Carbon-13 NMR Characterization of DGEBPA Epoxy Resins

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Synopsis

Carbon-13 nuclear magnetic resonance (NMR) has been used to investigate the structure and character of diglycidyl ether of bisphenol A (DGEBPA) epoxy resins more thoroughly than previously reported in the literature. It is shown that spectra, when run under quantitative conditions, can detect the loss of epoxides at the end groups by reactions such as hydrolysis. The products of acid hydrolysis of a DGEBPA resin are observed and assigned. It is further shown that the possibility of epoxide hydrolysis and impurities or structural irregularities can lead to inaccuracies in epoxy equivalent weight (EEW) calculations using a previously reported methodolgy. A new method is employed which can take into account loss of end group epoxides. Part of this new method consists of a measure of the epoxide to end group ratio (EER) which sheds light on the final possible quality of the cured resin. The EER value is shown to be in many ways more informative than the EEW measure which has the built-in assumption that there is an epoxide group for each end group.

INTRODUCTION

Epoxy resins have been an extremely important class of polymers for the past 20 years,[1,2] being used in a wide range of industrial products including adhesives, circuit boards, and structural composites. The properties of the cured resin are largely determined by the structure and quality (purity, molecular weight and distribution, etc.) of the starting resin. Consequently, the characterization of epoxy resins is necessary in order to correlate physical properties to the material properties.

Nuclear magnetic resonance has been a fundamental technique for characterization and analysis for many years. The use of proton NMR for the characterization of polymers is well documented.[3,4] Carbon-13 NMR has been used increasingly over the past several years for the characterization of polymers such as polystyrenes,[5-7] polyurethanes,[8] and other common important polymerics.[9-14] Indeed, the amount and quality of information obtained by carbon NMR is generally superior to that obtained by proton NMR. Several review articles exist which discuss the application of carbon NMR to polymers.[13-19]

There has been considerable work directed at the use of ^{13}C NMR in the characterization of epoxy resins. This effort was spearheaded by the work of Poranski, Moniz, et al., who initially looked at a wide range of commercial epoxy resins and curing agents by both proton and carbon NMR.[20] Subsequently, this group explored the use of ^{13}C NMR in characterization and quality control of epoxy resins.[21-23] In particular, they described a technique for determining the epoxy equivalent weight (EEW) using ^{13}C NMR.[21] This work has been expanded by others who used ^{13}C NMR to look at resin

formulation,[24] curing,[25] and the final cured material in the solid state.[26,27] Recently, two groups have begun making substantial contributions to the understanding of epoxide crosslinking mechanisms using boron and fluorine NMR.[28,29]

One aspect of epoxide resin characterization that has not been adequately addressed to date is what might be called the quality of the epoxidation. This topic is directly related to the EEW number, which is a measure of the equivalent molecular weight associated with each group. Prior to the work by Moniz and Poranski,[21] this value was determined by chemical analysis, infrared spectroscopy, and similar means. However, these techniques tend to be subject to uncertainties and are somewhat macroscopic in nature. It is possible to have a loss of epoxides with a corresponding change in EEW that does not adequately indicate a change in the functional character of the resin. Moreover, a direct method of looking at the epoxide groups and assessing their distribution and chemical evolution has not been fully developed.

This report describes the results of an investigation of a series of diglycidal ether of bisphenol A (DGEBPA) resins using ^{13}C NMR. It will be shown that additional information about the nature of the end group can be obtained. In particular, one can determine a ratio of the number of epoxide groups to the number of end groups, which will be called the epoxide to end group ratio or EER. Under ideal conditions this number should be unity. However, in reality the EER can be less than one. It will be further shown that hydrolysis of the end groups can be detected, and that because of built-in assumptions, the EEW value obtained by the methodology of Moniz and Poranski can be in error. An alternative method of determining the EEW will be provided. Finally, some implications of end group hydrolysis will be discussed.

