end-to-end distance. Because of this feature, i.e., the energetic symmetry and the geometric asymmetry of the conformational map, the value of C_∞ is close to that of a freely rotating chain. The value of $(C_\infty)_f$ corresponding to free rotation, with the geometry used here, is 1.736, which leads to $\langle r^2\rangle_0/\langle r^2\rangle_{0,f} = 1.03$. Thus, the symmetry of the energy surface permits treatment of the BPAPC and the other polycarbonates discussed above, as freely rotating chains, with each repeat unit segment represented by a virtual bond.[1,2] The calculated values of the temperature coefficient, $d(\ln C_\infty)/dT$ (in the range of 10×10^{-5} deg^{-1}), are also extremely small in these cases, indistinguishable from zero, i.e., that of the freely rotating chain.

The small values of the characteristic ratio and its temperature coefficient has been interpreted as due to the equal energy of the flat-helical and extended helical conformers.[6] In the crystalline state, the BPAPC assumes an extended 2-fold helical conformation.[23] An indirect evidence for the flat-helical conformations in polycarbonate is derived from the recent experimental observation[24] of a helix–coil transition in the mixed solvent system of 1,1,2,2-tetrachloroethane and *n*-propyl alcohol. The energies included in the partition function, Z', involve all the rotational states of both the skeletal and side group atoms. These energies could be used to calculate the conformational entropies in the manner described recently by Hopfinger et al.[25] to rationalize the differences in the glass transition temperatures of these polycarbonates.

Registry No. (4,4′-$HOC_6H_4C(CH_3)_2C_6H_4OH$)($HOCO_2H$) (copolymer), 25037-45-0; (4,4′-$HOC_6H_4C(CH_3)_2C_6H_4OH$)($HOCO_2H$) (SRU), 24936-68-3; (4,4′-$HOC_6H_4CH_2C_6H_4OH$)($HOCO_2H$) (copolymer), 29832-46-0; (4,4′-$HOC_6H_4CH_2C_6H_4OH$)($HOCO_2H$) (SRU), 28935-53-7; (4,4′-$HOC_6H_4CH(CH_3)C_6H_4OH$)($HOCO_2H$) (copolymer), 27815-48-1; (4,4′-$HOC_6H_4CH(CH_3)C_6H_4OH$)($HOCO_2H$) (SRU), 28774-91-6; (4,4′-$HOC_6H_4CHPhC_6H_4OH$)($HOCO_2H$) (copolymer), 29250-89-3; (4,4′-$HOC_6H_4CHPhC_6H_4OH$)($HOCO_2H$) (SRU), 31694-37-8; (4,4′-$HOC_6H_4CPh(CH_3)C_6H_4OH$)($HOCO_2H$) (copolymer), 29250-91-7; (4,4′-$HOC_6H_4CPh(CH_3)C_6H_4OH$)($HOCO_2H$) (SRU), 26985-42-2; (4,4′-$HOC_6H_4CPh_2C_6H_4OH$)($HOCO_2H$) (copolymer), 118631-41-7; (4,4′-$HOC_6H_4CPh_2C_6H_4OH$)($HOCO_2H$) (SRU), 28934-44-3; (4,4′-$HOC_6H_4C_6H_{10}C_6H_4OH$)($HOCO_2H$) (copolymer), 26471-16-9; (4,4′-$HOC_6H_4C_6H_{10}C_6H_4OH$)($HOCO_2H$) (SRU), 25135-52-8; (4,4′-$HOC_6H_4C{=}CCl_2C_6H_4OH$)($HOCO_2H$) (copolymer), 29057-43-0; (4,4′-$HOC_6H_4C{=}CCl_2C_6H_4OH$)($HOCO_2H$) (SRU), 31546-39-1.

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Long-Range Reading of Polypropylene Stereosequences: Undecad Assignment in Proton Spectrum by Two-Dimensional NMR Spectroscopy

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ABSTRACT: Application of 2D NMR spectroscopy to hemiisotactic polypropylene allowed us to resolve the proton methyl resonances of polypropylene at the nonad and undecad level. From the proton homonuclear *J*-resolved experiment, after strong digital filtering, the ^{1}H NMR spectrum devoid of homonuclear couplings was obtained at high resolution as a cross section of the 2D matrix at $^3J(CH_3–CH)/2$. Similarly, the $^{13}C–^1H$ correlated spectrum shows an unprecedented resolution, mainly in the methyl region. Thus, the assignment of the ^{1}H NMR spectrum was possible starting from ^{13}C resonances previously identified on the basis of a known stereosequence distribution.

