^{13}C nuclear magnetic resonance of propylene/butene copolymers. Reassignment of —PB— centred tetrads

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Three papers have appeared on the ^{13}C nuclear magnetic resonance (n.m.r.) spectra of propylene/butene copolymers[1-3]. Bunn and Cudby[1] published first, having studied a wide range of copolymer compositions and assigned all the resonances they observed in the spectra. Fisch and Dannenberg[2] examined copolymers with up to 13 mol% propylene and, in addition to assigning the resonances in their spectra, they showed that the ^{13}C n.m.r. spectra of these copolymers could be used for quantitative analysis. Randall[3] covered both instrumental conditions necessary to achieve quantitative results and assignments of the resonances.

The assignments in the latter papers agreed with Bunn and Cudby[1] except for Randall's assignment of the resonances from the –PB– centred α,α-methylene group. The difficulty which arises with this assignment is that only two resonances have been found which could arise from the four possible tetrads i.e. PBPP, PPBB, BBPB and PBPB. The authors of this note have reconsidered jointly their two sets of data, and combined with some better signal-to-noise spectra, have shown that neither of their previously published assignments for the resonances from the –PB– tetrads was correct. This report details the evidence on which we base a revised assignment. In the following discussion the chemical shift values quoted are those found in Randall's paper[3].

Bunn and Cudby studied copolymers having a wide range of comonomer composition including block and 'random' distributions, and based their assignments on an empirical approach. When Randall assigned the resonances of the –PB– α,α-methylenes, he assumed that the 43.1 ppm resonance, shown conclusively by Fisch and Dannenberg to arise from BBPB sequences, corresponded to the 43.3 ppm resonance in his work. Randall then deduced the assignments of the other three –PB– tetrad sequences by: (i) noting the intensity changes with composition; and (ii) the use of the relationships for tetrad concentrations and tetrad/triad concentrations[4]. However, he considered that the assignments were tentative for the –BP– centred tetrads, although reasonable considering the information available.

Re-appraisal of the data

The spectra of *Figures 1–3* were taken under conditions described previously[1], and show the region 40–50 ppm of the ^{13}C n.m.r. spectra of propylene/butene (P/B) copolymers. Copolymer A (*Figure 1*) contains a small amount of butene and the absence of a resonance at 40.3 ppm, arising from BB centred tetrads[3], shows that butenes are present as isolated units i.e. PBP. Thus only two –PB– centred tetrads are possible: PBPP and PBPB. The latter possibility can be eliminated, since an examination of the resonances of the propylene and methyl group failed to show the presence of –BPB triads. Thus the sequence PPBP gives rise to a resonance at 43.3 ppm in agreement with our previous assignment.

The spectrum in *Figure 2* is of a propylene/butene copolymer (copolymer B), low in propylene, and is the same polymer whose spectrum is given in *Figure 2a* of ref 1. The previously published spectrum showed that there are no significant levels of BPP and PBP triads (from the propylene α-methyl and butene branch methylene resonances respectively). Thus the 43.6 ppm resonance in *Figure 2* cannot arise from BBPP, PPBP or BPBP tetrad sequences since each contains BPP and/or PBP triads. Thus the 43.6 ppm resonance in *Figure 2* arises from BBPB tetrad sequences. When a spectrum was taken of a mixture of copolymers A and B, then two resonances are observed at 43.4 ppm and 43.6 ppm, showing that these are truly distinguishable. Thus, Randall's 43.6 ppm resonance corresponds to Fisch and Dannenberg's 43.1 resonance and is the BBPB tetrad. The relatively large discrepancy in these chemical shift values is not caused by a referencing zero error, as there is good agreement between

