Tetraglycidyl methylene dianiline (TGMDA)–analysis of the proton spectrum by two-dimensional n.m.r. spectroscopy

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The application of Fourier transform two-dimensional n.m.r. spectroscopy to the study of the epoxy resin monomer, tetraglycidyl methylenedianiline, TGMDA, is reported. The combination of homonuclear proton 2D-J resolved and shift correlated SUPERCOSY experiments permits the complete elucidation of the complex spectrum due to the glycidylamine region. Observation of long-range, four-bond coupling between the different methylene protons of the epoxy chain is also discussed.

(Keywords: tetraglycidyl methylenedianiline; nuclear magnetic resonance; proton spectrum two-dimensional analysis)

INTRODUCTION

Chemical characterization for quality control standards of organic polymers used in composites is receiving greater attention these days[1]. This can be achieved by employing standard analytical techniques such as infrared spectroscopy[2,3], differential scanning calorimetry[4], liquid chromatography[5] and magnetic resonance spectroscopy[6,7]. A recent example of these methods in the characterization of bisphenol-A epoxy resin was described by Wright[8]. In this paper the application of nuclear magnetic resonance (n.m.r.) techniques for the analysis of the proton (^{1}H) spectrum of the commonly used epoxy resin in the graphite fibre reinforced composite, tetraglycidyl methylenedianiline (TGMDA) is reported.

N.m.r. spectroscopy can be used for both qualitative and quantitative purposes. Qualitatively this can be accomplished by detecting any chemical shift changes that occur in the spectrum during crosslink reaction with a curitive or the appearance of a new resonance peak such as a hydroxyl peak in the curing reaction of TGMDA with DDS (diaminodiphenyl sulphone)[4]. Quantitative applications include determination of the resin-to-curing agent ratio in prepreg, impurity content, etc. To use the n.m.r. method effectively in this fashion it is necessary to have a complete assignment of the one-dimensional (1D) spectrum of the compound of interest. If such a spectrum is complex due to several couplings and overlap of different chemical shifts then one employs more sophisticated techniques such as two-dimensional (2D) n.m.r. methods.

The use of high-field 2D n.m.r. techniques to study a variety of systems from simple organic molecules to large proteins is well known, but applications to synthetic polymers, composites and epoxy resins have as yet been limited[9–16]. Homonuclear J-resolved and shift correlated experiments are the widely used methods for assigning different resonances, their coupling patterns and connectivities. The former type of experiment, such as 'J-spectroscopy', contains chemical shift information in one frequency dimension and spin–spin coupling on the other[17,18]. Two-dimensional experiments of this category contain no more information than the corresponding one-dimensional experiments, but present it in a more readily interpretable form.

The presence of a scalar coupling of either homo- or hetero-nuclei generates 'cross-peaks' at the resonant frequencies of the coupled nuclei when 'shift-correlated' two-dimensional spectroscopy (COSY) is employed. The observation of a cross-peak demonstrates that these nuclei are coupled to each other[19–23]. Whereas the J-resolved spectroscopy was of the conventional form, the shift-correlated 2D-spectroscopy employs the new pulse sequence SUPERCOSY, developed by Kumar *et al.*[24]. Even though this pulse scheme has potential application for larger biological molecules, because of reduced acquisition time to get intense cross peaks, we feel that it can be routinely applied to other systems as well.

EXPERIMENTAL

The commercial grade epoxy resin TGMDA, known as Hercules 3501-6 resin (MY 720), was obtained from Ciba-Geigy and was supplied to us by the Department of National Defence of Canada.

The n.m.r. experiments were carried out at 400 MHz on a Bruker WH400 spectrometer at room temperature. The proton 2D-J resolved and shift-correlated experiments used the Bruker software package. For the 2D-J resolved time-averaged proton-free induction decays 1024 data points were accumulated, using standard pulse sequence reported in literature, for 128 different values of t_1. A relaxation delay of 5 s was employed and 32 scans were accumulated for each t_1 experiment. Sine bell apodization was employed in both dimensions before Fourier transformation for a data set of a 256 × 1024 matrix.

The pulse sequence used for SUPERCOSY experiment has the additional advantage over that of the conventional COSY in that the intensities of the cross-peaks are enhanced by the introduction of two 180° pulses

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of the same phase with a delay $\Delta \simeq 0.3/J$ just before and after the mixing pulse. Recently it has been shown that with suitable adjustment of Δ, the pulse scheme can be optimised to display long-range couplings[16,25]. For the epoxy monomer reported here we have used a Δ value equal to 0.1 s. The data set consisted of a 256×1024 matrix. For each value of t_1, 32 free induction decays were accumulated. Sine bell apodization was applied in both the dimensions before Fourier transformation.

