hydrogen bonding. IR dichroism measurements were strongly dependent upon the hard domain morphology and the viscoelastic state of the soft segment matrix. The hard segments within domains intially orient transverse to the stretch direction whereas the soft segments orient parallel to the stretch direction. Small differences in the orientation behavior of the hydrogen-bonded and nonbonded urethane units at the hard domain interface were observed for each PEUU sample. These various trends could be interpreted in terms of the slightly different morphology of each sample.

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Registry No. 4,4'-Methylenebis(phenylene isocyanate)-ethylenediamine-poly(tetramethylene oxide) copolymer, 9053-66-1.

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^{13}C NMR Study of the Chain Dynamics of Polypropylene and Poly(1-butene) and the Stereochemical Dependence of the Segmental Mobility

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ABSTRACT: Carbon-13 spin-lattice relaxation times and nuclear Overhauser enhancements of polypropylene and poly(1-butene) have been measured in an *o*-dichlorobenzene-perdeuteriobenzene (9:1 (v/v)) mixture at 50 MHz. The relaxation data for the methine peak of polypropylene, including the 25-MHz data reported previously, were interpreted well in terms of the log χ^2 distribution model of the correlation time. The stereochemical dependence of the spin-lattice relaxation times was also observed for the methine peak of poly(1-butene) as well as polypropylene. The difference is small but significant and tends to be larger when the comparison is done on the correlation times determined with the log χ^2 distribution model. Both the correlation times and the activation energies of poly(1-butene) were considerably larger than those of polypropylene, which indicates that the greater bulkiness of the side group causes higher steric hindrance with the backbone chain.

Introduction

^{13}C NMR has been widely used to examine the chain dynamics of a number of polymers in bulk and solution.[1] One of the most important objectives of these studies is to determine the correlation times for the backbone motion of the polymer. The isotropic rotational diffusion model has been widely applied to describe the polymer motion. Detailed examinations of the relaxation data suggest that

Table I
Polymerization Conditions and Molecular Weights of Polypropylenes and Poly(1-butene)

sample	polymerization conditions		mol wt[a]	
	catalyst	temp, °C	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w \times 10^{-4}$
isotactic PP[b]	$TiCl_3$-$AlEt_2Cl$	41	13.1	133
atactic PP	$TiCl_3$-$AlEt_3$	41	7.1	113
syndiotactic PP	$V(acac)_3$-$Al_2Et_3Cl_3$	−78	9.9	18
isotactic PB	$Ti(OBu)_4$-$MgCl_2$-$AlEt_2Cl$	20		

[a] Determined at 135 °C by GPC. [b] Fraction insoluble in boiling heptane.

this model is inadequate for several polymers, e.g., poly(1-butene) (PB),[2] poly(methyl methacrylate),[3,4] polystyrene,[4,5] and so on. In the model, the chain motion is characterized by a single discrete correlation time. On the other hand, specific models that take into account the correlation time distribution, such as the Cole–Cole distribution or log χ^2 distribution, have been proposed and successfully applied to interpret the ^{13}C relaxation data of several polymers as well as the diamond-lattice model, invoking two discrete correlation times.[1] The interpretation of these models has already been given in detail in the review by Heatley.[1]

We have observed previously the ^{13}C NMR spin–lattice relaxation time (T_1) and nuclear Overhauser enhancement (NOE) of isotactic and syndiotactic polypropylene (PP) at 25 MHz and determined the correlation times for the segmental motion in terms of the isotropic rotational diffusion model.[6] In this paper, these relaxation parameters for isotactic, atactic, and syndiotactic PP's are obtained again by means of 50-MHz NMR spectroscopy, and the determination of the average correlation times for the backbone motion is performed more quantitatively in terms of the log χ^2 distribution model from the frequency-dependent relaxation data observed at two different magnetic fields.