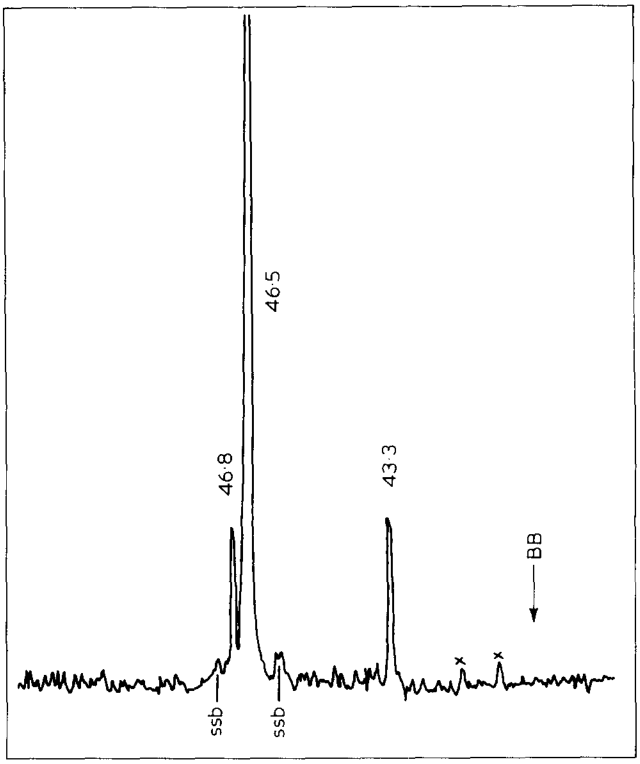

Figure 1 25.2 MHz ^{13}C n.m.r. spectrum of copolymer A, a propylene-rich copolymer with butene units as PBP sequences. Peaks marked x are from d_6-DMSO lock

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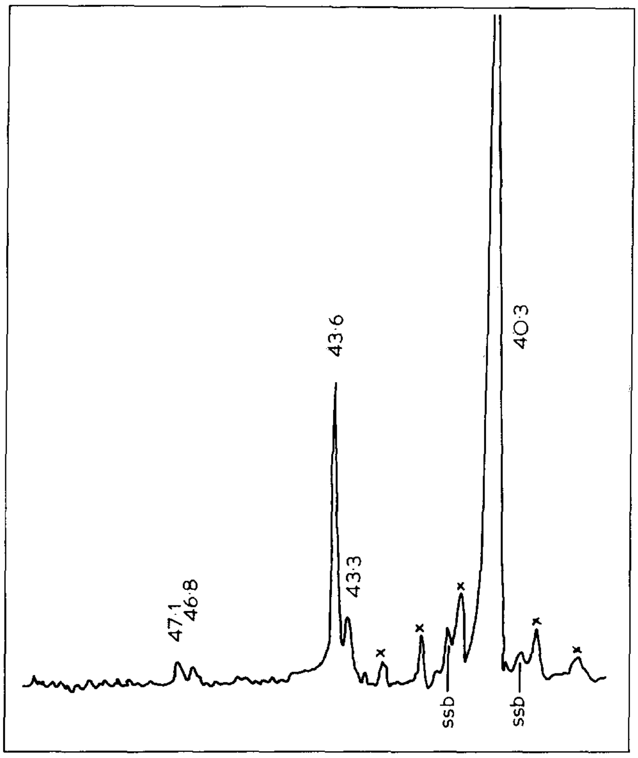

Figure 2 25.2 MHz ^{13}C n.m.r. spectrum of copolymer B, a butene-rich copolymer with nearly all the propylene copolymerized as BPB sequences. Peaks marked x are from d_6-DMSO lock

Randall's and Fisch and Dannenberg's data elsewhere in the spectra. Possible causes of the discrepancy are a solvent effect or a temperature variation[5] of the chemical shift value for the resonance of the BBPB tetrad. Randall used 1,2,4-trichlorobenzene at 123°C whilst Fisch and Dannenberg used deuterochloroform at 50°C.