RESULTS AND DISCUSSION

The one-dimensional proton spectrum of TGMDA in acetone-d_6 is shown in *Figure 1*, together with its structural features. The resonances in the region 6.7 to 7.2 ppm are due to aromatic protons and are easily assigned. The region between 2.7 and 4.0 ppm represents the resonances of protons of the glycidylamine group and that of the methylene protons in between the two phenyl rings.

A preliminary analysis of the proton and ^{13}C n.m.r. spectra of this epoxy was reported earlier in the literature[7,8] with a view towards employing n.m.r. as an analytical technique suitable for qualitative and quantitative quality control standards, but no detailed investigation seems to have been discussed. In order to unravel the complexity of the proton resonances of the epoxy region, we employed the 2D techniques and the analysis is presented below.

The protons of the glycidylamine group together with the methylene group proton connecting the two phenyl rings resonate between 2.7 and 4.0 ppm. The 2D-J contour plot shown in *Figure 2* clearly indicates the presence of 10 different chemical shifts; while the contour map in *Figure 3* shows the connectivities between these protons, giving rise to these resonances. The sharp resonance at 3.94 ppm is seen not to be coupled to any protons and we assign this to the methylene proton, which is in between the two phenyl rings. The remaining resonances in this region were assigned to the glycidylamine group. Before further discussion about the complete assignment of these protons, the following considerations are to be taken into account:

(a) There is an asymmetric centre at the carbon atom c (see *Figure 1*).

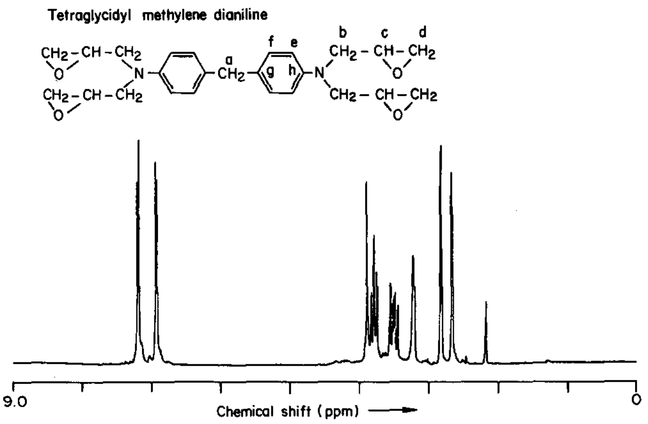

Figure 1 One-dimensional proton n.m.r. spectrum of TGMDA at 400 MHz in acetone-d_6. The truncated peak around 2.17 ppm is due to the solvent. The structural features of TGMDA are also shown as an insert

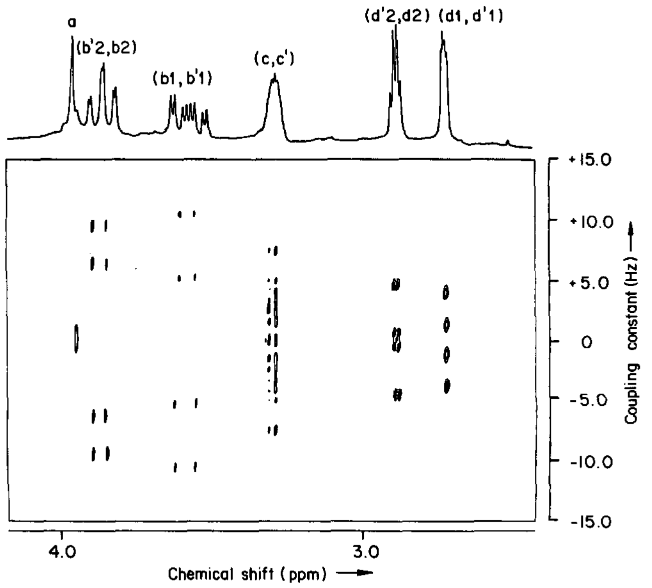

Figure 2 Proton homonuclear 2D-J contour plot of TGMDA. The normal 1D spectrum is shown at the top for convenience. $W1 = \pm 15$ Hz and $W2 = 700$ Hz; $X1 = 128$, $X2 = 1024$; $N1 = 256$, $N2 = 1024$. Sine bell apodization was applied in both directions before Fourier transformation