EXPERIMENTAL

Spectra were obtained using an IBM Instruments NR/80 NMR spectrometer using samples in 10 mm NMR tubes and an internal deuterium field lock. Spectra were acquired using 16K of data points and a spectral width of 5000 Hz with quadrature phase detection. The carbon resonant frequency was 20.13 MHz, and proton decoupling was carried out using broad band noise modulation about a center frequency of 80.06 MHz. The carbon ninety degree pulse was 9 μs, and typically either 8192 or 10,000 transients were accumulated for each spectrum using the Aspect 2000 computer. The pulse width and pulse repetition rate were chosen in order to permit full relaxation of the carbon magnetization for all resonances. These values were determined after measuring the spin-lattice relaxation times for a typical sample using the inversion–recovery pulse sequence.[30] Chemical shifts are referenced relative to the center peak of the perdeuterated DMSO solvent, which was assigned the value of 39.5 ppm. The temperature of the samples was 32°C.

Samples of DGEBPA resins were either Epon 1004, 1004F, or 2004, obtained from Shell, or DER 667 obtained from Dow Chemical and were

commercial samples from various production lots.* The Epon 1004 samples were reported from the vendor to have weight average molecular weights ranging from 3300 to 3610, number average weights ranging from 1610 to 1700, and EEWs ranging from 900 to 943. DER 667 is reported to have EER values ranging from 1600 to 2000. Commercial samples had various histories expected in an industrial environment. An additional sample of DGEBPA was obtained from DOW which was designed have a molecular weight similar to that of the DER 667 but be extensively hydrolyzed. This sample was reported by the vendor to have 0.6 wt% residual epoxide compared to the 2.4 wt% of DER 667. A completely hydrolyzed sample was also prepared in our laboratory by acid hydrolysis of a sample of DER 667 for comparison purposes.

RESULTS AND DISCUSSION

A typical spectrum of a DGEBPA resin in DMSO-d_6 is shown in Figure 1. Assignments are given in Table I along with assignments for bisphenol A (BPA) and epichlorohydrin. The carbons are labeled according to the convention of Poranski et al. in Ref. 20. There was no residual BPA observed

* The use of these materials is for experimental purposes only and is not intended to be an endorsement of any kind. Any material properties observed reflect the state of the materials when studied and are not intended to imply that those properties represent materials as it is produced by the respective manufacturer.
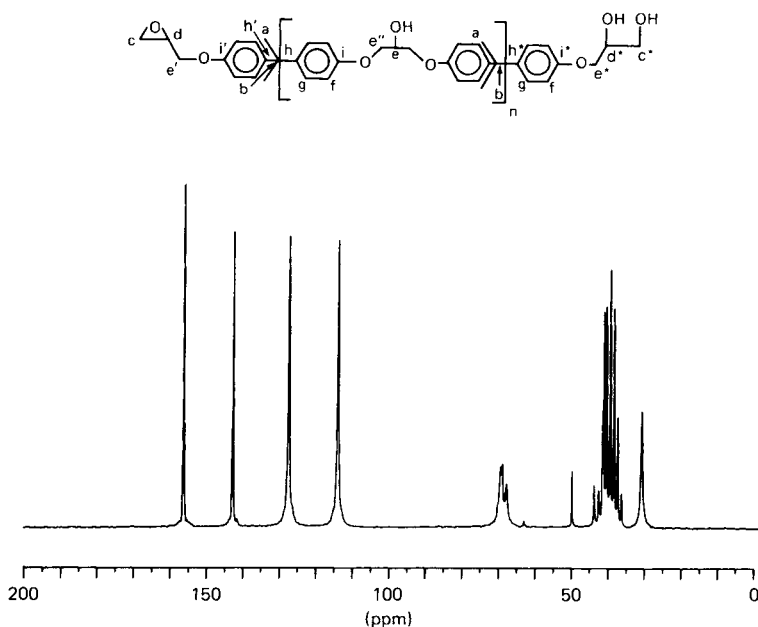

Fig. 1. ^{13}C-NMR spectrum of a typical DGEBPA epoxy resin (Epon 1004) at 20.13 MHz with DMSO-d_6 as the solvent. 8192 transients were accumulated according to the procedure described in the experimental section. Peaks are labeled according to the structure and are listed in Table I relative to TMS = 0 ppm assuming that the central peak of the solvent multiplet is at 39.5 ppm.

