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Effect of Stereosequence on Carbon-13 Nuclear Magnetic Resonance Spin–Lattice Relaxation Times of Polypropylene

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ABSTRACT: Carbon-13 spin–lattice relaxation times, T_1's, and nuclear Overhauser enhancements, NOE's, have been observed for isotactic and syndiotactic polypropylenes at 25 MHz in *o*-dichlorobenzene at 98 °C. Maximum NOE values were observed for both samples. The T_1 values of the isotactic sequences were considerably longer than those of the syndiotactic sequences. The minimum sequence length of meso additions resulting in a longer T_1 for the isotactic sequence was found to be in the range $2.0 \leq n_m \leq 4.8$. Moreover, the motion of the racemic units ($n_r = 2.0$) which exists in a highly isotactic sample was essentially independent of the motion of surrounding isotactic sequences.

Carbon-13 NMR spectroscopy has proved quite useful in studying the chain dynamics of a number of polymers in bulk and solution.[3] One of the most interesting observations is dependence of the ^{13}C NMR spin–lattice relaxation time, T_1, upon the stereochemical configuration of the polymer.

Randall[4] has reported that ^{13}C NMR T_1's of the isotactic sequences are considerably longer than those of the syndiotactic sequences in amorphous polypropylene (a maximum T_1 difference due to stereochemical configuration of 18% for methyl carbons, 44% for methylene carbons, and 51% for methine carbons) although the activation energies for the ^{13}C NMR relaxation process were independent of the configuration. A similar trend of T_1 dependence upon the stereochemical configuration has been observed for polymethacrylates[5–9] and poly(vinyl chloride).[10] Hatada et al.[8] have pointed out that the glass transition temperatures of the bulk polymethacrylates are considerably lower for the isotactic polymer than for the syndiotactic polymer; this fact may be additional evidence for a greater freedom in the segmental motion of the isotactic polymethacrylates deduced from the ^{13}C T_1 data. However, the origin of the T_1 dependence on the stereochemical configuration has scarcely been discussed.

In this paper, ^{13}C NMR T_1's of isotactic and syndiotactic polypropylenes are measured together with the nuclear Overhauser enhancement (NOE) to study the effect of the stereochemical configuration on the T_1's of polypropylene. From the results, the minimum sequence length of racemic or meso additions which give a T_1 value characteristic of the stereochemical configuration has been determined.

Experimental Section

The ^{13}C T_1 measurements were made on a JEOL PS-100 spectrometer equipped with a PFT-100 Fourier transform system operating at 25 MHz, using a 180°–τ–90° pulse sequence. ^{13}C–^{1}H NOE was determined by the gated decoupling method, using a JEOL FX-100 spectrometer at 25 MHz. The ratio of the pulse delay to T_1 was 10 for the gating experiment to avoid the problems noted by Opella et al.[11] The integrated intensities of each resonance peak were used in T_1 and NOE determinations. The standard errors in both determinations were about ±10%. The number of transients accumulated was 50–512. Solutions of polymers were made up in *o*-dichlorobenzene to 30–100% (w/v) (0.3–1.0 g of polymer/1 mL of solvent) without degassing and the temperature of observation was 98 °C.

The catalyst systems for the polymerization, the stereoregularity, the amounts of the chemical inversion, and the molecular weights of polypropylenes, PP's, produced are summarized in Table I. Sample 4 is the same one as reported previously.[12]

Results and Discussion

The ^{13}C NMR spectra of isotactic (sample 2) and syndiotactic (sample 3) PP's are reproduced in Figure 1, together with the peak assignments.[4,13–15] The observed T_1 values for the ^{13}C nuclei of all samples and NOE values for isotactic (sample 2) and syndiotactic (sample 3) PP's are summarized in Table II. The NOE values can be regarded as the theoretical maximum[16] of 2.988 within experimental error (±10%), indicating that T_1's of all the carbons in PP are determined by ^{13}C–^{1}H dipole–dipole interaction and that the extreme narrowing condition is satisfied.