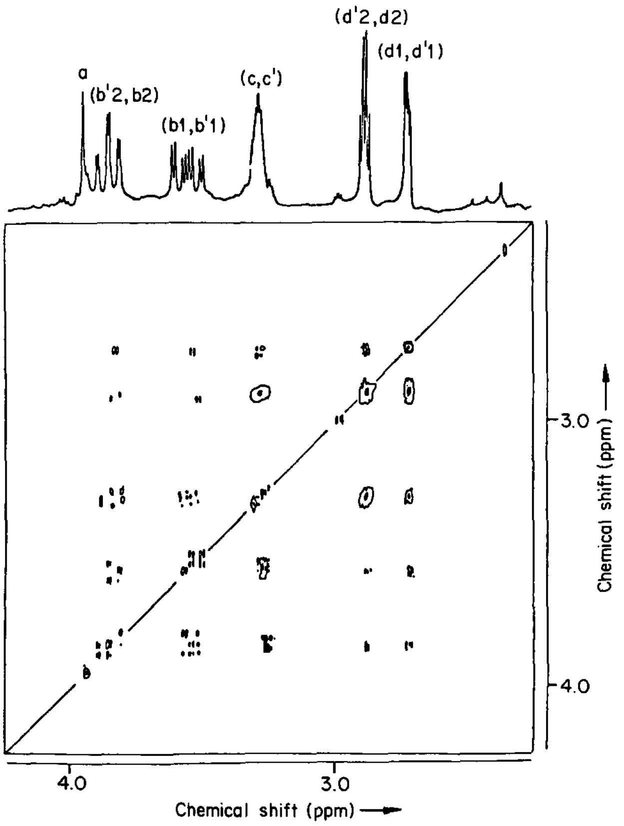

Figure 3 Proton homonuclear 2D shift-correlated SUPERCOSY contour plot showing the J connectivities between protons. $W1 = 800$ Hz, $W2 = 800$ Hz; $X1 = 128$, $X2 = 1024$; $N1 = 256$, $N2 = 1024$. For convenience the normal 1D spectrum is shown on the top of the contour plot. The lettering of peaks follows that shown in *Figure 1*, except the protons attached to the carbons are referred to here

(b) Any sample of TGMDA will have a 50–50% mixture of R and S epoxy chains. The presence of the asymmetric centre may lead to different chemical shifts and coupling constants in the R and S chains, which in turn means the protons in the methylene groups of the epoxy groups are probably inequivalent. We shall use the notation that the R and S chain are differentiated by a prime on the lettering shown in *Figure 1*, and a suffix 1 and 2 for the non-equivalent protons in the methylene group. Thus, for example, the types of methylene protons attached to a nitrogen atom in the glycidylamine group are b1, b2, b′1 and b′2.

From the contour plots of *Figures 2* and *3* we notice that there are only small chemical shift differences between the two asymmetric chains, and that the biggest chemical shift differences are observed for the methylene protons attached to the carbon atoms b and b′ (i.e. to the carbons attached to nitrogen). These values of chemical shifts are given in *Table 1*. The 2D-*J* contour plot (*Figure 2*) shows that each resonance of these protons is a doublet of doublets corresponding to couplings between the inequivalent protons on each methylene group and the coupling with proton attached to carbons c and c′. The resolution of the 2D homonuclear shift-correlated SUPERCOSY plot is also sufficient to resolve these small chemical shift differences between the asymmetric chains, and the different proton connectivities (b1,b2), (b′1,b′2), (b1,c), (b2,c), (b′1,c′) and (b′2,c′) are very clear. The coupling constants $J_{\mathrm{b1,b2}}$, $J_{\mathrm{b1,c}}$, $J_{\mathrm{b2,c}}$, $J_{\mathrm{b'1,b'2}}$, $J_{\mathrm{b'1,c'}}$ and $J_{\mathrm{b'2,c'}}$, as determined from the 2D-*J* plot are given in *Table 1* and compare well with those reported for other epoxies[15,16].

It is interesting to note that with the proper adjustment of the contour level the SUPERCOSY plot also revealed four-bond couplings of these protons (b1, b2, b′1, b′2) with that of the methylene group attached to carbons d and d′. The values of these long-range couplings, determined through simulation, were small, of the order of 0.1–0.3 Hz and were obscured by the natural linewidth of the spectra, which is around 2 Hz.

Considering the broadness of the peak around 3.30 ppm corresponding to the c and c′ protons in the 1D spectrum, the 2D-*J* plot is well resolved showing clearly the two chemical shifts as well as the different coupling constants. The proton connectivities of these two protons with the others are shown in *Figure 3*. The *J* values are as listed in *Table 1*.