TABLE I
¹³C Chemical Shifts for DGEBPA, BPA, and Epichlorohydrin Relative to TMS[a]

		Molecule	
Peak	DGEBPA	BPA	ECH
a	30.8	31.3	
b	41.2	41.3	
c	43.8		46.1
d	49.8		50.9
c*	63.0		
e	67.7		
e′	68.9		45.7
e″	69.3		
e*	69.3		
d*	70.1		
f	114.0	115.1	
g	127.5	127.7	
k*	142.5		
h	142.7	141.6	
h′	143.0		
i′	156.1		
i	156.4	155.2	
i*	156.8		

[a] Chemical shifts are referenced based on the central peak of the solvent multiplet (DMSO-d_6) being at 39.5 ppm. Assignments for BPA and ECH are based upon appropriate modification of DGEBPA structure shown in the figure. Peaks denoted with an asterisk are assigned to the hydrolyzed end group carbons as shown in Figure 1.

in the samples run, and there were no visible quaternary resonances to indicate any significant branching. Figure 2 consists of expanded sections of the spectrum in Figure 1. Among the features that one observes is the presence of resolved peaks of the end group aromatic carbons h′ and i′ and the separation of peaks e, e′, and e″. This is in contrast to the spectrum of the sample in CDCl₃ in which the peaks in the 65–70 ppm region and the h, h′, and i, i′ regions are less well resolved. This is apparently due to solvent effects resulting from the large dipole moment of DMSO, which has been found to be the best solvent tried to date. Also present are several additional resonances in the 60–75 ppm region that will be discussed later.

In order to obtain quantitative information from NMR spectra, the intensities of the peaks must correspond to the spin populations of the corresponding carbons. In the case of ¹³C spectra, one must avoid nuclear Overhauser enhancement (NOE) and allow enough time during the pulse repetition time to ensure full relaxation of all spins in question. The NOE effect can be avoided by decoupling only during acquisition of the free induction decay (FID), and full relaxation of magnetization can be guaranteed by setting the pulse repetition time and the pulse width appropriately after determining the spin lattice relaxation times, T_1, of the spins. Table II contains the spin lattice relaxation times for a typical DGEBPA resin as well as BPA, both in DMSO. In these experiments the experimental parameters were adjusted to account for T_1's that were twice as long as those that were actually observed.

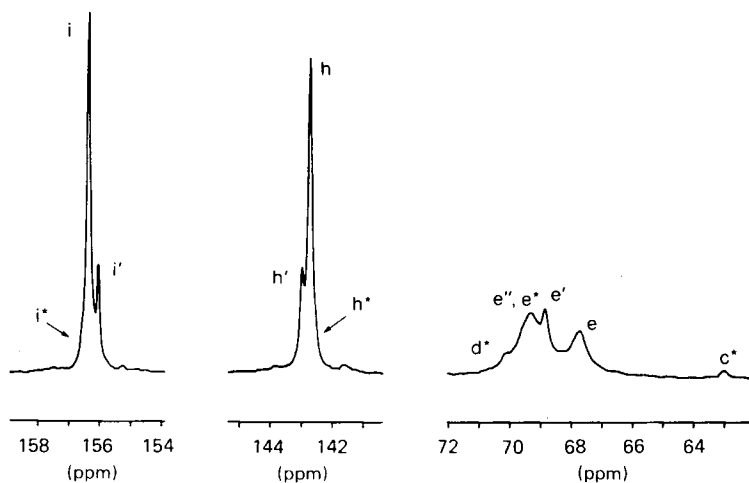The ability to observe the end group aromatics distinctly from the main