Let us compare the T_1's of the highly isotactic (sample 1), isotactic (sample 2), and syndiotactic (sample 3) PP's. The chemical inversion of propylene units is negligible or very low in these samples. The T_1 values for highly isotactic and syndiotactic PP's are essentially the same as those reported by Randall[4] for amorphous PP within experimental error. The T_1 values of the isotactic sequences are considerably longer than those of the syndiotactic sequences and the largest difference in T_1 is observed for the methine carbons. The difference in the T_1's of the corresponding ^{13}C peaks is not observed between highly isotactic and low isotactic samples. The average sequence length of meso additions in the chain can be determined from the expression[17]

$$\bar{n}_m = 1 + 2f_{mm}/f_{mr} \qquad (1)$$

where f_{mm} and f_{mr} were the triad fractions of mm and mr sequences, respectively. Using the triad distribution for the low isotactic sample shown in Table I, one finds the average sequence length of meso additions to be 4.8. This indicates that the minimum sequence length to give a T_1 value characteristic of the isotactic sequence is smaller than 4.8 meso units.

An interesting fact can be pointed out from a comparison of the T_1 values of these two isotactic polymers with those of syndiotactic polymer (sample 3). This is a remarkable decrease in the T_1 value of the meso methylene carbon in the syndiotactic sample. As a result, the difference in the T_1's between isotactic and syndiotactic sequences becomes small or almost negligible. The meso unit in the syndiotactic PP can be regarded as isolated in the chain because of the disappearance of the mm peak in the >CH– and $-CH_3$ regions (Figure 1). Then, the syndiotactic PP is presented by

...rrrmrrrrmrrr...

The longer T_1, characteristic of isotactic units, no longer appears when the isotactic unit is isolated in a long syndiotactic sequence block in the chain. The motion of the isolated meso unit may be influenced strongly by that of the racemic units: the isotactic T_1 is consistent with that of the syndiotactic sequence. Thus, the minimum se-

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Table I
Stereoregularities, Amounts of Chemical Inversion, and Molecular Weights of Polypropylenes

	polymerization conditions		stereoregularity triad fraction[a]			inversion,[b] mol %	mol wt[c]	
sample	catalyst	temp, °C	mm	mr	rr		$10^{-4}\overline{M}_n$	$10^{-4}\overline{M}_w$
1, highly isotactic[d]	$TiCl_3$-$AlEt_2Cl$	41	0.94	0.04	0.02	0	13.1	133
2, isotactic	$TiCl_3$-$AlEt_3$	41	0.50	0.26	0.24	0	7.1	113
3, syndiotactic	$V(acac)_3$-$Al_2Et_3Cl_3$	−78	0	0.26	0.74	2.6	9.9	17.8
4, syndiotactic	$VOCl_3$-$Al_2Et_3Cl_3$	−28	0.07	0.38	0.55	9.1	0.61	1.22

[a] Estimated from the triad peaks of the primary carbon resonance ($P_{\beta\beta}$). [b] Estimated from the ratio of the integrated intensities of $T_{\beta\gamma}$ to those of $T_{\beta\beta}$ for methine carbon.[12] [c] Determined at 135 °C by GPC (Waters Associates, Model 200). [d] Fraction insoluble in boiling heptane.

Table II
^{13}C Spin-Lattice Relaxation Times, T_1's,[a] and $^{13}C\{^1H\}$ Nuclear Overhauser Enhancements, NOE's (in Parentheses), for Polypropylenes in *o*-Dichlorobenzene at 98 °C

		CH_2			CH				CH_3		
		$S_{\gamma\alpha\alpha\gamma}$		$S_{\gamma\alpha\beta\gamma}$	$T_{\beta\beta}$		$T_{\alpha\beta}$	$T_{\beta\gamma}$	$P_{\beta\beta}$		
sample	concn, w/v %	m	r	t-t[b]	mmmm	CH*[c]	h-h[b]	t-t	mm	mr	rr
1, highly isotactic	30	0.54			0.92	0.67			1.51		
2, isotactic	30	0.55 (2.9)	0.38 (2.7)		0.93 (2.7)	0.66 (2.6)			1.54 (2.8)	1.32 (3.0)	1.23 (3.0)
3, syndiotactic	30	0.33 (2.9)	0.31 (3.1)			0.61 (3.0)				1.29 (2.7)	1.24 (2.8)
	50	0.32	0.32			0.58				1.30	1.25
4, syndiotactic	100	0.32	0.31	0.61		0.58	0.5	0.68	1.3	1.20	1.19