We have found positions for the resonances from PPBP and BBPB tetrad sequences. We now consider the BBPP tetrad sequence. The region associated with PP centred tetrads in *Figure 2* shows small resonances from BPPB (47.1 ppm) and BPPP (46.8 ppm). Thus, in addition to the majority of propylene being in BBPB sequences in this butene-rich polymer, small amounts are present as

BBPPBB (1)

BBPPPBB (2)

but longer P sequences are excluded because the resonance associated with PPPP is absent. Considering tetrad possibilities from (1) and (2):

(1) gives 1 BPPB and 2 BBPP

(2) gives 2 BPPP and 2 BBPP

Thus, if the small 43.3 ppm resonance in *Figure 2* occurs because of BBPP sequences then:

Intensity 43.3 ppm resonance = Intensity 46.8 ppm resonance

+ 2 x Intensity 47.1 ppm resonance

Visually, this seems to be the case, so in this spectrum the 43.3 ppm resonances arises from BBPP tetrads.

Additional evidence for the assignment of the BBPP tetrad at 43.3 ppm is shown in *Figure 3*. The same copolymer has been used to obtain this spectrum as was used for *Figure 2b* in Bunn and Cudby[1] but the signal-to-noise is considerably improved. Although the copolymer contains long sequences of propylene and butene, the ^{13}C n.m.r. spectrum does show resonances associated with PB centred tetrads. The propylene α-methyl groups show resonances characteristic of PPP and PPB triads, but only negligible amounts from BPB triads. Therefore, it seems unlikely that the 43.3 ppm resonance in this spectrum arises from tetrads containing BPB sequences. This rules out BBPB and PBPB and leaves PBPP and PPBP. Since there is no significant resonance from the butene branch methylene at the position associated with the PBP triads, the presence of the PBPP tetrads can be discounted. Thus the 43.3 ppm resonance in *Figure 3* arises from BBPP tetrad sequences. The sequence is presumably –PPPPBBB– which gives one PPPB sequence for each PPBB sequence: this is observed since the intensities of the 46.8 ppm and 43.3 ppm resonances are equal. As this copolymer was prepared by initially polymerizing propylene, then continuing the polymerization with a large excess of butene, any residual propylene after the first stage of the polymerization would have been polymerized in an excess of butene. It is reasonable that the small 43.6 ppm resonance in *Figure 3* occurs because of a small number of BBPB sequences.

The final tetrad to be considered is PBPB. In Bunn and Cudby's paper the spectrum from a P/B copolymer (*Figure 2*, ref 1) with about 10 mol % butene, mainly as PPBP tetrad sequences, also showed a resonance from BB centred tetrads. However, a small resonance at 43.04 ppm (corresponding to 43.6 ppm in Randall's paper) was observed; and as there were no BBB sequences (based on evidence from butene branch methylene resonances) Bunn and Cudby assigned this to PPBB sequences. We now know this conclusion to be incorrect for the following reasons. In propylene rich co-

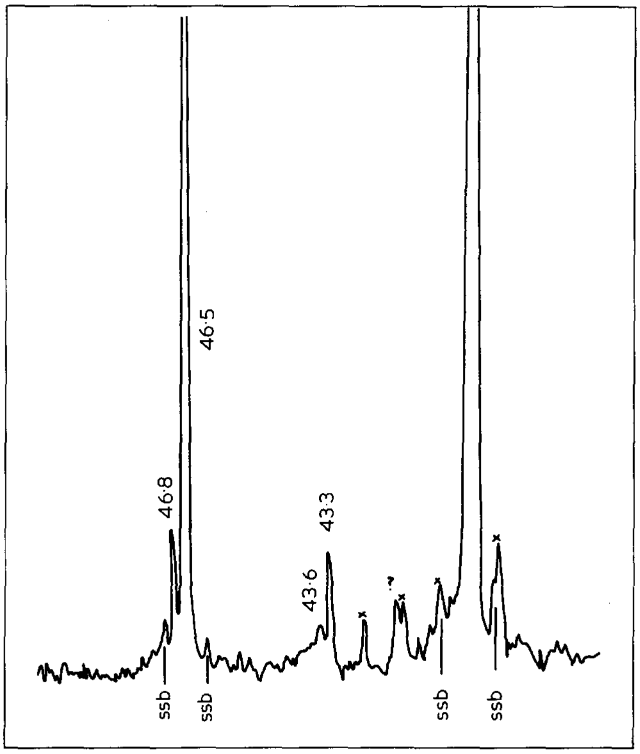

Figure 3 25.2 MHz ^{13}C n.m.r. spectrum of a propylene/butene block copolymer. Peaks marked x are from d_6-DMSO lock

