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Solid-state n.m.r. determination of residual unsaturation in styrene-cured polyester resins

Roger H. Newman* and Kevin H. Patterson†
Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand
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A resin containing fumarate, isophthalate and propylene glycol structural units was cured with styrene and characterized by ^{13}C solid-state nuclear magnetic resonance spectroscopy. The degree of residual polyester unsaturation was estimated from relative areas of peaks at 172 ppm (carboxylic carbon in saturated structural units derived from fumarate) and 165 ppm (carboxylic carbon in isophthalate and unreacted fumarate structural units). Decreasing the styrene content below 47% by weight resulted in residual polyester unsaturation. Results were interpreted in terms of a statistical model for copolymerization, providing evidence for low reactivity of fumarate structural units relative to diethyl fumarate and drawing attention to differences in reactivity between the resin system used in the present work and those used in earlier studies.

(Keywords: polyester resins; residual unsaturation; ^{13}C n.m.r.)

INTRODUCTION

Unsaturated polyester resins are condensation products of low molecular weight (1000 to 2000 Daltons) prepared from combinations of unsaturated and saturated dibasic acids or anhydrides with dihydric alcohols or oxides. Unsaturated structural units are fundamental to the reactivity of the resin. Most commercial formulations use maleic acid anhydride. The maleate structural units are almost all converted by *cis–trans* isomerization to fumarate units during condensation. Commercial products are commonly marketed as solutions in styrene. Addition of a source of free radicals initiates crosslinking reactions involving the styrene and fumarate double bonds, resulting in a rigid, three-dimensional polymer network.

Cured polyester resins have been characterized by ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy in the solid state[1,2]. This technique shows promise in revealing information that is difficult to obtain by more classical indirect means[1]. The earlier n.m.r. studies explored the sequence distributions of crosslinks[1] and the effects of crosslinking on nuclear spin relaxation[2]. The present work assesses use of n.m.r. in estimating another parameter, namely the degree of residual polyester unsaturation.

Resins containing residual unsaturation are sometimes described as 'undercured'. Styrene evaporation is a frequent cause of undercuring[3]. Prolonged heating will not solve problems with undercuring if all of the available styrene has been consumed through, for example, formation of pendent chains or microdomains of polystyrene in addition to the desired crosslinking bridges.

Appropriate styrene contents are sometimes calculated from a copolymerization model[4–7] using data published by Lewis *et al.*[8] for copolymerization of styrene with diethyl fumarate. Some published evidence supports the use of diethyl fumarate as a model for unsaturated structural units in polyesters, at least in the early stages of copolymerization[5,6]. We used ^{13}C n.m.r. spectroscopy to provide data for a more rigorous test.

EXPERIMENTAL

Materials

The commercial resin contained fumarate, isophthalate and propylene glycol structural units, and was supplied as a solution in styrene with a nominal styrene content of 45% by weight. The composition was confirmed by solution ^{13}C n.m.r. spectroscopy, using chemical shifts published for the relevant structural units[9,10]. In particular, peaks in the ranges 163.4 to 165.0 ppm and 167.1 to 168.1 ppm were assigned to fumarate structural units, while peaks in the ranges 165.6 to 167.1 and 168.6 to 170 ppm were assigned to isophthalate structural units. Relative strengths of these peaks indicated proportions of 48 moles fumarate to 52 moles isophthalate.

Additional styrene was added to some samples. Other samples were prepared by allowing some of the styrene to evaporate into room air, or by removing styrene under vacuum. A few samples were prepared by removing styrene and then replacing it, to confirm that any changes were reversible.

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* To whom correspondence should be addressed
† Present address: Allflex New Zealand Ltd, PB 11-003 Palmerston North, New Zealand

Curing was initiated by adding methyl ethyl ketone peroxide (1% by weight) as a 40% w/w solution in dimethyl phthalate. Cobalt naphthalate (nominally 0.27% by weight) was present, as a promoter, in the commercial resin solution as supplied. Samples weighing between 10 and 15 g were left at 23°C and 50% relative humidity for 4 days, then heated to 90°C for 60 min. Weight losses associated with styrene evaporation did not exceed 5%, and were taken into account in calculating product compositions. Powders were prepared by drilling holes with a 2 mm diameter drill bit or by milling fragments in a Retsch type ZM-1 Ultracentrifugal Mill (0.5 mm mesh).