One of the most interesting observations through the study of PP chain dynamics is the dependence of the relaxation data upon the stereochemical configuration; i.e., the isotactic sequences possess a less restricted segmental mobility than do the syndiotactic or other confirguational sequences.[6,7] However, essentially no dependence of T_1 on the configuration has been reported for predominantly isotactic PB.[8] This seems to be questionable in view of the close similarity in these polymer structures. Therefore, ^{13}C NMR relaxation parameters of PP and PB are observed carefully under the same experimental conditions in this paper. Actually, we will show that T_1 of an isotactic PB sample depends on the stereochemical sequence. The difference is small but significant. Moreover, the difference tends to be larger when the comparison is made on the average correlation times determined with the log χ^2 distribution model.

Thus, the relaxation behavior of the backbone motion of PP and PB is well interpreted in terms of the log χ^2 distribution model for the chain motion.

Experimental Section

The catalyst systems for the polymerization and the molecular weights of PP and PB are summarized in Table I. The ^{13}C NMR T_1 measurements were made on a JEOL FX-200 spectrometer operating at 50 MHz using a 180°–τ–90° pulse sequence. Each T_1 value was obtained by using between 10 and 13 τ values and using the peak areas, which were measured by weighing cut out traces of the peaks. The ^{13}C–^1H NOE value of the methine peak was determined by direct comparison of peak areas obtained with complete ^1H decoupling to the corresponding areas obtained with the gated ^1H decoupling method. Each spectrum was recorded with a 2000-Hz spectral width, 8K data points, and 150–200 accumlations, except for the NOE measurements, for which there were 300–500 accumlations. The polymer solution was prepared at a concentration of 0.2 g/cm^3 in *o*-dichlorobenzene-perdeuteriobenzene mixtures, at a 9:1 volume ratio of the two solvents, without degassing. The standard errors in the T_1 determinations were less than about ±5% for well-resolved resonances. The relative error in the NOE values was substantially greater (±10%).

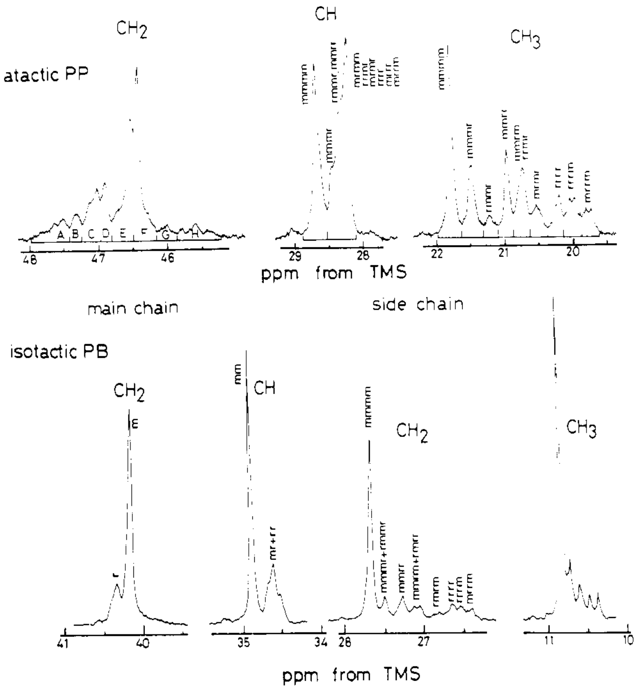

Figure 1. ^{13}C NMR spectra of atactic polypropylene and isotactic poly(1-butene) at 100 °C in a 20% (w/v) *o*-dichlorobenzene-deuteriobenzene (9:1 (v/v)) mixture. The spectra were recorded with a 2000-Hz spectral width, 8K data points, and 300 accumlations. The overlapping methylene resonance of polypropylene was arbitrarily separated into eight sections from A to H; assignments are given in the text.

