# High-resolution $^{13}C$ nuclear magnetic resonance studies of an unsaturated polyester in the solid state

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Unsaturated resins crosslinked with styrene, have been investigated by magic angle spinning-cross polarization (MAS-CP) $^{13}C$ n.m.r. and relaxation times in the rotating frame obtained. The relaxation times $T_{1\rho}$ obtained ranged from 2 to 34 ms, and were found to change with cure temperature in the polyester resin with a maximum value observed for all carbons when curing proceeded in the temperature region 80°C–90°C. The relaxation times evaluated indicate that more complete crosslinking occurs at temperatures in this temperature region indicating that there was a correlation between $T_{1\rho}$ and the cure temperature. There was also a common pattern for all carbon atoms and similarly a strong influence on relaxation time existed for all carbons in the cured polyester. The corresponding main-chain motions are mainly cooperative which, with a suggested spin-lattice relaxation mechanism will be a significant influence on the molecular mobility along with the cure temperature. This influence on the molecular mobility is dependent on the carbon chain polymer length and thereby on the number of endgroups in the carbon chain polymer.

**(Keywords: unsaturated polyester; $^{13}C$ nuclear magnetic resonance, solid state; relaxation time; cure temperature)**

## INTRODUCTION

Unsaturated polyesters are macromolecules with a polyester heterochain in which saturated and unsaturated acids are condensed with glycol. A three-dimensional structure is produced by crosslinking the heterochain through the unsaturated acid component with a vinyl monomer, e.g. styrene, by a free radical copolymerization to form a carbon chain polymer.

The polyester structure has been investigated using hydrolysis of the cured product and subsequent analysis of the carbon chain polymer[1]. Mechanical properties and the influence of the cure temperature on unsaturated polyesters have also been described[2]. Kinetic data evaluated from d.s.c. measurements on unsaturated polyesters have been used in a data simulation which was found to agree well with experimental data[3].

In recent years n.m.r. has been used to evaluate cured products. Chemical shifts have been evaluated for unsaturated polyesters by $^{13}C$ n.m.r. in the solid state[4].

The restriction of molecular mobility of an unsaturated polyester was examined[5] by combining pulse and wideline $^{1}H$ n.m.r. methods to follow the curing process into the solid state.

Measurements of the $T_1$ spin-lattice relaxation time by pulsed $^{1}H$ n.m.r. have been made to monitor the effect of the catalyst concentration on the unsaturated polyester resin[6].

An approach to understanding the microscopic origins of polymer motions in solids has been suggested[7], where a relationship between microscopic motion and macroscopic behaviour is proposed. This approach comprised $^{13}C$ n.m.r. in the solid state. This method, called high-resolution n.m.r. in the solid state[8], comprises high power resonant decoupling and high speed sample rotation at the magic angle, magic angle spinning (MAS) and cross polarization (CP). This produces a $^{13}C$ n.m.r. spectrum with acceptable resolution and the chemically different carbons can be identified by separate resonances[8]. In addition to the evaluation of chemical shifts there is one further advantage of combining CP and MAS in the high-resolution n.m.r. in the solid state which is that the resolution in the solid state allows individual carbon relaxation experiments to be performed.

The $^{13}C$ relaxation time in the rotating frame, $T_{1\rho}$, has contributions from spin-lattice and spin-spin relaxation[9]. If spin-lattice relaxation dominates the $T_{1\rho}$, then the result can be interpreted in terms of molecular motions in the polymer network. As a sufficient number of unique resonances exist in $^{13}C$ n.m.r., the results can be discussed in terms of methyl group rotation, aromatic ring rotation, main-chain and local motions, etc.[8,10,11] This presents an advantage over the more common proton relaxation measurements, in which efficient spin diffusion usually results in an averaging of relaxation behaviour over an ensemble of protons yielding a single relaxation time for all protons.

The aim of the work described in this paper was to investigate the differences in relaxation times for carbon atoms with cure temperature for unsaturated polyester in the kHz region by $^{13}C$ n.m.r. in the solid state.

