SHORT COMMUNICATIONS

$^{13}C=O$ NMR Signal Assignments for Poly(n-butyl methacrylate-co-methyl methacrylate). Application of $^{13}C-^1H$ Correlation Spectroscopy and ^{13}C Labelling

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In a recent report we described how long range $^{13}C-^1H$ chemical shift correlation spectroscopy[1] could be applied to give unambiguous peak assignments for pentads in poly(methyl methacrylate).[2] Recent papers by Brar et al.[3,4] on NMR analysis of copolymers of methacrylate esters prompted us to make this preliminary report on our efforts to apply $^{13}C-^1H$ correlation spectroscopy to the study of such copolymers.

In the previous study[2] we demonstrated that $^{13}C-^1H$ correlation spectroscopy on polymers could be rendered more practicable by the use of polymers prepared from monomers specifically labelled with ^{13}C. With 99% enriched monomer, the labelled carbons (and solvent) give rise to the only signals of significant intensity in the ^{13}C NMR spectrum. This facilitates the use of very narrow spectral widths (and thus high data point resolution) in the ^{13}C dimension without incurring problems due to spectal foldover and enables adequate signal-to-noise spectra to be obtained on dilute polymer solutions in a reasonable time.[2]
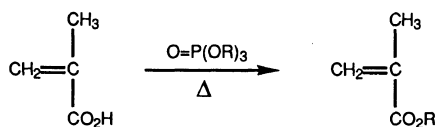
Alkyl *carbonyl*-^{13}C-methacrylates are readily prepared in high yields and purity by heating *carbonyl*-^{13}C-methacrylic acid with the appropriate trialkylphosphate and with simultaneous distillation of the product (Scheme 1).[5] Methyl *carbonyl*-^{13}C-methacrylate and butyl *carbonyl*-^{13}C-methacrylate were prepared in this manner. Copolymers ($\bar{M}_n$ ca. 100000) of these monomers were prepared at 60°C in benzene with AIBN as the initiator. Figures 1a—c show the ^{13}C NMR spectra of the copolymers.

The pattern of peaks due to MMA centred sequences and BMA centred sequences show close similarity (compare Figures 1b and c). However, the BMA centred sequences appear slightly to higher field (lower ppm). It is clear from the spectra that the chemical shift changes induced by tacticity are significantly greater than those induced by the monomer sequence distribution (the type of ester alkyl group). In the 62.9 MHz spectra, it appears that the chemical shift of the carbonyl carbon is sensitive to the configuration of the monomer unit at the heptad level (at least) but to the nature of the ester groups on adjacent units only at the triad level. This is demonstrated by the fact that the spectra of the copolymers shown in Figures 1b and 1c closely resemble
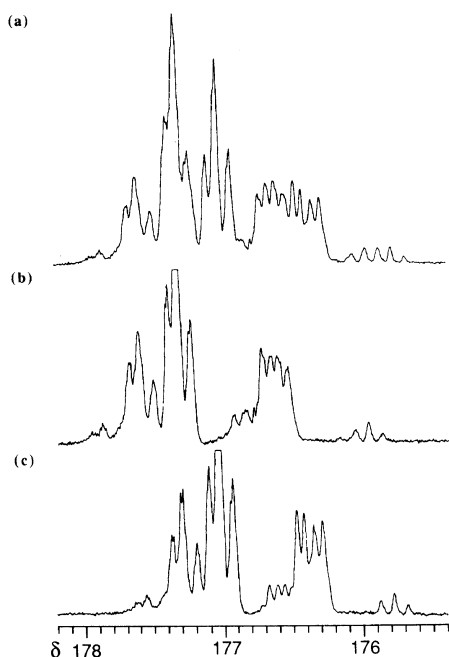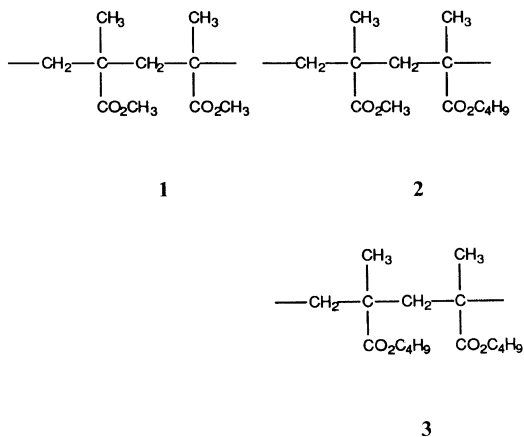
Scheme 1.

to rely on arguments other than solely statistical ones, when making NMR peak assignments, and illustrates how easy it is to be mislead by fortuitous agreement between calculated and observed peak intensities.