Results and Discussion

Peak Assignment. Figure 1 shows the ^{13}C NMR spectra of atactic PP and isotactic PB, together with the peak assignments. In the PP spectrum, the methyl carbon region is well resolved into nine peaks associated with individual pentads, and only two pentads overlap.[9] Moreover, the heptad assignment was reported by Tonelli et al.[10] for this region. For the methylene carbons, the region was arbitrarily separated into eight sections, A–H, as shown in Figure 1, because of the strong overlapping of the peaks. According to recent hexad assignments by Tonelli et al.[10] and Zambelli et al.,[11] each section involves the following hexad peaks: A, mrmrm, rrmrm, rrmrr, mrrrm; B, rrrrm, mrmmr; C rrmmr, rrrrr, mrmmm; D, rrmmm; E, mrrmr, rmmmr, rrrmr; F, mrrmm, rmmmm, mmmmm, rrrmm; G, rmrmr; H, rmrmm, mmrmm. The assignment is confirmed here for several hexad peaks from a comparison of the ^{13}C NMR spectra of isotactic, atactic, and syndiotactic PP's shown in Figure 2 as follows. The stereosequence involving the isolated meso units occurring in the syndiotactic PP is represented by ... rrrrrrrmrrrrrr.... This may be clearly concluded from the

Table II
Carbon-13 Spin-Lattice Relaxation Times (s) for Isotactic, Atactic, and Syndiotactic Polypropylenes and Isotactic Poly(1-butene) at 50 MHz in *o*-Dichlorobenzene–Perdeuteriobenzene (9:1) Mixture at 100 °C

		PP			isotactic PB		
		isotactic	atactic	syndiotactic			
CH_3	mmmm	1.72	1.74		sc-CH_2	mmmm	0.32
	mmmr	1.55	1.77			mmmr + rmmr	0.32
	rmmr		1.9			mmrr	0.32
	mmrr	1.69	1.73			mmrm + rmrr	0.3
	mmrm + rmrr		1.73	1.52		rmrm	0.3
	rmrm		1.88			rrrr	0.3
	rrrr		1.88	1.41		rrrm	0.4
	rrrm		1.80	1.5		mrrm	0.4
	mrrm		1.9				
					mc-CH_2	m	0.25
CH_2	A[a]		0.7	0.42 (rrmrr)		r	0.19
	B		0.7	0.4 (rrrrm)			
	C		0.63	0.36 (rrrrr)	mc-CH	mm	0.45
	D	0.50 (rrmmm)	0.57			mr + rr	0.41
	E		0.63	0.36 (rrrmr)			
	F	0.59	0.60				
	G		0.6				
	H		0.5				
CH	mmmm	1.15	1.21				
	I[b]	0.9 (mmmr)					
		0.8 (mmrr + mrrm)	0.94	0.75			

[a] The overlapping methylene carbon resonances were arbitrarily separated into eight sections from A to H, as indicated in Figure 1. [b] Pentad peak involving racemic unit.

heptad methyl resonance; i.e., the ratio of the peak areas of rrrmrr and rrrrmr is 1:1. Thus, the four peaks in the methylene carbon region of the syndiotactic PP spectrum that correspond to the A, B, C, and E sections in the atactic spectrum are assigned to the rrmrr, rrrrm, rrrrr, and rrrmr hexads according to the hexad assignment of both researchers.[10,11] Actually, the ratio of the peak areas of rrmrr, rrrrm, and rrrmr was 1:2:2. Similarly, the stereosequence in the isotactic PP is represented by ...mmmmmmmmrrmmmmmmmm.... Thus, section D involves the rrmmm hexad in the methylene region.

A pentad assignment was reported for the methine carbon region by Randall[7] and Tonelli et al.[10] although the splitting due to stereochemical configuration was small. This region was assigned as shown in Figure 1.

A stereochemically well-resolved spectrum was also observed for the isotactic PB used here, as shown in Figure 1. Peak assignments were made for the methine carbons as triads and for the side-chain methylene carbons as pentads, according to Mauzac et al.[12] The splitting due to stereochemical configuration is also clear for other carbons. The peak appearing at lower field in the main-chain methylene region is tentatively assigned to racemic dyads and the other peak to meso dyads. We believe that a detailed stereochemical assignment of PB will be performed in the future by theoretical calculations similar to those reported for PP.[10]

