Heteronuclear two-dimensional n.m.r. study of polymers: ^{13}C–^{1}H shift correlations for resonances from 1-cyano-1-methylethyl end groups

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End-group 1-cyano-1-methylethyl resonances from copolymers of phenyl methacrylate or methyl methacrylate with styrene have been examined using a phase-sensitive two-dimensional ^{13}C–^{1}H shift-correlation experiment. Proton shift values for the methyl resonances, totally obscured on one-dimensional ^{1}H spectra, could be identified and microstructural information observed.

(Keywords: polymerization; end groups; two-dimensional n.m.r.; methacrylates; styrene; azoisobutyronitrile)

Studies of initiator-derived end-group responses from polymers and copolymers have provided extensive information concerning the initial stages in polymerization processes. They also give data which may be of importance in connection with both chemical and physical properties of these materials. Radical initiation at 60°C of methyl methacrylate (MMA) and of styrene (STY) homopolymerizations using azobisisobutyronitrile (AIBN) enriched with ^{13}C gives rise to easily recognizable ^{13}C responses[1]. Relative velocity constants for addition of the 1-cyano-1-methylethyl radical to these and other monomers during copolymerizations using [^{13}C]AIBN can readily be determined[2]. Reactivities of monomers towards the 1-cyano-1-methylethyl radical at 100°C can be ascertained using end-group resonances derived from 1-cyano-1-methylethyl-azoformamide (AZOF) suitably enriched[3] with ^{13}C.

There are many situations where the extraction of quantitative information from end-group resonance signal data is problematical. For example, in the study of isotopically enriched chain ends derived from the 1-phenylethyl radical[4,5], it was necessary to employ difference spectroscopy techniques, which rely on the subtraction of backbone responses obtained from a second sample prepared under closely similar conditions using unenriched initiator. In the examination of polymers and copolymers of ethyl acrylate (EA) the two methyl resonances from 1-cyano-1-methylethyl end groups attached to this monomeric unit were almost coincident[6], in strong contrast to the situation when MMA is the first unit and where chiral effects induce a shift difference of 4–5 ppm between the two groups of resonances.

For most homo- and copolymers, direct observation of methyl proton resonances from 1-cyano-1-methylethyl chain ends is not possible, because first these protons cannot be isotopically enriched to increase their n.m.r. responses relative to those of other signals, and second they occur in a spectral region dominated by very intense aliphatic resonances arising from monomeric units.

Many two-dimensional (2-D) n.m.r. experiments now exist by means of which complex spectral systems can be rendered more amenable to study through the introduction of a second frequency axis. As part of our programme in the investigation of polymer end groups, phase-sensitive 2-D chemical shift correlation methods are being employed to generate chemical shift contour maps on which peak coordinates lead to simultaneous identification of ^{13}C and ^{1}H chemical shift positions for each resonance on the spectrum. The results of preliminary experiments are now reported.

A copolymer of phenyl methacrylate (PMA) and STY was prepared using [^{13}C]AIBN at 60°C, and a copolymer of MMA and STY was obtained using [^{13}C]AZOF at 100°C. Conditions were such that both materials contained enriched 1-cyano-1-methylethyl end groups attached in comparable proportions to each type of monomeric unit and sample purification by reprecipitation followed established procedures.

N.m.r. spectra were recorded at ambient temperature in $CDCl_3$ solution using a Jeol GSX-400 Fourier transform spectrometer fitted with a 5 mm multinuclear probe. For these preliminary 2-D experiments, the aliphatic spectral region was selectively observed using a ^{13}C spectral width of 4201.7 Hz and a ^{1}H spectral width of 1200 Hz (PMA-STY) or 1500 Hz (MMA-STY). Both ^{13}C and ^{1}H 90° pulse widths were directly determined for the samples under examination and a final $1/4J$ delay time was chosen, to ensure that all responses were positive. A total of 256 t_1 increments was collected, each from 96 acquisitions, and 2K data points. Processing involved 2 Hz exponential broadening for the ^{13}C (t_2 axis) and no broadening for the ^{1}H (t_1 axis) transform. Zero-filling was employed to yield a final data matrix containing 1K × 1K pairs of points.