The resonances in the region 2.7 to 2.9 ppm were assigned to protons attached to carbons d and d′. The *J*-resolved plot corresponding to these signals showed three chemical shifts instead of four, presumably because of overlap of two of the resonances into one. The plot further revealed that these are all quartets corresponding to a doublet of doublets due to couplings between the inequivalent protons on each methylene group and with protons attached to carbons c and c′. The different *J* couplings are as given in *Table 1*. *Figure 3* shows the proton connectivities.

Table 1 Proton chemical shifts and coupling constants of tetraglycidyl methylenedianiline (TGMDA)

Numbering of atoms[a]	Chemical shift[b] (ppm)	Couplings	Coupling constant (Hz)
a	3.94	–	–
b1	3.62	J_{b1b2}	15.94
b2	3.83	J_{b1c}	5.40
c	3.29	J_{b2c}	3.17
d1	2.72	J_{cd1}	2.70
d2	2.86	J_{cd2}	4.11
b′1	3.55	J_{d1d2}	5.70
b′2	3.87	$J_{\mathrm{b'1b'2}}$	15.84
c′	3.31	$J_{\mathrm{b'1c'}}$	5.40
d′1	2.72	$J_{\mathrm{b'2c'}}$	3.17
d′2	2.87	$J_{\mathrm{c'd'1}}$	2.70
		$J_{\mathrm{c'd'2}}$	4.11
		$J_{\mathrm{d'1d'2}}$	5.60
e	6.93		
f	7.19	J_{ef}	8.70

[a] See *Figure 1* for designation of the atoms. The prime signifies the chiral counterpart of a chain. The suffixes 1 and 2 indicate non-equivalent protons

[b] With respect to TMS

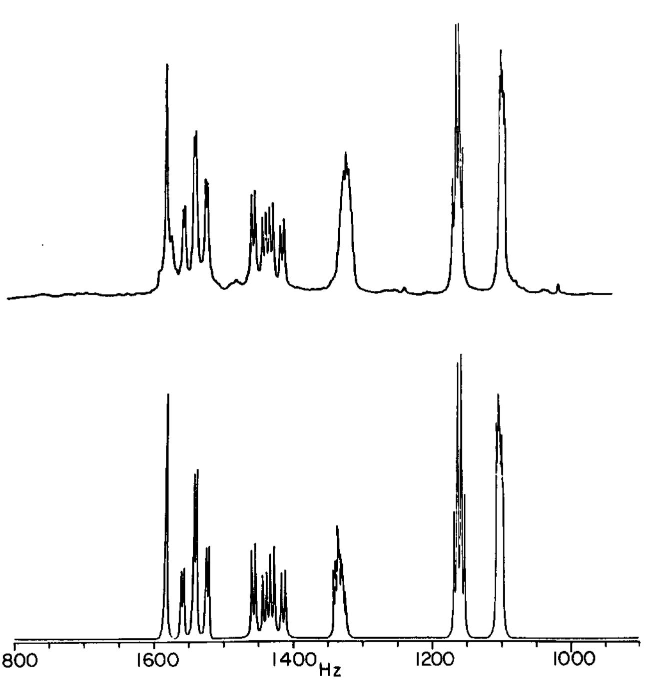

Figure 4 (A) Experimental proton spectrum of the glycidylamine region of TGMDA at 400 MHz. (B) Simulation of this region at 400 MHz using the chemical shift and coupling constant values listed in *Table 1*

In order to completely confirm the interpretation, a simulation of the proton 1D spectrum was carried out using the chemical shifts and coupling constants listed in *Table 1*. The spectral simulation was carried out on a Nicolet 1280 computer using the program NMRSIM. The simulation program has a limit of seven spins, and as a consequence the spectrum was simulated in two parts and combined; consequently the central part of the spectrum may not fully resemble the experimental one. The comparison of the experimental and the simulated spectrum at 400 MHz of the glycidylamine region is shown in *Figure 4*. The agreement is seen to be good but some impurity peaks are also clearly visible.

CONCLUSIONS

Through the complete agreement of the ^{1}H n.m.r. spectrum of tetraglycidyl methylenedianiline, TGMDA, this work demonstrates how 1D and 2D n.m.r. techniques can be used in the analysis and characterization of thermosetting synthetic polymers. The ability to make a full spectral assignment is invaluable in the study of the curing and ageing reactions of resin/curitive mixtures. For example, using ^{1}H n.m.r. the proposed hydroxyl group formation in the TGMDA/DDS crosslink reaction can now be investigated. With the values of the coupling constant presented in *Table 1*, it is also possible to deduce, to a certain limit, the conformation of the epoxy chain about the CH carbon atom.

Finally, the results show the powerful nature of the SUPERCOSY pulse sequence in the detection of short- and long-range couplings in these systems.

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