Spin–Lattice Relaxation Time. The T_1 data for PP and PB are given in Table II. In the case of PP, the T_1 values were determined for the pentad methyl signals and for eight sections from A to H of the methylene region. Determination of the T_1 values in the methine region was made for two peaks, i.e., mmmm and a peak containing other pentads, of atactic PP, for three peaks, i.e., mmmm, mmmr, and (mmrr + mrrm), of isotactic PP, and for one peak of syndiotactic PP. All T_1 values of PP observed at 50 MHz were longer than the corresponding values reported previously with 25-MHz NMR[6] although observed conditions differed slightly. The frequency-dependent T_1 behavior can be regarded as significant and indicates that T_1's are not in the extreme motional narrowing condition. This will be discussed in detail in the next section. A dependence of T_1 on stereochemical sequence was clearly observed for the methine carbon. The peak overlap might prevent clear observation of the stereochemical T_1 dependence for methylene and methyl regions in the atactic PP spectrum. Actually, the T_1 value of mmmrr, 0.50 s, was shorter than that of mmmmm, 0.59 s, in well-separated methylene peaks of isotactic PP, which was the same trend of stereochemical T_1 dependence as observed in the methine region, i.e., 0.8–0.9 s for mmmr, mmrr, and mrrm and 1.15 s for mmmm. As reported previously,[6] shorter T_1 values for all peaks were observed for syndiotactic PP compared with corresponding values for isotactic and atactic samples. Also, the difference in T_1 observed be-

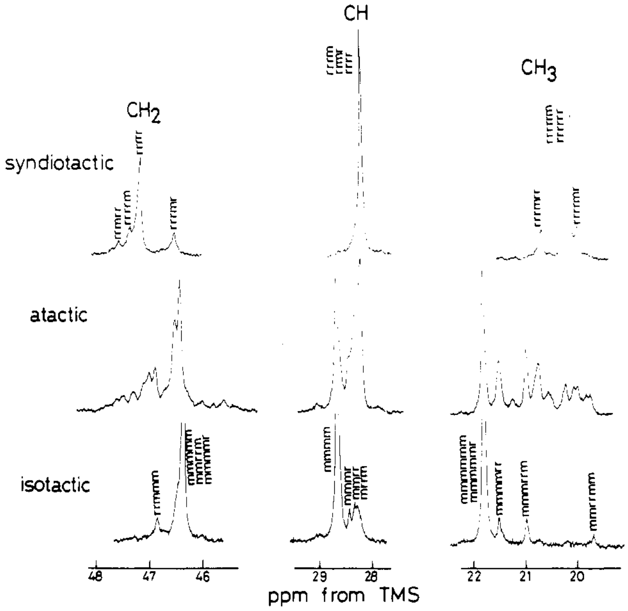

Figure 2. ^{13}C NMR spectra of syndiotactic, atactic, and isotactic polypropylenes at 100 °C in a 20% (w/v) *o*-dichlorobenzene–perdeuteriobenzene (9:1 (v/v)) mixture. The assignment of atactic polypropylene is given in Figure 1.

Table III
Average Correlation Times, τ, and Width Parameters, p, Determined from the Spin-Lattice Relaxation Times and Nuclear Overhauser Enhancements Observed at Two Magnetic Field Strengths at 100 °C for the Methine Peak of Polypropylene Using the log χ^2 Distribution Model of the Correlation Time

	50 MHz		25 MHz[c]			
	T_1, s	NOE	T_1, s	NOE	$\tau \times 10^{10}$, s	p
		Atactic Polypropylene				
mmmm	1.21	2.6	0.93	2.7	0.089	14
	(1.17)[b]	(2.58)	(0.96)	(2.65)		
I[a]	0.94	2.6	0.66	2.6	0.13	14
	(0.93)	(2.55)	(0.75)	(2.61)		
		Syndiotactic Polypropylene				
	0.75	2.7	0.61	3.0	0.28	25
	(0.74)	(2.71)	(0.65)	(2.80)		

[a] Pentad peak involving racemic units. [b] Calculated value. [c] From ref 6.