N.m.r. spectroscopy

Portions of about 0.3 g cured resin were packed in 7 mm diameter cylindrical sapphire rotors and retained with Kel-F end caps. The rotors were spun at 5 kHz in a Doty Scientific magic-angle spinning (MAS) probe. N.m.r. spectra were acquired with a Varian XL-200 spectrometer operating at a ^{13}C n.m.r. frequency of 50.3 MHz. Each 6 μs $\pi/2$ proton preparation pulse was followed by a 2 ms cross-polarization contact time, 30 ms of data acquisition and a 2 s pulse delay before the sequence was repeated. Most spectra were acquired with an interrupted decoupling pulse sequence[11] (*Figure 1*) in which the contact time was followed by a delay of $t_i = 42\,\mu$s without proton spin decoupling. Decoupler power was restored for a further delay $2T - t_i$ before data acquisition began. A 12 μs ^{13}Cπ pulse was applied during this delay so that the magnetization was refocused at the beginning of data acquisition. The value of T was set at one rotor period to ensure that the sequence suppressed signals affected by strong dipole–dipole interactions, i.e. signals from CH and CH$_2$, rather than signals affected by large chemical shift anisotropies[11]. At least 5000 completed transients were averaged for each spectrum, except for reproducibility tests in which the number of completed transients was 1400.

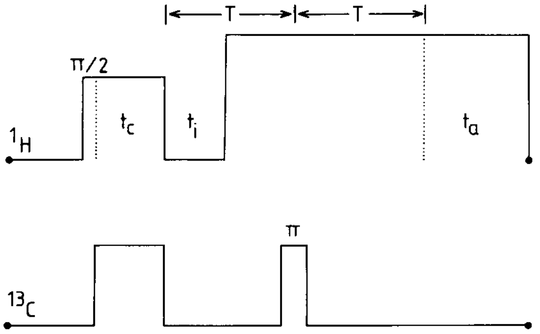

Figure 1 Schematic representation of the interrupted decoupling pulse sequence. Time intervals (not shown to scale) are: T = rotor period, t_c = contact time, t_i = interruption without decoupling, t_a = acquisition time

Table 1 Chemical shifts for non-protonated carbon atoms

Chemical shift (ppm)	Environment	Structural unit
131	aromatic	isophthalate
144	aromatic	styrene-derived[a]
165	carboxylic	isophthalate and fumarate
172	carboxylic	fumarate-derived[a]

[a] Structural units formed during curing

The reliability of the n.m.r. method was tested in a series of spin relaxation experiments on a sample of the resin cured with the styrene content as supplied. Relevant peak assignments (*Table 1*) are discussed below. The proton spin–lattice relaxation time constant was $T_1(\mathrm{H}) = 0.8$ s. Values of cross-polarization time constants (T_{CH}, *Table 2*) were much shorter than the proton rotating-frame relaxation time constant of $T_{1\rho}(\mathrm{H}) = 8.0$ ms, so it was possible to use a contact time much longer than T_{CH} without losing more than a fraction of the theoretical signal strength through rotating-frame relaxation. Signal strength decayed approximately exponentially through interrupted decoupling, with time constants (T_{DD}, *Table 2*) all much longer than the 42 μs interruption used in quantitative n.m.r. experiments.

Peak areas $A(\delta)$ refer to the centreband at chemical shift δ, without correction for spinning sidebands. Centreband signals accounted for at least 75% of signal strength (*Table 2*), the remainder being spread over sideband signals spaced at intervals of 100 ppm either side of each centreband.

Estimation of styrene contents

Lowering and raising styrene contents relative to an uncertain nominal value seemed likely to compound uncertainties. We therefore used n.m.r. peak areas to provide independent estimates of the styrene contents. Assignments in *Table 1* lead to a theoretical relationship of the form:

$$R = KA(144)/[A(165) + A(172)] \qquad (1)$$

where R is the mole ratio of styrene reaction products to fumarate double bonds and the corresponding reaction products. The factor K allows for the total number of moles of carboxylic carbon per mole of fumarate structural units, for differences in spin relaxation time constants and for differences in the proportions of signal strength spread into spinning sidebands. Rather than try to enumerate all of the contributing factors, we chose to use an empirical value of $K = 6.63$ based on a least-squares best fit (correlation coefficient = 0.998) for five samples prepared by adding a known amount of styrene to portions of the commercial resin solution. The best-fit calculations used a formula weight of 379 g polyester per mole of fumarate double bonds, based on the polyester composition discussed above. The least-squares fit also provided an improved estimate of 47% by weight styrene in the original resin solution. Reproducibility was tested by running one sample nine times on different days. The