Fig. 2. Expanded regions of the spectrum in Figure 1 showing details which are due chemical shift effects associated with the end groups. The peaks labeled h' and i' are resonances of the end group aromatics. The peaks labeled c* and d* are peaks resulting from hydrolysis of the terminal epoxides.

chain aromatics means that one can use the ratios of the monomer aromatic resonances h nd i and the corresponding resonances of the end groups to determine the average degree of polymerization of the sample. This has several advantages compared to the earlier method which relies on peaks c, d, and the total integral of the peaks e, e', and e''. First, the earlier method assumes that each monomer unit contains one epichlorohydrin-based linkage, while there may be more than one. Second, if some epoxides in the end groups have opened, the areas of the peaks c or d will not be equal to the peak e' as assumed. Also, if the epoxide ring opening occurs through

TABLE II
^{13}C Spin-Lattice Relaxation Times, T_1 for All the Carbons of a Typical DGEBPA Resin and BPA at 20.13 MHz and at 32°C in DMSO-d$_6$[a]

Peak	T_1 relaxation times (s)	
	DGEBPA resin	Bisphenol A
a	0.07	0.19
b	0.835	1.5
c	0.18	
d	0.42	
e	0.06	
e'	0.12	
e''	0.04	
f	0.08	0.13
g	0.08	0.13
h	1.1	1.5
h'	1.0	
i'	2.3	
i	1.1	1.1

[a] The DGEBPA resin had a number average degree of polymerization of 4.4. All values were determined using the inversion recovery pulse sequence. The T_1 values can be solvent dependent. In CDCl$_3$, the T_1 values are generally longer at similar concentrations.

hydrolysis, the resulting resonances will likely be in the same region as peaks e, e′, and e″. This can skew the results as illustrated in Table III, which shows the hypothetical results that would result for a sample with various degrees of hydrolysis. That the former can occur is supported by measured integrals of peaks e, e′, and e″ normalized to the integrals of peak f or g; in some samples the integral of e, e′, and e″ was larger than could be expected from the idealized monomer with a single $OCH_2CHOHCH_2O$ group. The later arguments are valid as demonstrated in the spectra of Figure 3, which shows the central regions of a commercial DGEBPA sample and the two hydrolyzed samples. The peaks at 63 and 71 ppm in two of the three samples are due to the CHOH and CH_2OH carbons of the $OCH_2CHOHCH_2OH$ hydrolysis product, respectively. The resonances due to the hydrolyzed end group are denoted as c*, d*, e*, h*, and i* as shown in Figure 1.

The ability to determine the molecular weight of a DGEBPA resin using the peaks h, h′, i, and i′ is dependent on the ability to resolve the individual peaks. In the case of the epoxidized and hydrolyzed end groups this requirement is satisfied if an appropriate solvent is used. The experimental chemical shift effects[31] for three end group substitutions are presented in Table IV. The differences between the respective chemical shift effects is clearly small. If there is a different substitution on the end group due to some other factor, it is possible that the resonances at positions h′ and i′ for this substitution will overlap with the resonances h and i. This may be a potential source of error in the methodology for molecular weight determination. However, there is no evidence to indicate that this is a source of error in the case of the neat resins.