Table IV
Average Correlation Times, τ, and Width Parameters, p, Determined from the Spin-Lattice Relaxation Times and Nuclear Overhauser Enhancements for the Methine Peak of Isotactic Poly(1-butene) Observed at Various Temperatures Using the log χ^2 Distribution Model of the Correlation Time

	T_1, s				NOE				$\tau \times 10^{10}$, s			
	55[a]	70	85	100	55	70	85	100	55	70	85	100
mm	0.25	0.29	0.35	0.45	2.3	2.4	2.5	2.6	1.4	1.0	0.79	0.56
									(18)[b]	(21)	(25)	(25)
mr + rr	0.21	0.26	0.33	0.41					2.0	1.3	0.89	0.67
									(22)	(23)	(26)	(28)

[a] Temperature (°C). [b] p value.

tween isotactic and atactic PP's was scarcely outside experimental error.

As shown in Table II, the T_1 values for isotactic PB were observed for the triad methine peaks and the dyad methylene peaks, which were tentatively assigned here in the main-chain carbon region, and for pentad side-chain methylene peaks. T_1 data are not given for the methyl peak of the side chain. The T_1 values were half of the corresponding values for PP. A stereochemical T_1 dependence was also observed for the main-chain methylene and methine peaks; i.e., the isotactic sequence was more mobile than the syndiotactic sequence. The difference was small but significant. This was confirmed from the T_1 observation of the methine peak as a function of temperature, as described below.

Average Correlation Time for the Backbone Motion of PP and PB. The average correlation times for backbone segmental motion of PP were determined from the frequency-dependent T_1 and NOE data for the methine peak by application of a log χ^2 distribution model to the correlation time. Since a detailed description of the correlation time determination in terms of the log χ^2 distribution has been given by Schaefer,[5] only calculated results are given here. These are summarized in Table III. The agreement between the calculated and observed values is good, taking into account the relatively large experimental error in evaluating T_1 and NOE values at 25 MHz. Thus, the relaxation behavior of PP can be well interpreted in terms of the log χ^2 distribution model of the correlation times. The segmental motion of syndiotactic PP is slower by a factor of 3 than that of the mmmm sequence or by a factor of 2 than that of pentad sequences involving racemic units in atactic and isotactic PP's.

The T_1 and NOE values of main-chain methine peaks were determined for isotactic PB and the backbone segmental motion was also interpreted in terms of the log χ^2 distribution model as a function of temperature. These data are listed in Table IV. With increasing temperature, both the T_1 and NOE values increase. The T_1 value of the mm triad is consistently larger than that of the (mr + rr) triad by 0.02–0.04 s over the observed temperature range. Although the difference in the T_1 observations is small, it becomes greater on comparison of the correlation time data determined from T_1 and NOE values. Thus, it is concluded that the isotactic sequences in PB possess a less restricted segmental mobility than do the syndiotactic or other configurational sequences, just as for PP.

Activation energies were determined from an Arrhenius plot of the correlation times as 22 kJ mol^{-1} for the mm triad and 23 kJ mol^{-1} for the (mr + rr) triad. Thus, no difference in activation energy was observed for these configurations. This finding is the same as for PP.[7] It is interesting to compare absolute values of segmental correlation times and the width parameter, p, for PB with the corresponding quantities for PP at 100 °C. The segmental motion of PB was slower than that of PP by a factor of 5–6. The activation energies for the motion of PB, 22–23 kJ mol^{-1}, were also larger than that of PP, 17 kJ mol^{-1}.[7] These were explicable in terms of the greater bulkiness of the side group, causing greater steric interference with the backbone in PB than in PP. Moreover, the smaller p value for atactic PP, 14, than for isotactic PB, 25–28, indicates that cooperative motions occur in PP over a longer range along the chain.[5] The ratio of the correlation time of the isotactic sequence to that of the syndiotactic sequence decreases in PB compared with that in PP, i.e., 1.20 for PB and 1.44 for PP. This might be interpreted qualitatively on the basis of the conformational analysis as well as the chemical shift predictions[10,11] if the configurational dependence of T_1 is related to the relative population of the preferred conformations in a given stereochemical sequence. In the meso dyad of PP and PB, the preferred conformations are |tg| and |gt|, where t and g represent trans and gauche, respectively. The notation follows that of Suter and Flory.[13] The relative probability of these conformations in the chain is the same because they are mirror images. On the other hand, the preferred conformations are |tt| and |gg| for the racemic dyad. Suter and Flory[13] estimated the partition function for the |gg| conformation as 0.6856 at 400 K and 0.6472 at 300 K relative to a value of unity for the |tt| state in PP, which means that the |tt| conformation appears more frequently. The preponderance in the time-averaged conformational probability causes a more restricted segmental motion in the syndiotactic sequence than in the isotactic sequence in a PP chain. This tendency differs for the racemic dyad in PB, contrary to the case of the meso dyad. According to Flory,[14] there are additional unfavorable interactions between the ethyl group of the side chain and the chain backbone when both adjoining skeletal bonds are t, i.e., |tt|. The statistical weight of such interactions was assigned to τ^* (<1), which causes a decrease in the relative population of the |tt| conformation and an increase of the |gg| conformation. Thus, the ratio of the segmental motion of the syndiotactic sequence to that of the isotactic sequence decreases in PB as compared to PP.