[a] In seconds. [b] t-t and h-h indicate tail-to-tail and head-to-head units, respectively. [c] CH* resonance has been assigned to mrmm, rrmr, mrmr, rrrr, mrrr, and mrrm by Randall.[4]

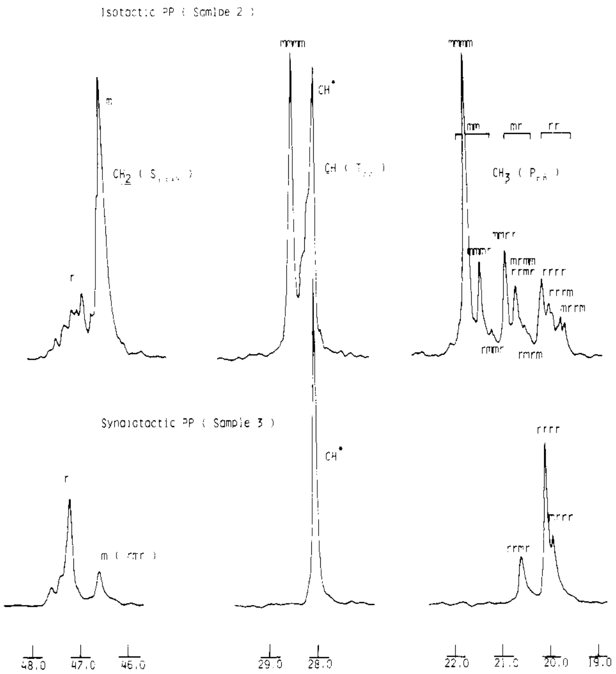

Figure 1. ^{13}C NMR spectra of isotactic and syndiotactic polypropylenes, samples 2 and 3, at 98 °C in 30% (w/v) *o*-dichlorobenzene. The number of transients accumulated with a repetition time of 10.0 s were 50 and 150, respectively. Spectra are calibrated in ppm from tetramethylsilane.

quence length of meso additions resulting in the longer T_1 for the isotactic sequence is

$$2.0 \le n_m \le 4.8 \tag{2}$$

This is, however, not observed for the racemic units in highly isotactic PP. The T_1 value of the CH* peak (pentad peak involving racemic units[4]) of the highly isotactic sample was the same as that of the corresponding peak of the isotactic PP. The characteristic shorter T_1 for syndiotactic sequences was maintained. Thus, the motion of the racemic units which exist in the highly isotactic PP is essentially independent of the motion of the surrounding isotactic sequences. A highly isotactic chain has been shown to contain short sequence blocks of racemic units, as represented by[14,18]

...mmmmmrrmmmmm...

It could be concluded that the shorter T_1 characteristic of the syndiotactic sequence appears even in the short block of two racemic additions.

The presence of the chemical inversion of the chain prevents the persistence of the head-to-tail sequence.[12] It is, however, noticed that the T_1's of the stereosequence in the syndiotactic sample containing the chemical inversion of 9.1 mol % (sample 4) are similar to those of the corresponding sample (sample 3) which consists mainly of head-to-tail units. This result again supports our conclusion that the T_1 value of PP is determined by the segmental motions involving a very limited number of head-to-tail units in the chain of polypropylene.

Taking into account the maximum NOE observation and assuming isotropic reorientation, one can calculate the PP correlation times, τ, by[19]

$$\tau = \frac{\sum r_{C\text{-}H}{}^6}{\gamma_C{}^2\gamma_H{}^2\hbar^2 N T_1} \tag{3}$$

which reduces to the numerical expression

$$\tau = 4.92 \times 10^{-11}/NT_1 \tag{4}$$

Correlation times for the segmental motion of samples 2 and 3 were calculated by using the methylene T_1's as follows: isotactic PP (sample 2), m, 4.5×10^{-11}, r, 6.5×10^{-11}; syndiotactic PP (sample 3), m, 7.9×10^{-11}, r, 7.9×10^{-11} (in s). The following may be pointed out as factors which contribute to the segmental motion of PP: (i) the conformational energy barrier; (ii) the energy difference between rotational isomeric states; (iii) the shape of the conformational energy surface.[3,20] However, we do not have sufficient information to discuss these terms at present. A quantitative analysis of the conformational energy surfaces of PP will be required to account for the stereochemical dependence of T_1.

