Acknowledgment. The generous financial support of this investigation by the National Science Foundation is gratefully acknowledged.

Appendix

The following remark was made by the Akron group: "The fallacy involved in uncritically relating reaction orders to association states can be seen in the following. Yamagishi et al.[5] examined the reaction between polystyryl lithium and 1,1-diphenylethylene in benzene in the presence of about 0.15 M diphenyl ether. . . . based solely on kinetic results they concluded that the presence of the ether failed to influence the association state of these polymers. . . . . Our measurements (determination of viscosity, our addition) on poly(styryllithium) and the 1,1-diphenylethylene capped poly(styryllithium) show that their average degree of association is considerably less than 2 in the presence of diphenyl ether, i.e., 25–60% of the chains can be present in the unassociated state under the conditions used by Yamagishi et al."

We checked this claim. Our results, shown in Table III, prove that the degree of association of lithium polystyryl in benzene is unaffected by the presence of diphenyl ether (0.15 M). This conclusion was confirmed by the independent study of Professor M. Van Beylen (The University, Leuven, Belgium), viz., flow time of benzene solution of polystyryl, concentration 5×10^{-3} M, dp 320: before diphenyl ether addition 628 s (average of six experiments); immediately after the addition (0.15 M) 624 s (average of four experiments). Two points need stressing. (1) Purified, and not commercial, ether has to be used, otherwise some carbanions are destroyed. (2) Prolong action of the ether gradually destroys the carbanions as revealed by the decrease of optical absorption at 334 nm.

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Carbon-13 NMR Spin-Lattice Relaxation Times of Inverted Monomeric Units in Polypropylene

TETSUO ASAKURA[1] and YOSHIHARU DOI*[2]

Department of Polymer Chemistry and Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan.

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^{13}C NMR spectroscopy has proved quite useful in determinations on both the stereochemical structure[3] and the chain dynamics[4,5] of polypropylene. Recently, we have demonstrated that ^{13}C NMR is sensitive to a specific sequence structure of propylene units resulting from propylene inversion along the chain of polypropylene.[6-8] The chemical shift assignment for ^{13}C resonances arising from head-to-head propylene units [$-CH_2-CH(CH_3)-CH(CH_3)-CH_2-$] and tail-to-tail propylene units [$-CH(CH_3)-CH_2-CH_2-CH(CH_3)-$] was made by using the Lindeman and Adams relationship.[9] More recently, the effect of stereosequence on the chemical shift of methyl-carbon resonances in the head-to-head propylene units was examined from the ^{13}C NMR analysis of model compounds of polypropylene and 30% enriched poly([3-^{13}C]-propylene) by Zambelli et al.[10,11]

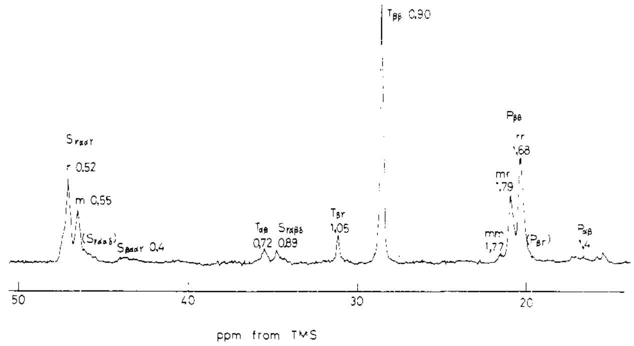

Figure 1. ^{13}C NMR spectrum of polypropylene at 123 °C in 100% w/v *o*-dichlorobenzene. The number of transients accumulated was 128.

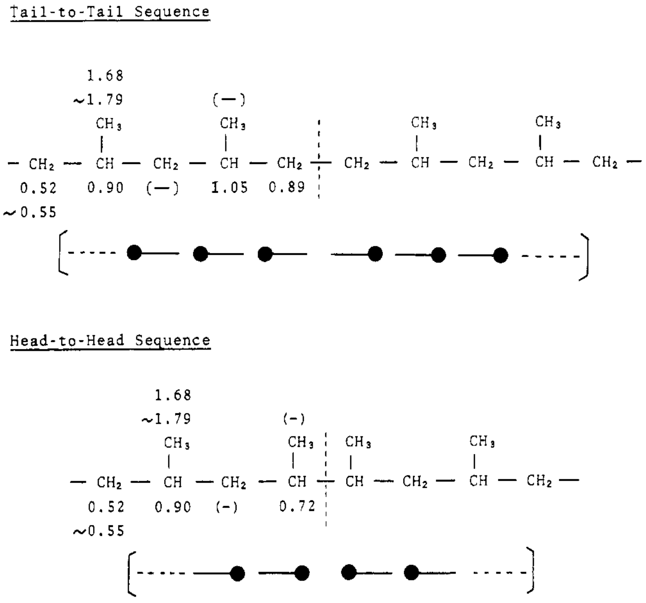

Figure 2. T_1 map of the polypropylene containing tail-to-tail and head-to-head units in 100% w/v *o*-dichlorobenzene at 123 °C (in seconds).

In the present study, the ^{13}C NMR spin-lattice relaxation times (T_1's) for specific carbon species of a polypropylene containing head-to-head and tail-to-tail units have been determined to confirm the previous chemical shift assignment and to obtain information on the main-chain motion near the reversal points in the polypropylene chain.