## EXPERIMENTAL

An aliphatic unsaturated polyester was synthesized by melt polymerization of fumaric acid (1 mole), adipic acid (2 moles) and 1,2-propylene glycol (3.2 moles) as described previously[12], and diluted with styrene to the azeotropic

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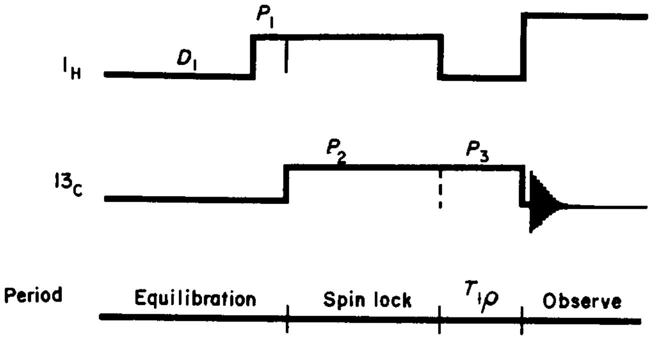

**Figure 1** Pulse sequences for the $T_{1\rho}$ experiments

ratio 1.8. Fumaric acid was used to achieve a *trans*-configuration in the unsaturated polyester.

Sheets of thickness 0.5 mm were made by curing the resin at predetermined temperatures and at calculated times as described previously[3,13]. Circular discs of diameter 8 mm were cut out from the sheets and stacked in a hollow rotor machined in Kel-F$^R$, which contained no protons.

$^{13}C$ n.m.r. CP-MAS spectra were obtained at 50.3 MHz with a Varian XL-200 NMR spectrometer with a high-power amplifier and a solid state probe. The frequency of the high-power decoupling field was near 45 kHz. All spectra were obtained at 20°C and the probe tuning was optimized before the experiments by Hartman–Hahn matching of each sample, adjusting with a hexamethyl benzene sample. The magic angle was also set with this sample using the aromatic resonance in the spectra. The pulse sequences for the $T_{1\rho}$ experiments are shown in *Figure 1*.

This sequence was used with the optimal contact time, $P_2 = 500$ms, delay time, $D_1 = 5$s, acquisition time, $AT = 0.064$, number of transitions, $NT = 8000$, sweep width, $SW = 16\,000$, Fourier number $FN = 4096$ and sensitivity enhancement $SE = 0.02$. Data from the holdtime $P_3$ was not stable for times less than 100 ms and ranged in the experiments at six to eight values from 100 to 1500 ms.

In these experiments the carbon magnetization was generated by cross-polarization, held spin-locked in the absence of a decoupling field for variable $P_3$ times, as described in *Figure 1*[14]. The relaxation time $T_{1\rho}$ is given by the extrapolation to zero of the logarithm of the relative peak height *versus* the holdtime $P_3$.

The pulsing program used by the Varian XL-200 NMR spectrometer for the elimination of spinning sidebands[15] gave spectra with improved resolution but the intensity of the centre peak became very sensitive to variations in rotation speed. There was too large a spread in the relaxation results even with variations in the rotation speed of just a few hertz and therefore this pulsing method could not be used here to evaluate the relaxation times.

The rotation speed was chosen at 2750 ± 5 Hz, where spinning sidebands did not affect the peak heights used here for relaxation measurements.

## RESULTS

A $^{13}C$ n.m.r. spectrum of the unsaturated cured polyester sheets is presented in *Figure 2* where line assignments were possible due to the reasonably well resolved lines for the cured polyesters.

In the heterochain we can assign the carbonyl groups from the fumaric acid and adipic acid residues to a single peak (h). The methine and methylene carbons adjacent to the carbonyl groups are assigned to peak (d). The methylene carbons and methine carbons from the propylene glycol are present in one peak (e). The methylene carbons in adipic acid, not bonded to a carbonyl group, give rise to peak (b). The contribution from the methyl group in propylene glycol in the heterochain is present as a separate peak (a). From the carbon chain sequences of crosslinked styrene, the contributions are one resonance from the quaternary carbon (g), and one resonance from the carbons in the aromatic ring (f). In the carbon chain polymer there are also methine and methylene carbons present (c). Spinning sidebands are indicated as (ss).