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Calculated Carbon-13 Nuclear Magnetic Resonance Chemical Shifts for Ethylene–Vinyl Chloride Copolymers

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ABSTRACT: ^{13}C NMR chemical shifts expected for the carbon atoms in ethylene–vinyl chloride (E–VC) copolymers are calculated as functions of the E and VC monomer sequence distribution and the stereoregularity of the VC sequences. The γ gauche effect, which results in upfield chemical shifts for those carbon atoms in a gauche arrangement with carbon or chlorine substituents in the γ position, is utilized, together with the predicted bond rotational state probabilities obtained from Mark's conformational model of E–VC copolymers, to calculate the ^{13}C NMR chemical shifts for carbons in the various microstructural environments possible in E–VC copolymers. The methine and methylene carbon chemical shifts are predicted to occur over ~6- and ~30-ppm ranges, respectively, solely as a result of different monomer sequence distributions. The several-fold greater range of methylene carbon chemical shifts is due to the downfield shift produced by the presence of different numbers of deshielding chlorine atoms in the β position. In nearly all cases the effects of monomer sequence distribution and stereosequence are clearly separable and should be experimentally resolvable. The predicted chemical shifts are in excellent agreement with the ^{13}C NMR spectra reported by Keller and Mugge for chlorinated polyethylene and observed by one of us for reduced poly(vinyl chloride).

Introduction

^{13}C NMR spectroscopy[1-3] is currently the most powerful probe of polymer microstructure. The utility of this spectroscopic method is a consequence of the extreme sensitivity of the observed ^{13}C chemical shifts to local elements of polymer structure, such as sequence of comonomer units,[2,3] stereoregularity,[3] inverted monomer addition,[4] branching,[5] etc. Recently[6] the full potential of structural information contained in the ^{13}C chemical shifts observed for synthetic polymers has been realized through our ability to predict the relative chemical shifts produced by different polymer microstructures.

The relative chemical shifts of a carbon atom depends on the number and kinds of substituents attached to it. ^{13}C NMR studies[7-10] of hydrocarbons and their derivatives have established substituent rules which can be used to produce accurate estimates of the observed chemical shifts. As an example, each carbon substituent α or β to the observed carbon produces a downfield shift (deshielding effect) of ca. +9 ppm relative to an unsubstituted carbon. By contrast each carbon γ substituent yields an upfield shift (shielding effect) of ca. −2 to −3 ppm.

The shielding effect produced by a γ substituent has been demonstrated[6,11-17] to require a gauche arrangement between the observed and substituent carbons (see Figure 1). The frequency of such γ gauche arrangements depends on the microstructure of the polymer in the vicinity of the observed carbon. It is possible to evaluate the frequency of γ gauche interactions and the resultant relative ^{13}C chemical shifts from a knowledge of the polymer chain conformational characteristics and the magnitude of the upfield shift produced by each γ gauche interaction.

This approach[6] has been successfully applied to predict the ^{13}C NMR chemical shifts expected for the various carbon atoms in polypropylene[18] and its oligomers,[12,15] ethylene–propylene copolymers,[13,17] poly(vinyl chloride)[14] and its oligomers,[14] the oligomers of polystyrene,[16] and several fluorinated polymers.[19] The effects of stereosequence, comonomer distribution, and defect structures have all been successfully accounted for, thereby providing detailed microstructural descriptions of these polymers. In the present work we extend this approach to the copolymers of ethylene and vinyl chloride (E–VC).

Calculation of ^{13}C NMR Chemical Shifts

Mark's[20] rotational isomeric states model of E–VC copolymers is used to calculate[21] bond rotation probabilities necessary to the evaluation of the number of γ gauche interactions involving a given carbon atom. On the basis of our previous studies,[14] we adopt the following γ gauche

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