^{13}C Spin Relaxation Parameters of Branched Polyethylenes. Ramifications for Quantitative Analysis

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ABSTRACT: The carbon-13 spin relaxation parameters of ethylene–*n*-alkane copolymers and low-density (branched) polyethylene were determined to establish conditions for the quantitative analysis of the branching and chemical nature of the side groups as well as to obtain information about the chain dynamics. The spin–lattice relaxation times of the different carbons are such as to require long ($\simeq$30 s) delays between scans to prevent variable saturation of the resonances. Full nuclear Overhauser enhancement factors are observed which simplifies the quantitative analysis. The measured T_1's indicate that longer chain branch length increasingly restricts main chain motion near the branch points. The segmental motions of the side chains are relatively rapid, with especially rapid internal motion noted for the chain-end CH_3 groups.

In the past several years ^{13}C NMR spectroscopy has been used increasingly to study synthetic high polymers.[2] This technique has proven quite useful in the determination of polymer microstructure such as stereoirregularity as well as an analytical tool for compositional studies.[3] The nature of Fourier transform techniques, which are now invariably used to acquire the data, requires a relatively detailed knowledge of the relaxation parameters of the particular polymer[4] investigated if the subsequent analysis is to be quantitative and unambiguous. For example, the choice of pulse delays and, possibly, pulse angles is dependent upon the spin–lattice relaxation times (T_1's) of the nonequivalent polymer carbons. Thus a true equilibrium spectrum must satisfy the condition that a spectrum is pulsed (acquired) only after a time of approximately 4–5 × T_1(max) has elapsed since the last pulse. This is sufficient time to allow the magnetization that is to be sampled to recover to 98% of its equilibrium value. T_1(max) is the longest relaxation time of the carbons of interest in the molecule. Although shorter delays used in conjunction with less than 90° pulse angles may be optimally used for certain small ranges of relaxation times, the presence of a number of quite different relaxation times makes quantitative analysis impossible in this limited nonequilibrium situation. Delays that are too short with respect to some T_1's will result in preferential saturation of those carbon resonances; thus integrated peak intensities will be misleading.

Another problem of concern is the possibility that different carbons in the same molecule possess different nuclear Overhauser enhancements (NOE). The concentration of different groups or isomers obtained from the integrated intensities may be seriously affected by such a phenomenon. This problem can be circumvented by the use of gated decoupling[5] or chemical modification of the sample[6] (addition of a paramagnetic reagent). However, both of these techniques lower experimental efficiency in terms of the time required to obtain a spectrum since the NOE is eliminated.

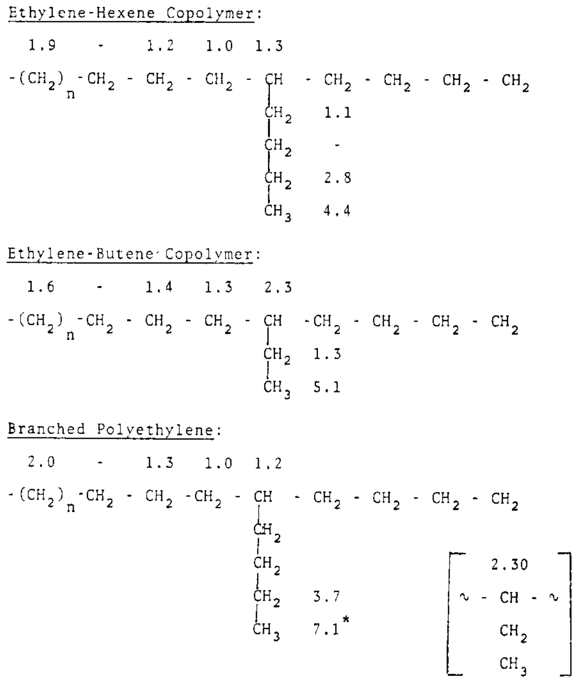
The aforementioned problems have been generally recognized and alluded to in the literature.[6b] However, due to the time-consuming experiments required for determination of the relaxation parameters, there is a relative paucity of data for most polymers and little application of these concepts to quantitative compositional analysis.[4h] It has been recently shown that tacticity differences in polypropylene result in quite different T_1's.[4d] These findings further emphasize the need for establishment of the necessary conditions for quantitative analysis of a given polymer.

A series of ^{13}C NMR studies of low-density polyethylenes[7–11] have addressed themselves to the problem of the quantitative analysis of the branching and the chemical nature of the side groups. Those results were obtained without the necessary detailed relaxation data, although it was generally suggested[7–11] that caution need be taken in interpreting the results for that reason. The use of hydrocarbon standards for deriving the optimum experimental conditions[8] is not an adequate substitute for the direct measurement of the relaxation parameters.

This present study was undertaken in order to determine the requisite relaxation parameters and thus establish the proper experimental conditions for a quantitative analysis of low-density polyethylene and related copolymers. Moreover, these relaxation parameters give insight into the solution molecular dynamics of the main chain and side chain carbons of branched polyethylenes. Two ethylene–alkene copolymers, ethylene–butene-1 and ethylene–hexene-1, as well as a conventional branched polyethylene sample were studied for this purpose. The ^{13}C T_1's were obtained in 118 °C and 67.905 MHz using a Bruker HX-270 spectrometer. An inversion–recovery sequence (T–180°–t–90°) was used to measure the relaxation times in all cases. The 90° pulse angle was 71 μs. The results are summarized in Figure 1. The possible effect of the long pulse width was negated by the small chemical shift rang for the resonances under investigation, in conjunction with the use of quadrature detection which increases the effectiveness of the available pulse power using proper placement of the carrier frequency.