polymers, BB sequences would be present as –PPBBPP– and the intensity of the resonance from the PPBB tetrads would be twice the intensity of the resonance from the PBBP. This is not the case, as in *Figure 2* ref 1 the intensity of the 43.04 resonance is very nearly equal in intensity to resonance from the PBBP tetrad and not a factor of two as required. Additionally the evidence cited earlier showed that the PPBB tetrads give rise to the higher field –PB– resonance (43.3 ppm). Therefore, in view of the composition of the copolymer, the 43.04 ppm resonance in *Figure 2c* of Bunn and Cudby's paper[1] is assigned to PBPB sequences, not PPBB.

The necessary tetrad relationship[4]

$$\mathrm{PPBB + PPBP = PPPB + 2BPPB} \qquad (3)$$

is satisfied for the spectra shown in *Figures 1–3* and *Figure 2c* in Bunn and Cudby's paper. In copolymer A (*Figure 1*) the tetrad sequences PPBB and BPPB are absent and the intensities of the 46.8 ppm and 43.3 ppm resonances are equal so:

$$\mathrm{PPPB = PBPP}$$

Copolymer B has no PPBP sequences and the resonance intensities are such that:

$$\mathrm{PPBB = PPPB + 2BPPB}$$

In the earlier discussion of *Figure 3* we showed that BPPB and PBPP ≈ 0 and that the 46.8 ppm and 43.3 ppm resonances were equal so that:

$$\mathrm{PPPB = PPBB}$$

thus (3) is satisfied for *Figure 3*.

The spectrum in *Figure 2c* of Bunn and Cudby's paper shows no evidence for BPPB sequences. Therefore (3) reduces to:

$$\mathrm{PPBB + PPBP = PPPB}$$

The PPBB and PPBP tetrad sequences give a resonance at 42.76 ppm and is seen to be equal in intensity to the 46.10 ppm resonance assigned to BPPP tetrad sequences.

The assignments for –BP– centred tetrads we now propose are:

$$\left.\begin{array}{l}\text{PBPP and PPBB 43.6 ppm}\\ \text{BBPB and PBPB 43.6 ppm}\end{array}\right\}\ \text{Randall's chemical shift valu}$$

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Association behaviour of poly(4-vinylbiphenyllithium) and substituted polydienyllithiums in n-hexane

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In connection with a systematic study of the anionic copolymerization of 4-vinylbiphenyl with substituted butadienes, using organolithium initiators, we required information about the degree of aggregation of the living polymers derived from these monomers. A survey of the literature revealed that the most convenient means to this end is by measurement of the viscosity of concentrated solutions which conform to the equation:

$$\eta = KM^{3.4} \qquad (1)$$

in which η is the viscosity, M the molecular weight and K a constant. It has been shown that this equation is valid provided that:

$$\nu_2 M > 2M_e \qquad (2)$$

where ν_2 is the volume fraction of polymer and M_e is the molecular weight between entanglements[1,2].

Morton and coworkers[3–5] devised a procedure whereby the flow time of a solution of polystyryllithium in a viscometer could be measured under high vacuum, both before and after terminating the carbanions with a trace of alcohol. Designating these flow times, respectively, as t_a and t_t, these are related to the mean degree of aggregation N of the living polymer by the equation:

$$t_a/t_t = N^{3.4} \qquad (3)$$

An important extension of this procedure was developed by Morton *et al.*[6]: by 'capping' polystyryllithium by the addition of a *few* units of isoprene or butadiene they were able to establish unequivocally that all three of these active chain ends are virtually completely dimerized. These results have been confirmed by light-scattering studies[6,7].

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