A semilog plot of data from successively increasing $P_3$ holdtimes gives one $T_{1\rho}$ for each cure temperature of the carbons in the polyesters and is presented in *Figure 3*. When the $T_{1\rho}$ data were plotted against cure temperature the results shown in *Figure 4* were obtained. For all carbons there were maxima in the temperature region 80°C–90°C.

The heterochain carbon lines relax relatively fast with no signal left after 6 ms, with the exception of the carbonyl groups for which values up to 34 ms were found. In the carbon chain polymer the methine and methylene carbons relax at nearly the same time as the protonated carbons in the heterochain. The carbons of the phenyl ring relax relatively slowly, up to 15 ms for the quaternary carbon and up to 7 ms for the other carbon atoms.

The rotation speed is of importance as spinning sidebands can affect other peaks in the spectra. Spinning sidebands can be identified by variations in the rotating speed as the position in the spectrum is changed with

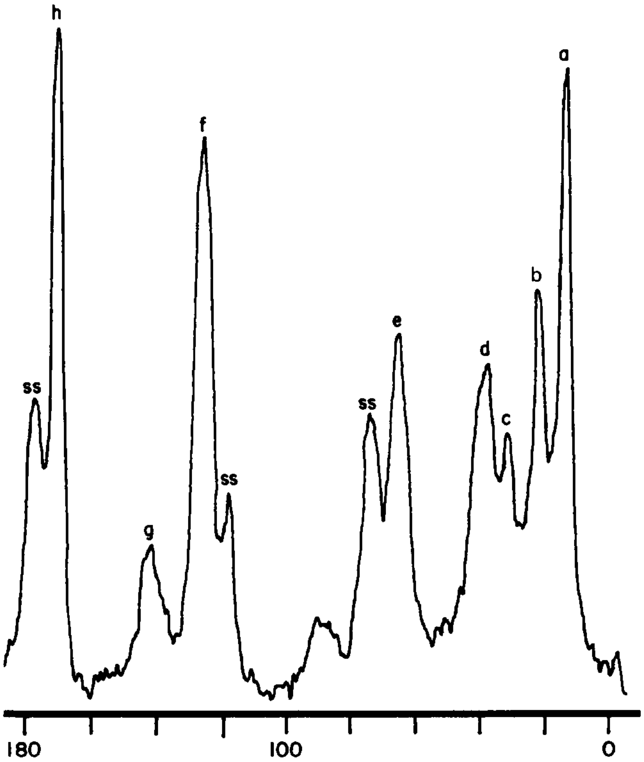

**Figure 2** Solid state $^{13}C$ n.m.r. spectrum of an unsaturated polyester with azeotropic composition and *trans*-configuration in the polyester unsaturations

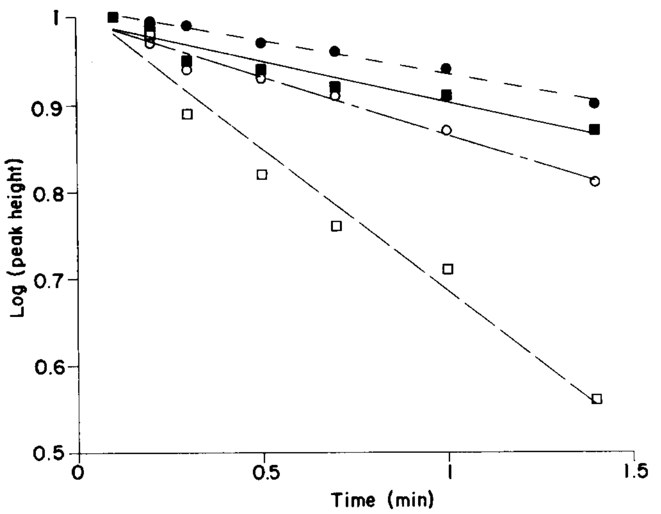

**Figure 3** Semilog plot of peak height for the carbons in the spectra *versus* time of absence of the decoupling field for evaluation of $T_{1\rho}$: ■, a; □, b; ●, g; ○, h