Nuclear Overhauser enhancements were complete for all measured carbons in the branched polyethylene sample.[16] These results are not unexpected in the light of the report by Inoue et al.[12] for molten linear polyethylene which has a maximum NOE at 140 °C and the results for a 50% crystalline linear polyethylene which also has a maximum NOE at 45 °C.[13] Thus, for these systems differential nuclear Overhauser enhancment does not affect compositional analysis. This result, anticipated by Bovey et al.,[9] is now established. The large range of T_1's observed for the different carbon atoms, however, indicates that the previous studies did not utilize sufficient pulse intervals to avoid preferential saturation of some carbon signals. In time averaging, scan intervals of 0.4 to 10 s are not sufficient to prevent preferential saturation of the side chain and quite possibly even the main chain CH_2 carbons not located near chain branches. For full quantification a scan interval approaching 30 s would be desirable provided that spectrometer sensitivity is sufficient to avoid extended averaging (we in fact used 35 s for the NOE pulse intervals and 20 s for the T_1 measurements reported here). On the Bruker HX-270 using a 13-mm sample tube, only 150–200 scans were required to obtain spectra of the quality shown in Figure 2.

In addition to establishing the conditions for quantitative analysis the ^{13}C T_1's presented in Figure 1 also give significant insight into the molecular dynamics of the ethylene copoly-



*May be slightly longer since delay time in inversion-recovery pulse sequence was too short.

Figure 1. T_1 map of ethylene copolymers and branched polyethylene in 40% w/v trichlorobenzene. Data obtained at 118 °C and 67.905 MHz.

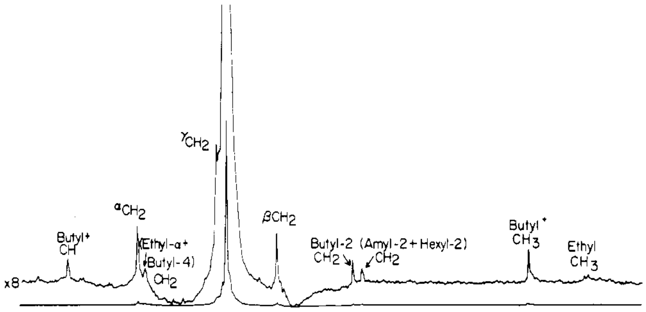


Figure 2. ^{13}C NMR spectrum of a branched polyethylene in 40% w/v trichlorobenzene at 118 °C and 67.905 MHz, 200 scans, 35 s delay, 12 kHz sweep width, 13-mm sample tube, 8K data points (only region from ~9–40 ppm shown).

mers and branched polyethylenes in concentrated solutions. The internal mobility of the polymer side chains as well as segmental flexibility of the main chain are indicated by the longer T_1 values for the peripheral carbons and for the chain CH_2 carbons not located near branches. Quantitative comparison of these ^{13}C T_1 data requires multiplication of each T_1 value by N, the number of directly bonded hydrogens for each carbon. The NT_1 values thus obtained relate more directly with motion.[14] It must also be noted that many of the resonances are actually composite resonances with contributing carbons from different branch types. Therefore, the analysis of the T_1 data in terms of chain dynamics is of a more semiquantitative nature. The relatively long T_1's and full NOE's confirm that the extreme narrowing condition is fulfilled and further obviate the need for invoking a distribution of correlation times for any discussion of dynamics. For example, in the ethylene–hexene copolymer the side chain CH_2 carbon NT_1 values of 2.2 and 5.6 s show increasing motion relative to the main chain junction CH carbon NT_1 of 1.3 s. Furthermore, the main chain CH_2 carbon T_1's adjacent to the branch site show a similar degree of internal motional freedom. We note that the CH_2 carbon NT_1 for the main chain carbons far removed from branch sites is only 3.8 s which is significantly lower than the side chain NT_1 for the third removed CH_2 carbon.

The NT_1 value of the side chain CH_3 carbon of the ethylene–hexene copolymer, 13.2 s, is indicative of a high degree of internal motion for the symmetrical methyl as expected from other studies.[15] It is interesting that in the ethylene–butene copolymer the side chain methyl is slightly more mobile (longer NT_1) than in the hexene copolymer despite the shorter chain segment connecting the methyl group to the main chain. The CH carbon at the branch point is distinctly more mobile in the butene copolymer than in the copolymer containing the longer side chain.

A similar motional behavior is manifest in the low density polyethylene sample where the observed NT_1 value for the long side chain CH_3 groups (i.e., CH_3's attached to butyl chains and higher, Bu^+) is over 20 s. Since this resonance has contributions from many branch types, the resultant T_1 would be expected to be different (and longer) from that obtained for the butyl methyl carbon of the ethylene–hexene copolymer. The motional behavior at and near the branching site is also similar for the polymer relative to the copolymers, where the presence of side chains of increasing length restricts mobility to a greater and greater extent even at the branch point.

Although the amyl-CH_2-3 and hexyl CH_2-3 T_1's could not be measured, a rough estimate of the T_1 of the composite amyl-CH_2-2 and hexyl-CH_2-2 resonance yields a value of approximately 7 s. This is a lower limit as the pulse delay was too short in the inversion–recovery sequence.

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