Figure 1 shows the complete 2-D correlation map for the aliphatic signals of the PMA-STY copolymer. This sample was chosen because on both the ^{1}H and the ^{13}C spectra very strong aromatic resonances are located outside the chemical shift ranges chosen for the 2-D acquisition. There is no evidence for any of these resonances being 'folded' into the region under examination. When a normal ^{13}C spectrum was determined for the aliphatic region using an identical observation window, a weak response from a 'folded' $CDCl_3$ solvent

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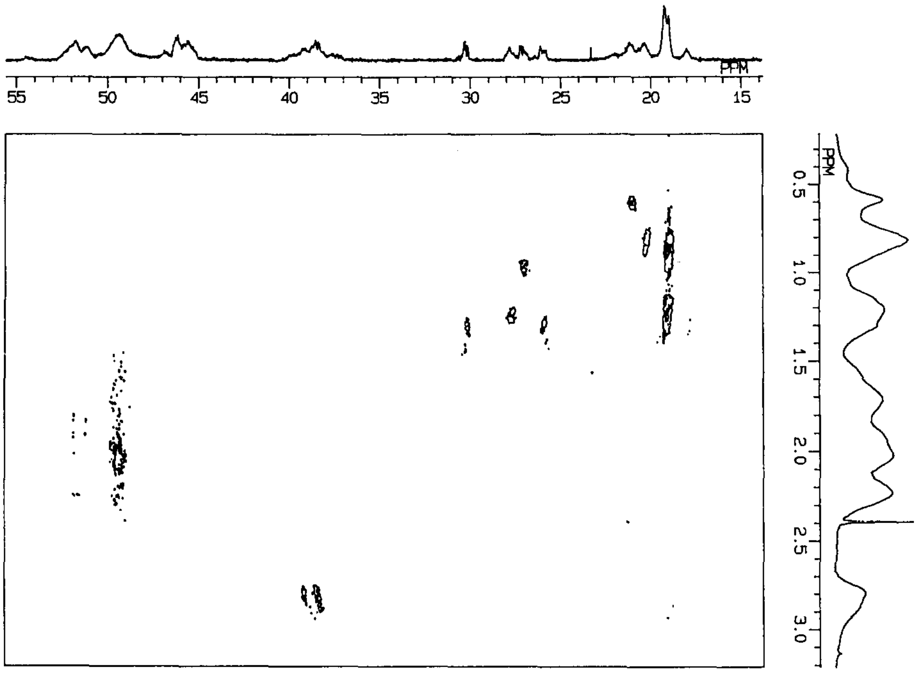

Figure 1 Phase sensitive ^{13}C–^{1}H correlation plot for the aliphatic region from a PMA-STY copolymer

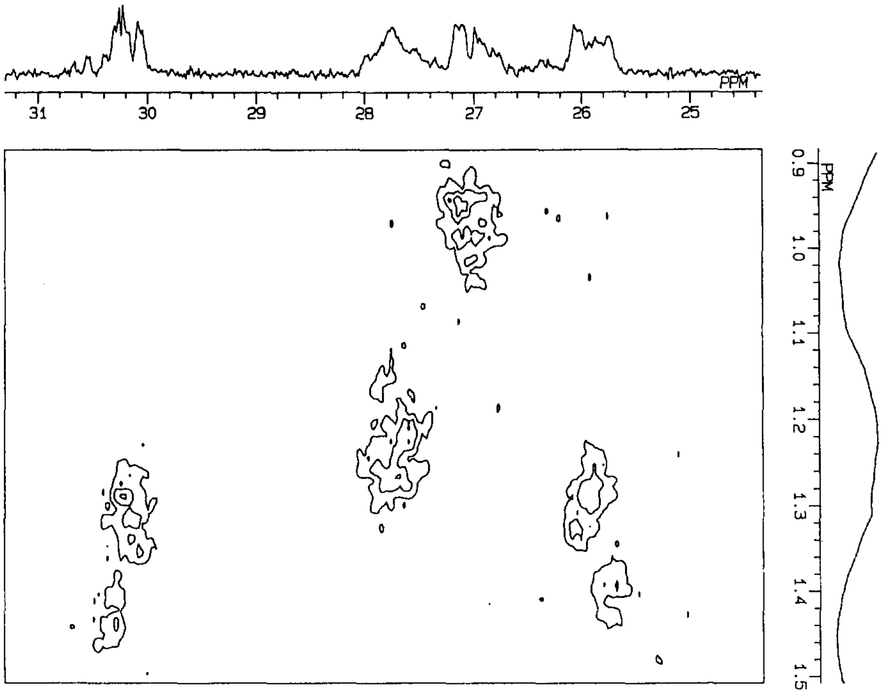

Figure 2 Expanded 2-D correlation plot for ^{13}C-enriched methyl resonances from 1-cyano-1-methylethyl end groups attached to a PMA-STY copolymer

resonance was observed but no aromatic carbons could be seen. Under the conditions employed for the 2-D experiment, only protonated carbons are detected; thus no weak folded $CDCl_3$ response is present, nor are any signals seen from the quaternary carbons in PMA units (although the latter may be seen on the carbon axis one-dimensional (1-D) spectrum which is derived from high-resolution data rather than a projection).

The 2-D responses from ^{13}C-labelled end-group carbons are shown in detail in *Figure 2*. The structures of such end-group signals from methacrylate-STY copolymers are complex. The two well-separated ^{13}C methyl signal regions from initiator fragments attached to PMA units fall at 30–31 and 25.6–26.4 ppm; those on STY units are intermediate at 27.3–28.1 and 26.6–27.3 ppm.