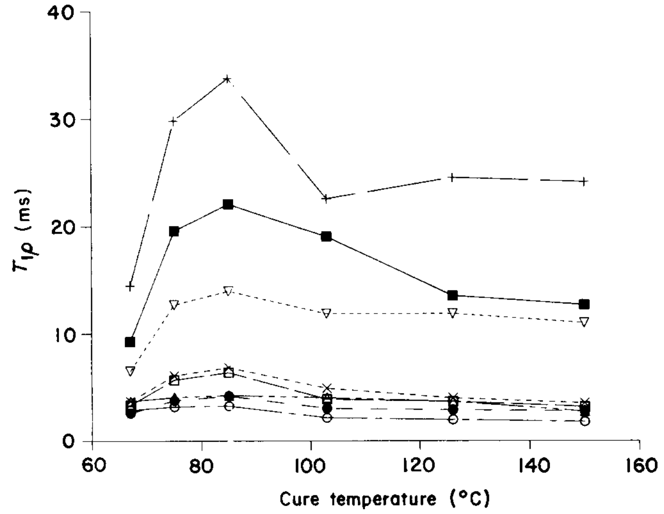

**Figure 4** $T_{1\rho}$ at 45 kHz for carbon atoms of an unsaturated polyester cured at different temperatures. The methyl group from the propylene glycol residue (a) ■; the methylene carbons in adipic acid not bonded to a carbonyl group (b) □; methine and methylene carbons present in the carbon chain polymer (c) ●; the methine and methylene carbons adjacent to the carbonyl groups (d) ○; the methylene carbons and methine carbons from the propylene glycol (e) △; the aromatic ring except the quaternary carbon (f) ×; the quaternary carbon (g) ▽; the carbonyl groups from the fumaric acid and adipic acid residues (h) +

rotation speed. These spinning sidebands occur at shift differences in multiples of the rotation speed (in Hz) on both sides of the peak they are emanating from and the two nearest ones have the strongest signal and may influence the determination of the relaxation times of the peaks they are overlapping. $T_{1\rho}$ also becomes shorter with increasing rotation speed as seen in *Figure 5*.

## DISCUSSION

There was a significant change in the relaxation times with curing temperatures. The same tendency was observed for all carbon peaks in any spectrum. All carbon atoms had a maximum in the temperature region 80°C–90°C. To interpret these data we must consider the nature of the relaxation of the rotating frame.

$T_{1\rho}$ has contributions from spin-lattice and from spin-spin mechanisms, and the effect on $T_{1\rho}$ has been determined by two different procedures[9,16]. Spin-lattice relaxation is an effect from the modulation of internuclear dipolar interactions by molecular motions at the rotating-frame Larmor frequency. Spin-spin relaxation, on the other hand, originates from modulation of the dipolar interactions by spontaneous rigid lattice proton spin fluctuations.

The values of $T_{1\rho}$ found experimentally can thus be explained by two alternative mechanisms, or a combination of them.

### *Spin-spin relaxation*

Spin-spin relaxation originates from modulation of the dipolar interactions by spontaneous rigid lattice proton spin fluctuations and is a depolarization process, which is exactly the reverse of the cross-polarization in an 'ADRF' experiment[9]. $T_{\mathrm{CH}}$(ADRF) experimental measurements require a complicated nine-step procedure[16]. A calculation of the ratio of $T_{1\rho}$ to $T_{\mathrm{CH}}$(ADRF) determines the extent of spin-spin contributions to $T_{1\rho}$ and will permit an estimate of spin-spin contributions to the observed carbon rotating-frame relaxation times.