Figure 1. Carbonyl regions of the 62.9 MHz ^{13}C NMR spectra (chlorobenzene-d_5, 100°C) of (a) poly(n-butyl methacrylate-*carbonyl*-^{13}C-*co*-methyl methacrylate-*carbonyl*-^{13}C), (b) poly(n-butyl methacrylate-*co*-methyl methacrylate-*carbonyl*-^{13}C) and (c) poly(b-butyl methacrylate-*carbonyl*-^{13}C-*co*-methylmethacrylate).

the NMR spectra of the corresponding homopolymers of MMA[5] and BMA respectively but with each resonance tripleted. This is further supported by the recent work of Hatada et al.[6] who reported spectra for stereoregular MMA–EMA copolymers. Thus, we believe the peak assignments reported for BMA–MMA copolymers by Brar and Kapur[4] are in error. These authors assigned signals in the carbonyl region to only compositional triads and ignored the possible effects of tacticity on chemical shifts.

The appearance of the carbonyl region is strongly solvent dependent. We found chlorobenzene-d_5 at 100°C to be the preferred solvent. No resolution due to monomer sequence distribution was observed with deuterochloroform as solvent (as used by Brar and Kapur). This example highlights the need

It was hoped that signals might be unambiguously assigned at the triad level by examining the 2D NMR contour plot. For example, one can envisage that backbone methylenes should be correlated to two methoxyls (if part of a MMA–MMA dyad **1**), to a butoxyl and a methoxyl (if part of a BMA–MMA dyad **2**), or to two butoxyls (if part of a BMA–BMA dyad **3**).

The ^{13}C–^{1}H correlation spectrum of the doubly labelled copolymers is shown in Figure 2. Strong cross peaks corresponding to the methoxyl hydrogens are visible and a cross section parallel to the ^{13}C axis through these peaks shows strong similarity to the spectrum shown in Figure 1b. However, cross peaks to the butoxyl methylene are essentially absent. The cross peaks to the butyl methylene were also found to be very weak in the ^{13}C–^{1}H correlation spectrum of BMA homopolymer.

A number of factors may contribute to the extreme weakness of cross peaks due to the butoxy methylene. First, it should be noted that if the butoxy methylene of a BMA unit gives rise to a first order triplet in the ^{1}H spectrum, then the absolute intensity of the cross peak to
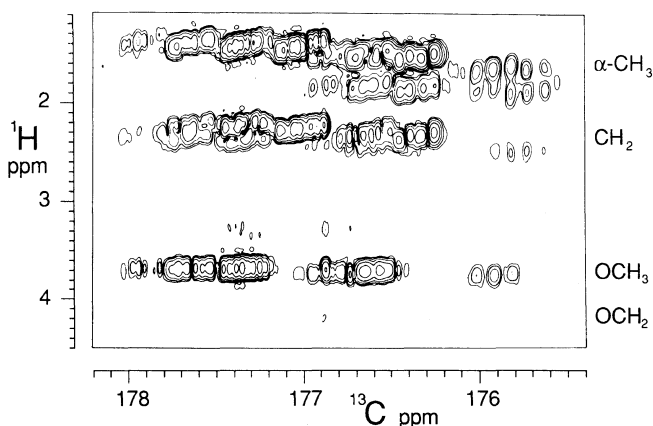
Figure 2. Contour plot from $^{13}C-^1H$ correlation spectrum (chrorobenzene-d_5, 100°C) of copolymer of poly(n-butyl methacrylate-*carbonyl*-^{13}C-*co*-methyl methacrylate-*carbonyl*-^{13}C). Acquisition parameters were the same as used previously.[2]

the butoxy methylene is expected to be at most 33% of that of the methoxyl (the methoxyl of a MMA unit appears as a singlet).

Secondly, the values of the coupling constant based delays (τ_1 and τ_2) set in the pulse sequence[7] may not be optimal. A range of values of τ_1 and τ_2 (corresponding to $^3J_{CH}$ in the range 4—20 Hz) were tested without improving the results. Large values of τ_1 and τ_2, corresponding to $^3J_{CH} < 5$ Hz made the pulse sequence excessively long with respect to the relaxation times resulting in poor overall signal strength.

Thirdly, while values of $^3J_{CH}$ to the hydrogens of freely rotating vicinal methyl and methylene groups in esters have been found to lie in the range 3.2—4.5 Hz,[8] the coupling constant $^3J_{CH}$ may be lower (or higher) than the expected value if the butoxy group is not able to undergo free rotation and the two methylene hydrogens are non-equivalent. The butoxy methylene hydrogens are vicinal to the carbonyl carbon and the value of the coupling constants should obey a Karplus relationship.[9] Under these circumstances it is

also not possible to rule out second order effects.

Studies on these systems are continuing.

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