There are two alternative strategies for molecular weight determination. In the first, the peaks h, h′ and h* or i, i′ and i* are either resolved using resolution enhancement procedures in the spectrometer software or fitted using three simulated Lorentzian lines. The resulting degree of polymerization is determined by the equation: $DP = I_h/(I_{h'} + I_{h*}) = I_i/(I_{i'} + I_{i*})$. In the second, the integral of peaks c, d, c*, and b* are used. Rather than deal with systematic errors in deconvoluting the aromatic resonances, the integral of peaks c, d, h′, and i′ and peaks c*, d*, h*, and i* are assumed

TABLE III
Results for the Calculation of Degree of Polymerization and EEW Using the Method of Poranski and Moniz[20] for the Hypothetical Case of a DGEBPA Sample of Degree of Polymerization of Four for Several Percentages of End Group Epoxidation[a]

% epoxidized end groups	Case 1		Case 2		"Actual" EEW
	$n = DP$	EEW	$n = DP$	EEW	
100	4.0	766	4.0	766	766
90	5.26	952	5.33	962	851
80	6.0	1061	6.17	1086	958
75	6.44	1126	6.67	1160	1021
50	10.0	1651	10.67	1750	1532
20	26.0	4010	28.67	4405	3830

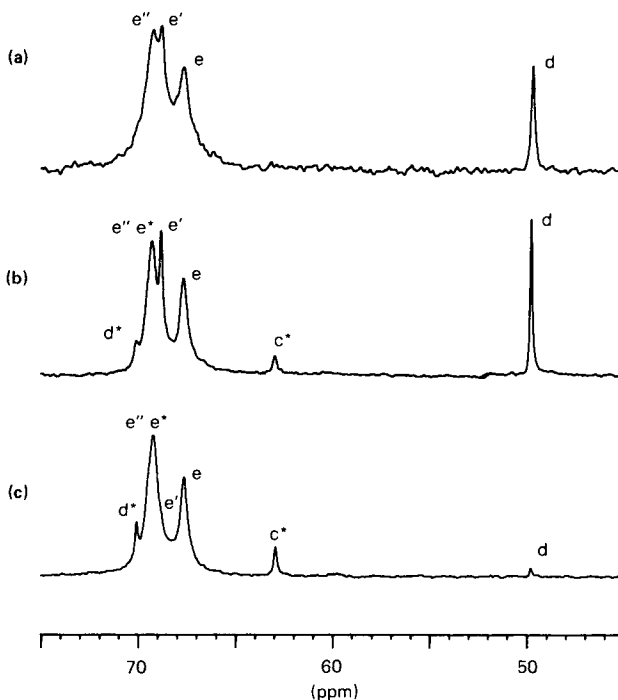[a] In case 1 and 2, one and both of the hydrolyzed epoxide carbons are counted in the "e" region, respectively.

Fig. 3. Central resion of the ^{13}C NMR spectrum of two virgin DGEBPA epoxy resins, (a) and (b), and an experimentally hydrolyzed resin, (c). Peaks c* and d* are due to the CH$_2$OH and CHOH groups resulting from hydrolysis of the epoxide. Peak e* is due to methylene e', which has been shifted by the hydrolysis.

to be equal. Thus, the degree of polymerization can be determined using the equation: DP = $[(I_h + I_{h'} + I_{h\cdot})-(I_d + I_{c\cdot})]/(I_d + I_{c\cdot})$. It was found that the later case was most consistent since the resonances d and c* are resolved without any overlap with other resonances. Resonances f or g can also be used to account for the intensity of the aromatic resonances as well.

The ratio of the number of epoxy groups to the total number of end groups can be determined using the resonances c, d, c*, and d*. Again, because resonances d and c* are well resolved, the epoxy to end group ratio was determined using the equation EER = $I_d/(I_d + I_{c\cdot})$.

The results of calculations based on the new methodology for a set of representative samples is presented in Table V, which also contains cor-

TABLE IV
Experimental Chemical Shift Effects (ppm) of Three Types of Aromatic Ring Substitution Observed in DGEBPA and BPA Samples[a]

Substituent	C1	Ortho	Meta	Para
—H	0	0	0	0
—OH	+26.9	−12.7	+1.4	−7.3
—OCH2CHOCH2	+27.8	−13.8	+1.2	−5.9
—OCH2CHOHCH2OH	+28.5	−13.9	+1.1	−6.4

[a] The results are based upon the assumption of additivity.