Theoretical expressions for $T_{\mathrm{CH}}$(ADRF) have been derived[17,18]. A phenomenological expression[16] for methylene carbons was found to be in good agreement with experimental data, and the assumption is made that the variations of $T_{\mathrm{CH}}$(ADRF) depend on changes in the proton local field $H_{\mathrm{L}}$. It would seem to be reasonable to suggest that similar relationships between $T_{1\rho}$ and $H_{\mathrm{L}}$ are also at hand for the other carbon atoms with an increase in $T_{\mathrm{CH}}$(ADRF) with increasing $H_{\mathrm{L}}$. If the $T_{1\rho}$ values of the carbons are dominated by spin-spin relaxation then the change in relaxation time must correspond to a change in the dipolar local field. The dipolar local fields are functions of internuclear distances and of averaging of the dipolar interactions by fast motions. There is probably a marginal change in the dipolar interactions by changing to fast motions in the network but the experimentally found increase in $T_{1\rho}$ would correspond to an increase in $H_{\mathrm{L}}$ and thereby a decrease in internuclear distance, which would indicate more complete crosslinking. This is in

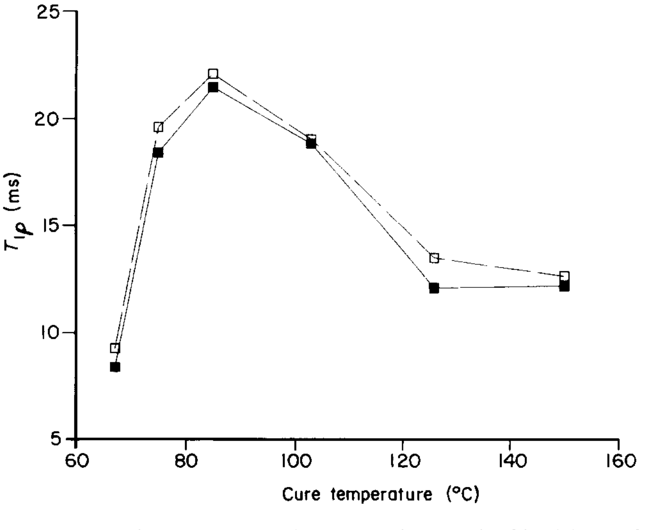

**Figure 5** $T_{1\rho}$ for the methyl carbon at rotation speeds of 2750 (□) and 3500 Hz (■)

accordance with other results, e.g. the same tendency with a maximum in this temperature region was found for reacted groups in the polyester[3], mechanical strength and $T_g$ for a glass fibre-polyester composite[2] and molecular weight of the carbon chain polymer[1] in cured unsaturated polyesters.

### *Spin-lattice relaxation*

The relaxation times in the rotating frame, $T_{1\rho}$, is probably dominated by spin-lattice relaxation which here would mean that there are significant changes in the molecular mobility with cure temperature in the cured polyester. Measurements of $T_{1\rho}$ at room temperature provide information on molecular motions in the kHz frequency range. $T_{1\rho}$ was found to describe a maximum with increasing cure temperature and the corresponding molecular mobility will thereby go through a minimum with increasing cure temperature. Restriction in mobilities for the carbons are brought about by the crosslinking reaction and then the relaxation time will be influenced by the reaction efficiency and crosslinking density. The most complete reaction will then proceed at around 85°C for this polymer system. This is also in accordance with the experimentally found relationships for the above mentioned maximum in the temperature region 80°C–90°C for reacted groups in the polyester[3], mechanical strength and $T_g$ for a glass fibre on polyester composite[2] and molecular weight of the carbon chain polymer in the polyester[1]. The amount of reacted groups influences the crosslinking density and thereby the molecular mobility as was similarly found in this $T_{1\rho}$ experiment. It was found that after a maximum, the molecular weight, $M_n$, decreased with increasing cure temperature varying between 4000 and 12 000. Thus the number of end groups increases with cure temperature.