Table 2 Results from experiments on three signals in the ^{13}C n.m.r. spectrum of resin cured with the styrene content as supplied

Chemical shift (ppm)	T_{CH} (ms)[a]	T_{DD} (ms)[b]	Centreband[c] strength
144	0.3	0.3	0.75
165	0.5	>0.4	0.88
172	0.4	>0.4	0.88

[a] Cross-polarization time constant
[b] Time constants for signal decay resulting from interrupted decoupling
[c] As a fraction of total signal strength, the remainder being distributed among spinning sidebands

standard deviation of the nine n.m.r. estimates of the ratio R was 0.15, for a mean value of 3.0.

RESULTS AND DISCUSSION

Signal assignments

Paci *et al.*[1] commented on problems with overlapping peaks in ^{13}C n.m.r. spectra of solid styrene-cured polyester resins. The interrupted decoupling pulse sequence reduces the level of interference by suppressing signals from CH and CH_2 groups, as illustrated in *Figure 2*. A strong signal at 129 ppm in *Figure 2a* was assigned to CH groups in the phenyl rings of styrene units and the aromatic rings of isophthalate units. This signal was suppressed by interrupted decoupling (*Figure 2b*), although a weak residual signal was observed in some samples cured with a high styrene content (*Figure 3a*). This peak was therefore not used for quantitative n.m.r. experiments. A signal at 131 ppm, revealed by interrupted decoupling, was assigned to non-protonated aromatic carbon in isophthalate units[9]. Suppression of the signal at 129 ppm permitted more reliable measurements of the area of a band centred on 144 ppm, assigned to C1 of aromatic rings in structural units derived from styrene. This band sometimes showed signs of partial resolution into components at 142 and 146 ppm, with variations in relative strengths, as expected for styrene units in sequences of different lengths[6]. A peak at 165 ppm was assigned to carboxylic carbon in unreacted fumarate and isophthalate structural units[9,10] and a peak at 172 ppm was assigned to carboxylic carbon in the saturated reaction products derived from fumarate structural units. A chemical shift of 173 ppm has been reported for the dimethyl ester of adipic acid, a closely-related model compound[12]. The peak at 172 ppm was relatively weak in spectra of samples cured with relatively low styrene contents (*Figure 3b*), as expected for incomplete reaction of available fumarate. Signals outside the range shown in *Figures 2* and *3* were suppressed by interrupted decoupling.

Residual unsaturation

The ratio $A(172)/[A(165) + A(172)]$ was used as a measure of the content of saturated products derived from fumarate structural units, expressed as a fraction of total dibasic acid structural units. Observations for one sample (see Experimental) suggested that the ratio of response factors for peaks at 165 and 172 ppm would not differ from unity by more than a few percent, so the n.m.r. results were not adjusted to allow for differences in spin relaxation time constants or proportions of signal strength spread into spinning sidebands. Fumarate units accounted for a mole fraction of 0.48 of dibasic acids in the original resin, so any deviation of the ratio below 0.48 was taken as evidence for residual unsaturation.

Reproducibility was tested by running one sample nine times on different days. The mean value of $A(172)/[A(165) + A(172)]$ was 0.445 and the standard deviation was 0.021. For a detection limit set at twice the standard deviation, 8% of the original fumarate structural units would have to remain unsaturated to produce a detectable deviation from a peak area ratio of 0.48. All of the points plotted in *Figure 4* were obtained from spectra run for longer periods of time, so that the signal-to-noise

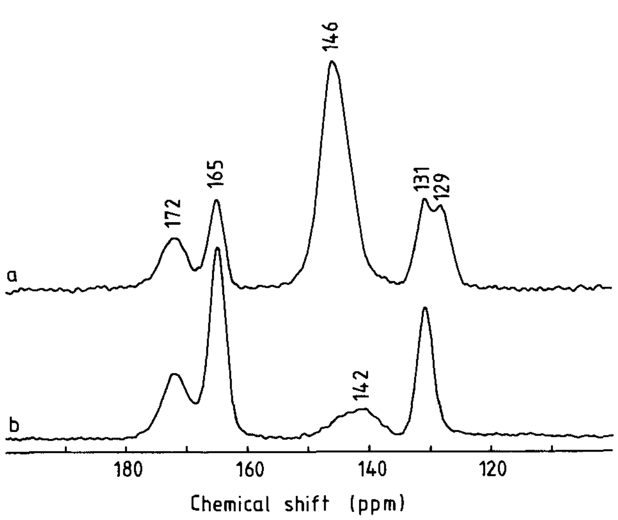

Figure 3 Portions of ^{13}C n.m.r. spectra of solid styrene-cured polyester resin obtained with interrupted decoupling. Mole ratios of styrene to fumarate were (a) $R = 16$, (b) $R = 1.6$. Vertical scaling factors chosen arbitrarily