TABLE V
Results of EER, EEW, and MN Determinations for Seven Commercial and One Modified
DGEBPA Resins Lots Using the ^{13}C NMR Analysis Described in the Text[a]

Sample	DP	MW	EER	EEW	EEW[p]
Epon 1004, 9BHN222	3.9	1503	0.75	1002	1021
Epon 1004, 10CHN210	4.1	1562	1.0	781	810
Epon 1004, 11CHN211	4.1	1562	0.75	1041	1098
DER 667	7.9	2683	0.9	1490	1415
XPR 544, hydrolyzed DER	7.9	2683	0.1	>10,300	1075
Epon 1004F, WT8211192	3.7	1444	1.0	722	742
Epon 2004, 9CHN601	4.6	1709	1.0	855	1417
Epon 2004, 5EHN601	4.4	1650	1.0	825	919

[a] EEW[p] is the epoxy equivalent weight determined by the method of Poranski and Moniz.[20]

responding results based on the method of Ref. 21. One can see that there are differences in the EEW values between the two methods which are due to the hydration of end groups. The difference between the two values increases with increasing hydrolysis as reflected by the EER values provided by the new method. Moreover, one can see that the EEW values do not *a priori* reflect the character of end groups, i.e., the degree of hydrolysis, since EEW values can increase by changes in the molecular weight and not necessarily loss of epoxide functionality. The disparities are most obvious for the highly hydrolyzed samples for which the number average molecular weights are normal but the EEW number is very large. However, even for cases in which the degree of hydrolysis is low, the nature of the polymer is not completely revealed by the EEW value.

It should be emphasized that the hydrolysis of the epoxide groups as observed by NMR is not a phenomenon that is confined to DGEBPA type resins but can indeed be expected to occur in other classes of epoxy resins as well. The presence of the epoxide group and its susceptibility for reaction are the primary factors that result in the hydration. The structure of the polymer is secondary in importance. Insofar as it has pointed out that there are lot to lot variations within a manufacturing site, at different manufacturing sites, and as a function of transport storage conditions,[32,33] it is also likely that environmental factors that can result in hydrolysis can be similarly variable.

The significance of the loss of epoxide functionality seems obvious. If, say, half of the epoxides were to be lost by some means, the physical performance would clearly suffer due to reduced crosslink density. The correlation between crosslink density which is varied by changing molecular weight, assuming 100% epoxide functionality, and physical properties compared to the correlation between crosslink density which varies because of epoxide functionality will be different due to the existence of free chain ends in the latter case. For example, the physical properties of a cured resin of molecular weight x and complete end group crosslinking due to 100% epoxide functionality at the end groups will be superior to a cured resin of molecular weight $0.5x$ and a 50% epoxide end group functionality (EER = 0.5) even if all remaining epoxidized end groups were to undergo crosslinking reactions. It remains to be determined at what level of hy-

drolysis the physical properties will deteriorate below acceptable levels. This is not to say that loss of and group functionality is a major problem in the epoxy industry, only that it should be considered and monitored.

CONCLUSIONS

The ability of ^{13}C NMR to determine the degree of end group hydrolysis and molecular weight in DGEBPA resins has been shown. The determination of the epoxy to end group ratio is a new measure of the character of such materials which supplements the information previously provided by the epoxy equivalent weight determination. In applications in which the potential for end group hydrolysis is high, the ability to measure the end group functionality may be important when the crosslink density of the cured material is an important determinant of final material performance. Although it is not clear what the long term effects of environmental factors can have upon the epoxides, some fragmentary evidence suggests that in some applications the hydrolysis of end groups can occur during resin storage or processing due to ambient moisture. This is true not only for DGEBPA type resins but for other classes of epoxy resins as well. The use of carbon NMR to characterize the resins with respect to molecular weight and the quality of epoxidation would be a valuable technique in these cases.

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