The carbon chain molecular weights will to some extent also influence the molecular mobility as the end groups are more mobile. They will also make the crosslinked polymer more flexible as they do not contribute to the network. The significant maximum in $T_{1\rho}$ would then be a combined effect of the highest crosslinking density and highest carbon chain molecular weights at these temperatures.

The relaxation times are short in comparison with reported values for $T_{CH}$(ADRF)[9] and it has been found[10] that organic glassy polymer systems, near room temperature, possess a wide variety of molecular side and main-chain segmental motions even at temperatures well below their glass transition temperature $T_g$. Shorter $T_{1\rho}$ values indicate a greater average mobility for polymers well under the $T_g$[10], which, by dynamical mechanical analysis, was found to be in the range 70°C–75°C for this cured unsaturated polyester[2]. The suggestion is that the $T_{1\rho}$ values found in these experiments are dominated by spin-lattice relaxations and depend on molecular motions in the polymer network, although spin-spin effects cannot be excluded without a careful determination of $T_{CH}$(ADRF).

Some $^{13}C$ nuclei have shifts with no overlapping from other $^{13}C$ nuclei and would thereby be expected to be better suited to describe changes in molecular mobility. The peaks involving just one kind of carbon are few and they are the carbons of the methylene groups in the adipic acid residues not bonded to carboxyl groups, the methyl group in the propylene glycol in the polyester heterochain and the quaternary carbon in the phenyl ring.

The carbons occurring together in the same peaks are chemically very similar. In the heterochain polymer there are the carbonyl groups from the fumaric and adipic acid residues, the methylene carbons from the adipic acid residues and the methine carbons from fumaric acid residues adjacent to carboxylic groups and the methylene carbons and methine carbons from the propylene glycol. There are methine and methylene carbon signals from the carbon chain polymer. Quaternary carbon signals from the carbons in the aromatic ring are combined in one single peak. There were no significant differences in the relaxation patterns for peaks involving one or two kinds of carbons.

The relaxation times would be faster for carbons having many protons. Carbons without adjacent protons, the quaternary carbon in the phenyl group and the carbonyl carbon, are, as expected, slower relaxing carbons. Also the aromatic carbons in the phenyl group relax relatively slowly.

It is probable that the methyl carbon relaxes slowly because it is isolated from communication with other nuclei by its fast rotation.

The relaxation times in the kHz region changed for all carbons in the same manner with the cure temperature. These relaxations can be related to the molecular mobility as suggested and then there will be some differences in the kinds of molecular mobility.

The mobilities of the polymer segments have an influence on the carbons in the heterochain and the carbon chain polymer. The methyl group, as a side group, can move more independently of the heterochain by, for example, rotation. In polystyrene the phenyl ring undergoes translation or is rotating, flipping or wiggling[19]. These motion alternatives can also occur in the phenyl side groups in the carbon chain polymer.

## CONCLUSION

From these experiments we have found that there was a correlation between $T_{1\rho}$ and the cure temperature. There is also a common pattern for all kinds of carbon atoms, a strong influence on relaxation time exists in a similar way for all carbons in the cured polyester. From this information we understand that the corresponding main-chain motion would be mainly cooperative. With a suggested spin-lattice relaxation mechanism there will be a significant influence on the molecular mobility with the cure temperature. This influence on the molecular mobility depends on the carbon chain length and thereby on the number of endgroups.

Whatever the dominating mechanisms are for $T_{1\rho}$, spin-lattice or spin-spin relaxation, the results indicate that the cured unsaturated polyesters change significantly in the molecular structure with cure temperature. There is a more complete crosslinking reaction with a more tightly bonded network at the cure temperatures corresponding to the relaxation time maximum.

The changes in relaxation times with cure temperatures probably correspond to structural changes. If this is true then the $^{13}C$ n.m.r. in solid state will be very useful when evaluating curing and postcuring mechanisms. Influence of, for example, mechanical stresses and immersion in water on the molecular structure of the matrix or of composites could well be evaluated using this method.

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