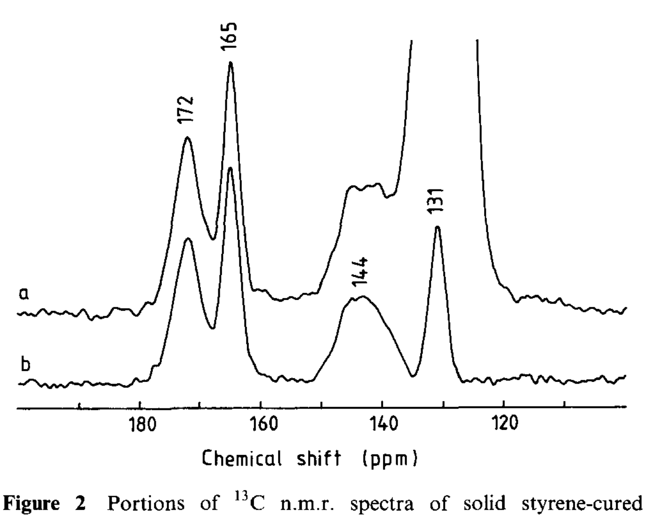

Figure 2 Portions of ^{13}C n.m.r. spectra of solid styrene-cured polyester resin obtained (a) without and (b) with interrupted decoupling. The mole ratio of styrene to initial polyester unsaturation was $R = 0.46$. Chemical shifts are shown above selected peaks

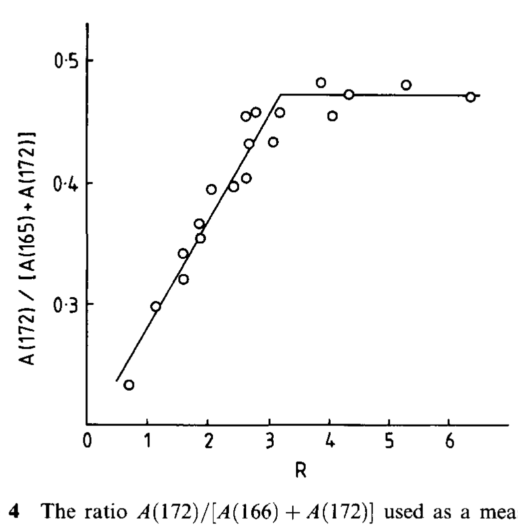

Figure 4 The ratio $A(172)/[A(166) + A(172)]$ used as a measure of fumarate reaction products, deviation below 0.48 being taken as an indication of residual unsaturation. Solid lines represent least-squares best fits. Values of R were determined by n.m.r.

ratio was at least doubled and the detection limit roughly halved.

The 14 points plotted for $R < 3.2$ all fell close to a least-squares best-fit straight line as shown in *Figure 4*. The correlation coefficient was 0.96. The five points plotted for $R > 3.2$ all fell close to a horizontal line drawn through the mean value of $A(172)/[A(165) + A(172)] = 0.472$. A mean value of 0.477 was obtained for three further samples with R in the range 9 to 16, i.e. outside the range plotted in *Figure 4*. The two straight lines meet at $R = 3.2$, corresponding to a styrene content of 47%. These results confirm that the nominal styrene content of the commercial resin solution was very close to the minimum value required to prevent residual unsaturation.

Theoretical residual unsaturation

The consumption of monomers in radical copolymerization can be described by an equation of the form[8]:

$$d[M_1]/d[M_2] = ([M_1]/[M_2])(r_1[M_1] + [M_2])/(r_2[M_2] + [M_1]) \qquad (2)$$

where $[M_1]$ and $[M_2]$ are concentrations of unreacted monomers, r_1 is the ratio of rate constants for the reaction of an M_1-type radical with M_1 and M_2, respectively, and r_2 is the ratio of rate constants for the reaction of an M_2-type radical with M_2 and M_1, respectively. In the present work, M_1 is styrene and M_2 is polyester unsaturation, i.e. fumarate structural units.