Examination of the ^{1}H shift axis shows that the shift positions can be clearly observed for protons attached to both enriched methyl sites, for each of the two types of chain end. As is seen from the 1-D ^{1}H spectrum, these resonances could never be directly observed for they are located under bulk polymer responses which are orders of magnitude greater in intensity.

It is apparent that cross peaks from enriched sites

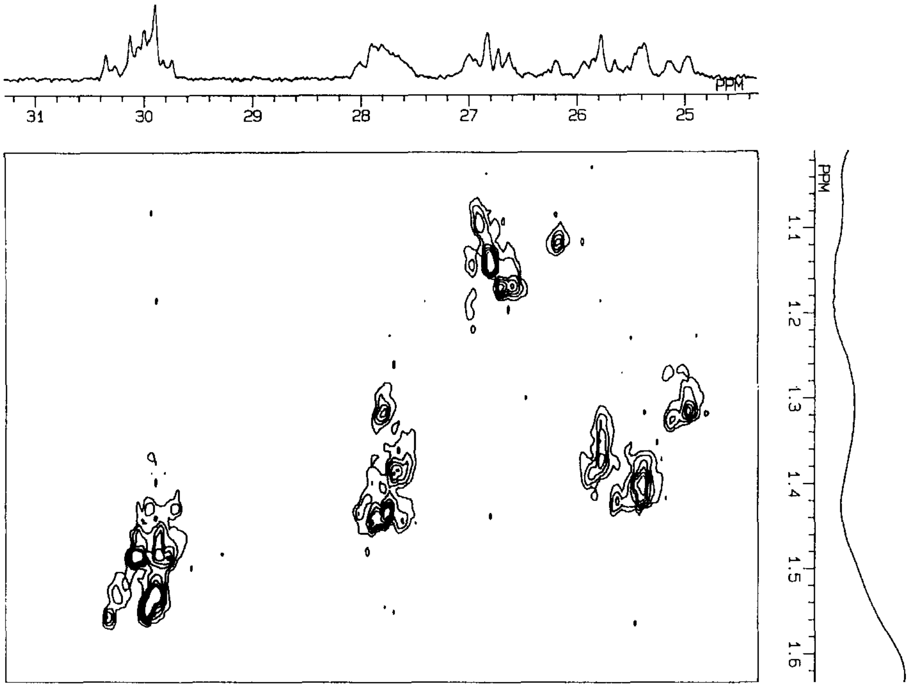

Figure 3 Expanded 2-D correlation plot for ^{13}C-enriched methyl resonances from 1-cyano-1-methylethyl end groups attached to a MMA-STY copolymer

adjacent to either PMA or STY units are totally separated from all other responses on the 2-D map and that they contain considerable structural detail. It is of interest that, on the proton axis, the shifts from methyls next to STY units are well separated, and they are upfield from the closer spaced methyls at PMA sites.

Relative sizes for these cross peaks should be obtainable from determination of peak volumes. Although the PMA methyl proton resonances are similar in their chemical shift ranges, the carbon shifts are well separated and the two components are therefore readily observed. If for an EA polymer[6], proton shifts from the corresponding end-group methyls were resolvable, separate observation of the two signal sets would then become possible. In general, provided that proton shifts for end-group resonances are distinct from proton shifts for in-chain signals, they would be separately observable on a 2-D map even when, as for example with the 1-phenylethyl end groups[4,5], they are overlaid by non-enriched backbone resonances on the 1-D ^{13}C spectrum.

Figure 3 shows an expansion of the 1-cyano-1-methylethyl end-group cross-peak region for the MMA-STY copolymer. Although the aliphatic proton chemical shift range is greater due to the presence of methoxyl resonances, there is still no interference from the aromatic protons of STY units. There is extensive structural complexity which arises both from tacticity variation and from copolymer sequence effects.

Experimental conditions have not yet been optimized. It is likely that improvements in 2-D spectral resolution will be achievable. For these relatively sharp resonances from end-group methyls, it is probable that the application of maximum entropy processing methods during the second (i.e. t_1) Fourier transform would give rise to significant sharpening. Such approaches to resolution enhancement in the manipulation of 1-D (natural) polymer spectra[7] have already proved to be very promising.

As is seen in *Figure 1*, ^{13}C–^{1}H cross peaks from the broad in-chain polymer resonances are also obtainable. The experiment described here was not intended to afford optimum responses for such systems; the use of different heteronuclear correlation experiments, where the evolution period is minimized in order to attenuate problems arising from rapid relaxation processes, could yield better results. A modified long-range COLOC correlation experiment has already been used[8] for the examination of one-bond ^{13}C–^{1}H correlations in cases where very broad resonances precluded application of more conventional 2-D approaches.

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