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A possibility of direct observation of residual styrene in crosslinked polyesters by solid state ^{13}C NMR methods

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SUMMARY

The cross and direct polarization NMR in solid state was employed to study crosslinked polyesters. It was demonstrated that direct-polarization solid state NMR spectra provide an evidence for the presence of residual styrene. In cross-polarization solid state NMR experiment styrene is discriminated against due to its high mobility at ambient temperature.

INTRODUCTION

The unsaturated polyesters (**UPE**) crosslinked by styrene are most widely used in many significant markets, such as machine, electrical, and engineering areas (1) as thermoset resins. The properties of UPE/styrene systems depend on the completion of the reaction between styrene and UPE and on the structure of the polymer network obtained. Investigations of the UPE/styrene systems have revealed that a conversion of double bonds is not complete and a degree of conversion of styrene is low as compared to that of UPE (2). Electron microscopic studies have shown that microstructure of UPE/styrene systems consist of both overlapping high crosslinked domains ("microgel" particles (3)) and amorphous styrene-rich boundary regions with a small density of crosslinking (3,4). It was also concluded that at high styrene concentration the residual styrene acts as a swelling agent of the microgels (3).

Recently solid state cross-polarization NMR method was applied to determine a degree of conversion of styrene in UPE/styrene crosslinked resins (5). In the authors' opinion the absence of significant NMR signal around 114 ppm from vinyl β-carbon of styrene means negligibly small amount of residual styrene. In our work both cross and direct polarization solid state NMR methods were employed to obtain information about residual styrene present in the network of a UPE/styrene thermoset resin.

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EXPERIMENTAL

The UPE resin used in this study was synthesized from a mixture of maleic and phthalic anhydrides. Propylene glycol was used as a diol. The number average molecular mass of the UPE was 2000. The solution of UPE in styrene with an initiator (2% methylethylketone peroxide with 0.2% cobalt naphthenate promoter) was degassed. The system was cured between glass plates for 48 h at 25°C, followed by postcuring for 24 h at 60°C.

High-resolution solid-state ^{13}C NMR spectra were recorded at ambient temperature on a Varian VXR-300 spectrometer operating at a ^{13}C resonance frequency of 75.4 MHz equipped with a solid state probe (Doty Scientific). Both direct (**DP**) and cross (6) (**CP**) polarization techniques with 13 μs 90° pulses for both protons and carbons were used. In order to attain a good signal-to-noise ratio a number of transients in DP experiments was five times of that in CP experiments. The matched spin lock CP transfer employed ^{13}C and ^{1}H magnetic fields of 19.2 kHz; contact time- 0.5 ms. Heteronuclear high-power proton dipolar decoupling (**DD**) field strength was 55 kHz, and a repetition time- 30 s. Chemical shifts were referenced relative to TMS. The sample spinning at magic angle (**MAS**) was carried out at 5.5-6 kHz.

RESULTS AND DISCUSSION

The ^{13}C CP/DD/MAS NMR spectrum is shown in Figure 1a. It closely resembles solid state spectra of similar systems reported by Bellenger at all. (5). This spectrum reveals the absence of any signal around 114 ppm, which could be assigned to vinyl β-carbons of styrene. Figure 1b presents the spectrum recorded without DD during acquisition (CP/NoDD/MAS). All the resonance peaks due to protonated carbons tend to disappear. On the other hand the peaks arising from nonprotonated carbons, i.e. nonprotonated aromatics and carbonyls (signals near 135 ppm and 165 ppm, respectively) do not vanish completely. The latter carbons are not directly bound to protons and are still visible because of a long carbon-proton distance.

The disappearance of all peaks from protonated carbons in CP/NoDD/MAS spectrum as compared to CP/DD/MAS experiments indicates that molecular motion of carbons observed in CP/DD/MAS spectrum is slow relative to the frequency of dipolar decoupling field (of the order of tens kHz). This is not surprising as such frequencies of motion are typical in solid polymers (7). Thus, an appropriate correlation time of this motion, τ_c, is $\tau_c >> 10^{-6}$s at ambient temperature. Finally, we can expect that CP/DD/MAS spectrum is dominated by heavily crosslinked domains in our system.

The spectra shown in Figure 2 were obtained by DP technique. It is clear that aside from all the peaks visible