An 'azeotropic ratio' R_a is defined as the value of $R = [M_1]/[M_2]$ for which the relative proportions of the two unreacted chemical species are expected to remain constant throughout copolymerization[13,14]. The condition for an azeotropic mixture is[14]:

$$R_a = [M_1]/[M_2] = (1 - r_2)/(1 - r_1) \qquad (3)$$

Values of $r_1 = 0.30$ and $r_2 = 0.07$ have been published for copolymerization of styrene and diethyl fumarate[8]. These lead to a predicted value of $R_a = 1.33$. Results plotted in *Figure 4* show that relative proportions of styrene and polyester unsaturation did not remain constant at this value of R. About 40% of the original polyester unsaturation remained unreacted after all of the styrene had been consumed.

Funke *et al.*[5] estimated a value of R_a for a different resin system by determining the point of intersection of tangents drawn through the initial and final portions of a plot related to that shown in *Figure 4*. The procedure of Funke *et al.* leads, in the present work, to an estimate of $R_a = 3.2$. It is not possible to estimate values of both r_1 and r_2 from an experimental value of R_a, but it seems reasonable to assume that any decrease in the rate of reaction of fumarate with styrene would be accompanied by a decrease in the rate of reaction of fumarate with fumarate. In other words, the condition $r_1 > 0.3$ would be accompanied by $r_2 < 0.07$. With this constraint on r_2, and a value of $R_a = 3.2$, equation (3) provides an estimate of r_1 in the range 0.69 to 0.71.

Computer simulations were used for more rigorous tests of the effects of lowering the rate of the reaction between styrene and polyester unsaturation, compared with the rate of reaction between styrene and diethyl fumarate. Progress towards copolymerization was calculated by numerical integration of equation (2) until one of the reactants was entirely consumed.

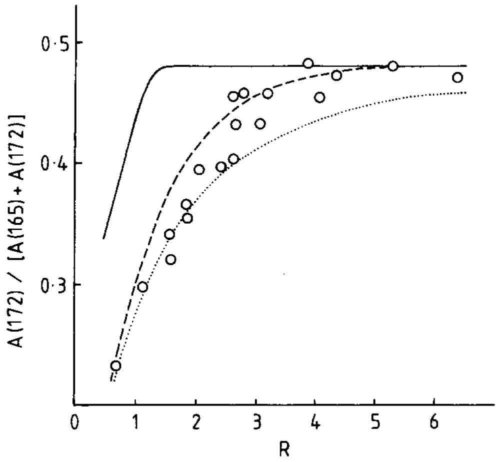

Figure 5 Theoretical curves calculated for a simple statistical model of copolymerization with $r_1 = 0.30$ and $r_2 = 0.07$ (solid line), (b) $r_1 = 1.0$ and $r_2 = 0$ (broken line), (c) $r_1 = 1.4$ and $r_2 = 0$ (dotted line). Experimental data as for *Figure 3*

Figure 5 shows that the simple statistical model of copolymerization with $r_1 = 0.3$ and $r_2 = 0.07$ fails to predict the experimental observations. The fit could be improved by increasing r_1 and decreasing r_2. Values of $r_1 = 1.4$ and 1.0 provided reasonable fits over the ranges $R < 2$ and $R > 3$, respectively, but it was not possible to obtain good fits over both the low-R and high-R ranges. The trial value of $r_2 = 0$ used in *Figure 5* corresponds to a negligible rate for a reaction involving pairs of fumarate double bonds. The quality of the fit in *Figure 5* began to deteriorate further for trial values of $r_2 > 0.01$, but was already so poor that the experimental data could not be used to estimate a reliable value of r_2.

The best-fit value of $r_1 = 1.2$ is considerably higher than the value of 0.7 estimated from equation (3) and the apparent azeotropic ratio. This observation suggests that the method of estimating R_a by drawing tangents is not reliable. In particular, it can lead to an estimated value of R_a even when $r_1 > 1$. The concept of an azeotropic ratio becomes meaningless when $r_1 > 1$ and $r_2 < 1$, as can be demonstrated from the form of equation (3).

Jacobs and Jones[15] have discussed evidence for a heterogeneous matrix structure in styrene-cured polyester resins. This is thought to result from the formation of a weakly linked network, i.e. a gel, followed by diffusion of styrene to localized domains in which chain propagation is relatively active. The copolymerization model could not be expected to describe such a process. In particular, diffusion of styrene between localized domains would result in styrene sequences that are fewer but longer than predicted by the copolymerization model. Levels of residual fumarate unsaturation would therefore be higher than predicted.