Figure 1 shows a ^{13}C NMR spectrum of the predominantly syndiotactic polypropylene ([*rr*] = 0.55, [*mr*] = 0.38, and [*mm*] = 0.07), together with the T_1 value in seconds for each peak.[12] For convenience, the T_1 map of polypropylene is given in Figure 2, based on the chemical shift assignments[6] as shown in Figure 1.

The methylene carbon in tail-to-tail units has a T_1 which is 62–71% longer than the methylene carbon T_1 in head-to-tail units. Similarly, the methine carbon T_1 in tail-to-tail units is 17% longer than the methine carbon T_1 in head-to-tail units. In contrast, the methine carbon T_1 in head-to-head units is 20% shorter than the methine carbon T_1 in head-to-tail units. Thus the tail-to-tail units are more mobile (longer NT_1) while the head-to-head units are less

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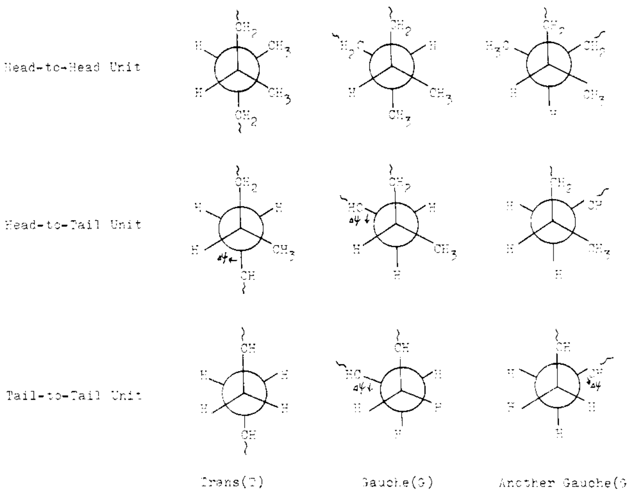

Figure 3. Newman projections of the three-state rotational isomeric states in head-to-head, head-to-tail, and tail-to-tail unit conformations. $\Delta\psi$ represents a distortion of the internal rotational angles from the exact staggering.

mobile (shorter NT_1) than the head-to-tail units. This motional behavior is easily understandable by comparing the conformational environment around the reversal points in the chain with that of head-to-tail unit sequences. According to the three-state rotational isomeric state (RIS) model[13] for polypropylene, each conformational state is assigned to one of the three states, i.e., trans (*T*), gauche (*G*), and another gauche (*G'*), as shown in Figure 3. The repulsive interaction restricting chain rotation occurs in the gauche arrangement between the carbon atom of interest and the carbon atoms separated by three bonds (γ substituents). The number of the carbon atoms participating in the steric repulsion decreases in the order of head-to-head, head-to-tail, and tail-to-tail units, though the repulsive interaction may release by a slight destortion of internal rotational angles ($\Delta\psi \simeq 20°$)[14,15] from the exact staggering as shown in Figure 3. As a result, the motions of CH, CH_2, and CH_3 groups increase in the order of head-to-head, head-to-tail, and tail-to-tail units. Thus, the ^{13}C NMR spin–lattice relaxation data support the previous chemical shift assignment for ^{13}C resonances arising from propylene inversion.

In the sequences containing regular head-to-tail propylene units, the T_1 values of both the methyl and methylene carbons are longer for the isotactic configurational sequences than for the syndiotactic configurational sequences. The dependence of the T_1 values of polypropylene on stereosequence has been pointed out by Randall.[5]

Experimental Section

The polypropylene sample was prepared with a $VOCl_3$–$Al_2Et_3Cl_3$ catalyst system in heptane at −28 °C. It had $\bar{M}_w = 12200$ and $\bar{M}_n = 6100$. It was determined from the ^{13}C NMR spectrum to have a 9.1% content of inverted propylene units.[7] ^{13}C NMR spin–lattice relaxation time measurements were made on a JEOL PS-100 Fourier transform system operating at 25.14 MHz, using a $180°–\tau–90°$ pulse sequence. Eight τ values were used in the measurement, and the integrated intensities of each resonance peak were used in T_1 determinations. The standard errors in T_1 values determined by the method of least squares were less than ±10% for well-resolved ^{13}C resonances, while they were about ±20% for the ^{13}C resonances of $S_{\beta\alpha\alpha\gamma}$ and $P_{\alpha\beta}$ species. The temperature for observation was 123 °C, and the solution was made up in *o*-dichlorobenzene to 100% w/v (1 g of polymer per 1 mL of solvent)[16] without degassing.

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Communications to the Editor

Synthesis and Morphological Behavior of a New ABC Three-Block Polymer

A carefully prepared specimen of a well-designed block copolymer such as an SBS thermoplastic elastomer is known to exhibit a regular periodic microphase structure which depends primarily on the volume fraction of the constituent blocks[1] and also, to some extent, on the conditions of preparation. Recently, studies on several ABC three-block polymers have been reported.[2-5] However, their morphologies are still not clearly understood, partly because of the complexities of their domain structure and partly because of the difficulty in staining these specimen to distinguish three phases. For instance, in the case of a polystyrene (PS)–polyisoprene (PI)–poly(2-vinylpyridine)

Table I
Characteristics of Polymer Samples

	block mol wt, $10^{-3}M_n$		
code	PS	PB	P4VP
SBP-1	20.2	22.0	32.3
SBP-2	23.3	45.2	22.3
SBP-3	13.0	76.7	22.8

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