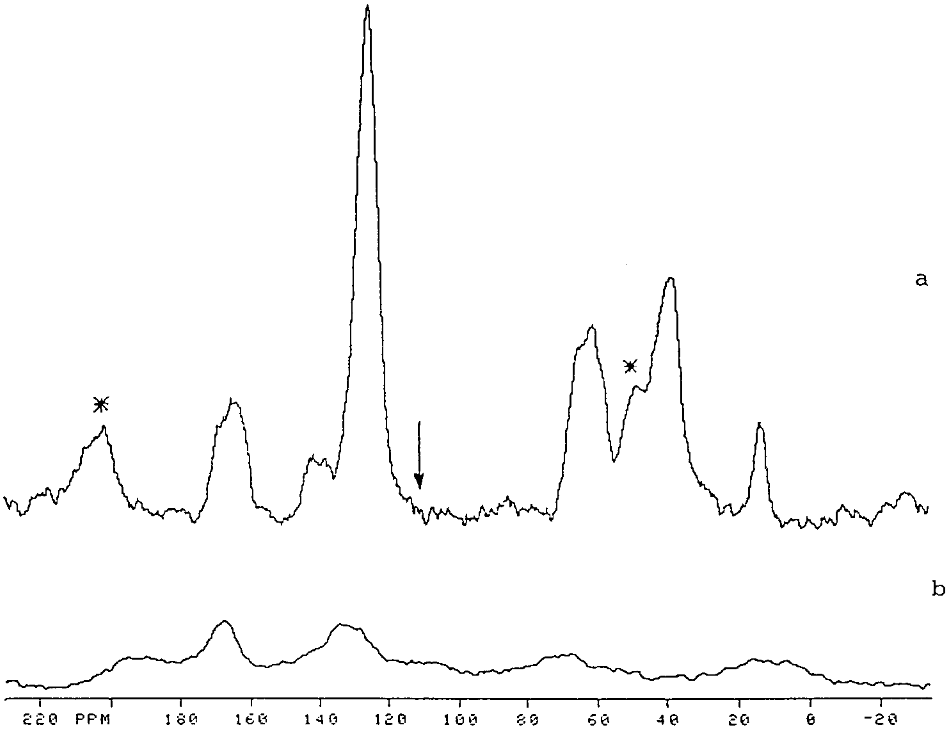

Figure 1. ^{13}C solid state NMR spectra obtained by CP/MAS techniques (number of transients is 200): a- with DD ; b- without DD. The arrow corresponds to a chemical shift value of 114 ppm. The spinning sidebands are denoted by the asterisks.

in CP/DD/MAS experiment, the DP/DD/MAS spectrum (Figure 2a) contains a signal around 114 ppm from the vinyl β-carbons of styrene indicating the presence of residual styrene in crosslinked resin. The spectrum does not reveal any changes upon annealing of the sample for 24 hours at 100°C. Hence a process of additional postcuring at this temperature does not remove the residual amount of styrene.

The spectrum in Figure 2b recorded without DD during acquisition displays overlapped broad signals due to vinyl β-carbon (signal around 114 ppm) as well as protonated and nonprotonated aromatic carbons and vinyl α-carbon of styrene (signal around 130 ppm). A comparison of both spectra (with and without DD) shows that the signals due to styrene's carbons do not vanish when the decoupler is turned off and a molecular motion of styrene is fast relative to the frequency of dipolar decoupling field. Thus correlation time of molecular motions of styrene is $\tau_c << 10^{-6}$s.

In addition we can gain some information about ^{13}C spin-lattice relaxation time, $T_1(C)$, at ambient temperature.

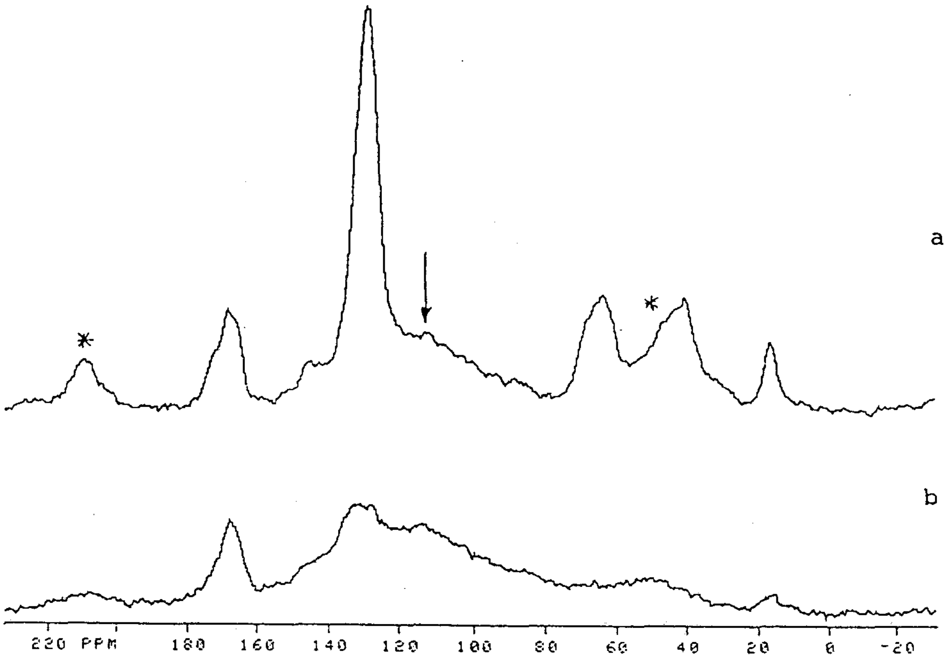

Figure 2. ^{13}C solid state NMR spectra obtained by DP/MAS techniques (number of transients is 1000): a- with DD; b- without DD. The arrow corresponds to a chemical shift value of 114 ppm. The spinning sidebands are denoted by the asterisks.

A comparison of DP/DD/MAS spectrum with the same spectrum obtained with much shorter repetition time (2 s) shows that the amplitude of signals due to styrene's carbons does not vary, because of a short value of $T_1(C) < 0.4$ s. On the other hand,a comparison of DP/DD/MAS and CP/DD/MAS spectra (Figures 1a and 2a) demonstrates that even 30 s repetition time is not sufficient for complete relaxation of the carbons of polymer, at least in heavily crosslinked domains; hence $T_1(C)$ of these carbons is longer than 10 s. In fact, the value of $T_1(C)$ determined by the method of Torchia (8) was, for instance, ca. 30 s for protonated aromatics.

As shown, the signals from styrene's carbons at ambient temperature can be observed only in the DP experiment. However they are very broad and no quantitative analysis of the number of the residual double bonds of styrene can be made at present. Investigations at lower temperatures are required to make styrene's carbons observable in CP/MAS experiment, which combined with dipolar decoupling should facilitate an evaluation of the amount of styrene in this system.

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