Wycherley[4] predicted failure of the copolymerization model beyond gelation in a paper published in 1957. We suggest that imperfections in the fit between theoretical curves and experimental data, evident in *Figure 5*, reflect changes in chain propagation processes imposed by gelation.

Commercial cured products

We examined both surfaces of a commercial fibreglass reinforced petroleum storage tank manufactured from resin obtained from the same source as that used in the present work. We found that the content of styrene reaction products was high on one surface ($R = 4.9$) and low on the other surface ($R = 2.1$) relative to the nominal value ($R = 3.0$). The peak area ratios $A(172)/[A(165)+A(172)]$ were 0.48 and 0.23, respectively. In other words, there was no detectable residual unsaturation on one surface, while about half of the original polyester unsaturation remained unreacted on the other surface. These results show that n.m.r. spectroscopy is sufficiently sensitive to detect variations in compositions, even within a single manufactured object.

Comparison with other studies

Residual unsaturation has been studied by a number of different methods, including chemical degradation[5,16], refractive indices[3], resistivity[17] and infra-red spectroscopy[3,6,16,17]. Of these methods, infra-red spectroscopy has been the most commonly used. The procedure described by Learmonth and Pritchard[3] is based on detection of a band at 985 cm^{-1}, assigned to fumarate unsaturation. The carbonyl band at 1737 cm^{-1} is used as an internal standard. Infra-red spectroscopy has an advantage over n.m.r. spectroscopy in that the experiments are faster. On the other hand, the n.m.r. method seems more reliable. The n.m.r. spectrum shows fewer peaks than the infra-red spectrum, and the baseline is more clearly defined across a wide range of styrene contents (*Figure 3*). Glass reinforcing fibres contribute signals to the infra-red spectra, but not the ^{13}C n.m.r. spectrum. The n.m.r. method can also provide more information, providing estimates for both the styrene/fumarate feed ratio and the degree of residual unsaturation from a single spectrum. The profile of the band centred on 144 ppm might also provide quantitative information about styrene sequence lengths[1,6,7] once precise chemical shifts have been tabulated for the component signals in solid-state n.m.r. spectra.

Despite the diversity of experimental methods available, there have been few systematic studies of residual unsaturation. Four are mentioned here.

Funke *et al.*[5] used styrene to cure a resin prepared from fumaric acid, adipic acid and 1,6-hexanediol. They found levels of residual unsaturation consistent with an azeotropic ratio of 1.3, and concluded that diethyl fumarate was a good model for polyester unsaturation. Their results were consistent with a reactivity ratio of $r_1 = 0.3$. The polymer chains studied by Funke *et al.* would be far more flexible than those studied in the present paper, so problems with steric interactions and rigidity of an intermediate network might not have been as obvious.

Learmonth and Pritchard[3], and Birley *et al.*[6], studied styrene curing at a single styrene content. Learmonth and Pritchard used an orthophthalic polyester resin and a styrene content corresponding to $R = 3.45$. They showed that 96% of fumarate double bonds reacted during curing. Birley *et al.* used a terephthalic polyester resin and a styrene content corresponding to $R = 1.48$. They concluded that the reaction proceeded almost as predicted for copolymerization of diethyl fumarate and styrene, i.e. with $r_1 = 0.3$, at least over the first 15 h. About 86% of the fumarate double bonds reacted over this period. Birley *et al.* stated that the simple statistical treatment failed to describe the course of further curing.

Hayes *et al.*[16] studied two resins, both containing fumarate and propylene glycol structural units. One resin contained additional orthophthalate structural units. In both cases the levels of residual polyester unsaturation were similar to those observed in the present work, at corresponding styrene contents. In particular, Hayes *et al.* found that about 40% of the fumarate double bonds remained unreacted at $R = 1.3$, as in the present work. The results of Hayes *et al.* were therefore not consistent with copolymerization with $r_1 = 0.3$.

CONCLUSION

Comparisons between results presented in this paper and in other papers draw attention to differences in the minimum styrene content required to suppress residual unsaturation or 'undercuring' in different resin/initiator/promoter systems. The variations can be interpreted as reflecting differences in reactivity ratios used in a copolymerization model, although the effects of gelation on chain propagation processes might also contribute to deviations from predictions based on data for copolymerization of diethyl fumarate and styrene.

The results also demonstrate the usefulness of solid-state ^{13}C n.m.r. spectroscopy in determining the styrene content at which residual unsaturation can be suppressed.

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