Two-dimensional NMR spectroscopy has proved to be a useful tool for increasing resolution, achieved by spreading the spectrum along a second dimension. The best results have been obtained for biological macromolecules, for which overcrowding of resonances entirely precludes the analysis of certain spectral regions.[1,2] In the field of synthetic polymers a number of applications of 2D NMR have appeared in the past few years.[3-8]

Two-dimensional studies of polypropylene tacticity have

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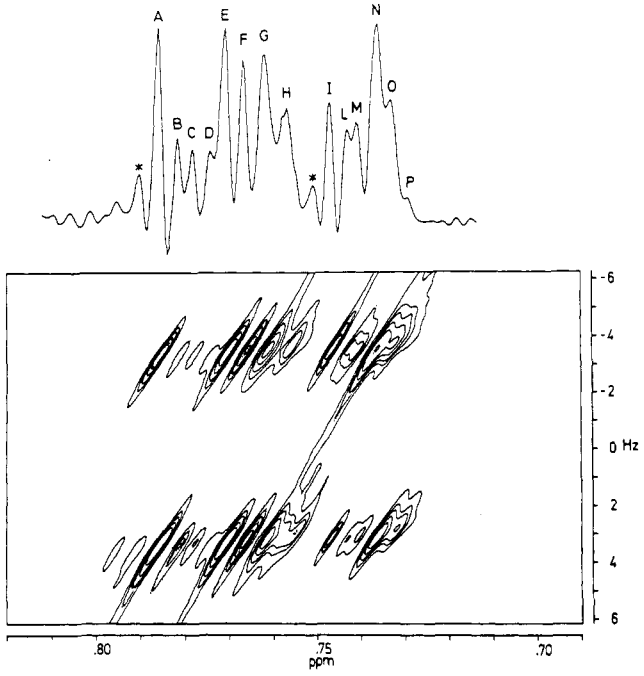

Figure 1. 270-MHz ^1H homonuclear J-resolved spectrum of hemitactic polypropylene: methyl resonances. The section obtained ±3.25 Hz after symmetrization is shown at the top. Resonances are labeled as in Table I. Asterisks denote minor spectral distortions.

recently led to refining and correcting assignments in the ^{13}C NMR spectrum at the hexad level,[9] but low resolution along the n_1 axis prevented accurate assignments of proton resonances. Actually, polypropylene is a case less favorable than others (e.g., poly(methyl methacrylate)) in which the spectral resolution is comparably high in both the ^1H and ^{13}C dimensions.[10]

To obtain the recognition and assignment of long stereosequences in polypropylene in both the hydrogen and carbon dimensions, we have applied 2D NMR spectroscopy to hemiisotactic polypropylene (hit-PP).[11] This can be regarded as a reference compound, containing only couples of m or r diads; as a consequence there is a dramatic selection and a characteristic statistical distribution of stereosequences.[12] The reduced overlap among NMR signals allowed us to assign the ^{13}C NMR spectrum of polypropylene at the level of 11 monomer units.[13,14]

In this paper spectra of polypropylene showing very high resolution in both proton and carbon dimensions were obtained with 2D methods. In particular, a proton spectrum was recorded exhibiting a large number of sharp peaks that were neither detected nor assigned before.

Figure 1 shows the methyl resonances in the ^1H homonuclear J-resolved NMR spectrum of hit-PP, at 270 MHz. Coupling to the methyl protons splits all signals along the n_1 dimension by the vicinal ^3J of 6.50 Hz. The fact that all couplings between CH_3 and CH protons in hit-PP are identical makes it possible to obtain a sort of "homodecoupled" methyl spectrum, i.e., devoid of J(H–H) interactions, in which only chemical shift effects are present. This "homodecoupled" spectrum is simply obtained by taking a section at $n_1 = \pm 3.25$ Hz, after symmetrization of the 2D matrix. With respect to the projection along n_1, following a 45° tilt, usually performed to remove homonuclear couplings, this section is free from instrumental distortions.

The resolution thus achieved in the proton spectrum after removal of the homonuclear interactions is much higher than that obtainable by irradiating the CH resonances in a conventional decoupling experiment. The

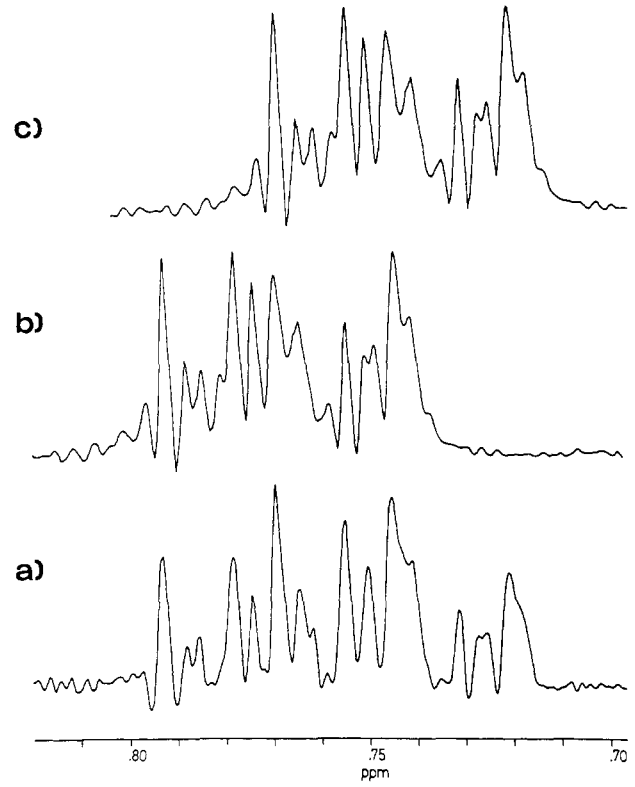

Figure 2. (a) Proton methyl spectrum of hemitactic polypropylene as run at 270 MHz; (b and c) J-resolved spectra, as in Figure 1, shifted from one another by 6.5 Hz. (a) is composed almost exactly of (b) plus (c).

latter would require a high power for the decoupling channel, producing distortions and Bloch–Siegert shifts. The "coupled" spectrum can be exactly reproduced by the addition of two "decoupled" spectra, shifted in relation to each other by 6.5 Hz by the vicinal coupling constant $J(CH_3CH)$ (Figure 2). Only the signals marked with an asterisk do not appear in the spectrum of Figure 1, and they thus are not the polymer signals.

In principle it should be possible to deduce the assignments from the known statistical pattern of hemitactic polymers[12] in a way similar to that used for assigning ^{13}C NMR at the undecad level.[13,14] However, the strong digital filtering, while increasing resolution, alters the line shapes, so that direct assignments based on signal intensities become impossible. Spectral simulation taking into account the particular line shapes after the digital treatment is in progress.

To overcome this problem, a ^{13}C–^1H heteronuclear correlated spectrum was obtained. in the CH_3 region, which is shown in Figure 3 together with the reference carbon spectrum, we obtain a major piece of information. In the ^{13}C spectrum run at 67.9 MHz only a few signals are added in respect to preceding reports. Therefore they were labeled as indicated in ref 13 and 14. The splittings for signals numbered 4 and 5 are due to sequences longer than nonads, and signal number 8 contains the contribution from different pentads, as already stated. Overall, it is possible to detect 21 signals. The cross peaks in the 2D spectrum allow the transfer of the assignments previously given for the methyl resonances in the carbon spectrum to the proton spectrum. Two assignments and the correspondence between the two groups of signals are shown in Table I.

As a general observation, despite the high resolution observed, the proton spectrum unlike the carbon spectrum is not divided into well-defined groups of resonances (pentads). However, from the 2D spectrum in Figure 3 it

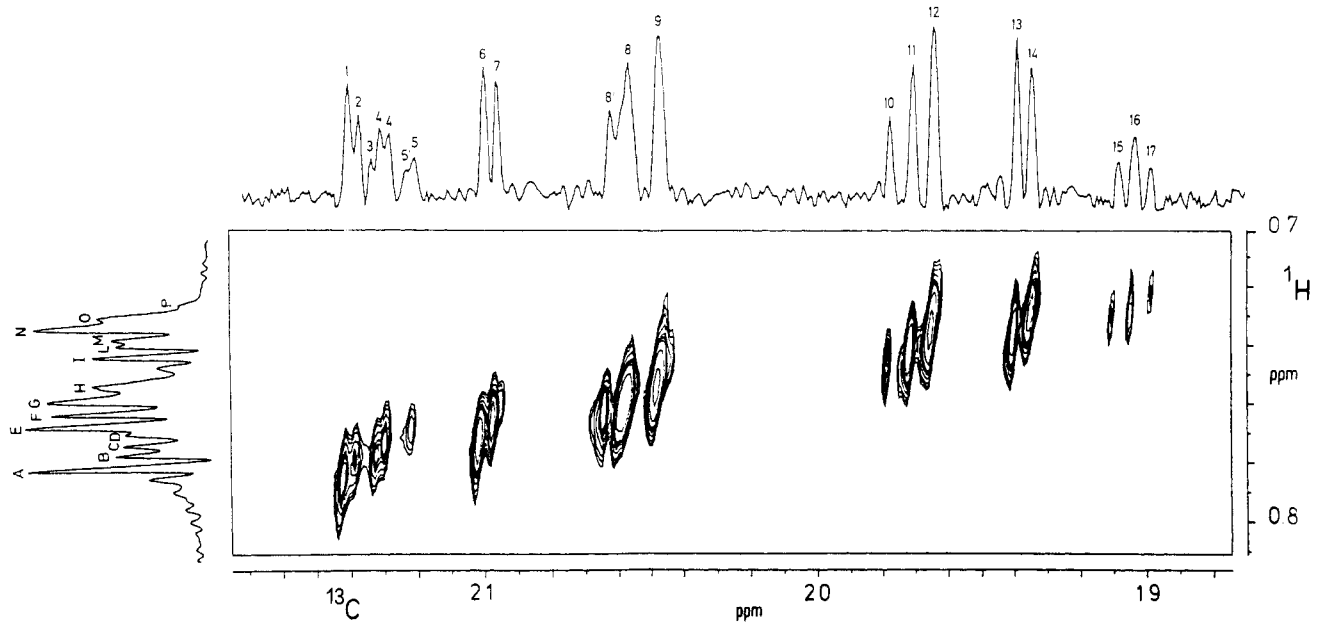

Figure 3. ^{13}C–^{1}H heteronuclear-correlated spectrum of hemitactic polypropylene: methyl resonances. The ^{13}C reference spectrum is shown on the n_2 axis, while the ^{1}H spectrum on the n_1 axis is the same, homodecoupled spectrum as in Figure 1, due to the characteristics of the 2D experiment. Carbon resonances are labeled as in ref 13.

Table I
^{1}H NMR Methyl Signals of Hemitactic Polypropylene

^{1}H signal	chemical shift	theoret area	^{13}C signal	sequence[a]
A	0.7812	6	1	*mm-mm-m.m-mm-mm*
A			2	*mm-mm-m.m-mm-rr*
A			3	*rr-mm-m.m-mm-rr*
B	0.7763	2	4	*mm-mm-mm.mm-rr*
C	0.7738	2	4′	*rr-mm-mm.mm-rr*
D	0.7686	2	5′	*mm-rr-mm.mm-rr*
D			5	*rr-rr-mm.mm-rr*
E	0.7664	4	6	*mm-mm-m.m-rr*
F	0.7624	4	7	*rr-mm-m.m-rr*
G	0.7572	12	8′	*rr-m.m-rr*
G			8	*mm-mm.rr*
H	0.7523	8	9	*rr-mm.rr*
I	0.7431	2	10	*mm-rr.rr-mm*
L	0.7390	2	11	*mm-mm-rr.rr-rr*
M	0.7373	2	11	*rr-mm-rr.rr-rr*
N	0.7328	10	12	*rr-rr.rr-rr*
N			13	*rr-mm-r.r-rr*
O	0.7306	7	14	*mm-mm-r.r-rr*
O			15	*rr-mm-r.r-mm-rr*
O			16	*mm-mm-r.r-mm-rr*
P	0.7293	1	17	*mm-mm-r.r-mm-mm*

[a] A dash divides one triad (*mm* or *rr*) from the other. The resonating carbon (or hydrogen) is located where a point appears along the sequence.

is clear that the signals show high resolution in both dimensions within the same pentad. In addition, no inversions in the order of the chemical shifts in the carbon and in proton spectra are observed in each pentad. This fact enabled us to assign proton chemical shifts at a far higher level than that accessible from the proton spectrum alone.

Despite the fact that the proton spectrum generally contains less information than the carbon spectrum, the proton methyl resonances in Figure 3 can be assigned at the undecad level. A remarkable complementariness can be observed between the sensitivity of both nuclei. In the carbon spectrum the isotactic pentad shows seven resolved signals in the 21.2–21.5 ppm range, corresponding to only three signals in the proton spectrum. On the other hand three signals are detected between 19.6 and 19.8 ppm in the carbon spectrum, due to the syndiotactic pentad, but the resolution in the proton spectrum is higher. Five clear signals are present: M and N correspond to signal 11 of the carbon spectrum, I and L to signal 10.

As already pointed out by other authors, *J*-resolved spectroscopy applied to synthetic polymer analysis highlights the information of the hydrogen chemical shift, often obscured by homonuclear couplings.[10] In the present case the particular features of the sample stress this observation. In the past the crowding in a narrow spectral region and the overlapping of some signals has made it impossible to accurately interpret the most informative parts of the hydrogen spectrum of polypropylene.

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