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Registry No. Atactic PP, 9003-07-0; isotactic PP, 25085-53-4; syndiotactic PP, 26063-22-9; isotactic PB, 25036-29-7.

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Branch Structures in Poly(vinyl chloride) and the Mechanism of Chain Transfer to Monomer during Vinyl Chloride Polymerization

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ABSTRACT: The detailed microstructure of poly(vinyl chloride) (PVC) has been determined from the ^{13}C NMR spectra of PVC samples that had been subjected to reductive dechlorination with tri-*n*-butyltin hydride or tri-*n*-butyltin deuteride. From the information thus obtained and other pertinent facts, several important features of the vinyl chloride polymerization mechanism have been deduced. Investigation of a PVC specimen prepared in bulk at 100 °C has shown that 2,4-dichloro-*n*-butyl, 2-chloroethyl, and chlorinated long-branch segments are present and that all of these arrangements are tertiary-halogen-containing sites. The former structures are generated by free-radical "back-biting" routes, whereas the latter one appears to arise via chain transfer to the polymer by a growing-chain carbon radical. Identification of the long-branch points has been facilitated by the observation of a unique resonance for this grouping in the 50.31-MHz ^{13}C spectrum of reductively dehalogenated PVC. No evidence has been obtained for the occurrence of chlorinated *n*-propyl, *n*-amyl, 2-ethyl-*n*-hexyl, or 1,3-diethyl branch segments in PVC itself, but in keeping with our earlier findings, the presence of a chloromethyl branch structure containing tertiary hydrogen has been confirmed. For a series of PVC samples prepared at temperatures ranging from 43 to 100 °C, the branch concentrations have been demonstrated to lie in the following order: chloromethyl > 2,4-dichloro-*n*-butyl > 2-chloroethyl > long. The concentration data indicate that the activation energy for 2-chloroethyl branch formation is significantly greater than that for 2,4-dichloro-*n*-butyl branch production, an observation that may account for the failure of other workers to detect any ethyl branches in some samples of reductively dehalogenated PVC. In the case of the 100 °C bulk polymer, each number-average molecule has been found to contain one $-\mathrm{CHClCH_2CHClCH_2Cl}$ long-chain end. The presence of this structure and the previously verified occurrence of chloroallylic long-chain ends in PVC are shown to establish the mechanism for chain transfer to monomer during the free-radical polymerization of vinyl chloride. This mechanism involves the addition, to the monomer, of an actual or incipient chlorine atom which results from the β scission of a chain-end radical that is formed via head-to-head monomer addition. The effect of tertiary halogen on PVC thermal stability is discussed, and earlier attempts to detect this grouping in the polymer are critically reviewed. Comments also are made with regard to the efforts of previous workers to identify the long-chain ends in PVC using NMR techniques. Finally, the presence of the $-\mathrm{CHClCH_2CHClCH_2Cl}$ chain end is shown to rationalize much of the published chemical evidence for the existence of head-to-head linkages in the polymer.

Recent work in these laboratories has shown that reduction with tri-*n*-butyltin hydride can effect the essentially quantitative conversion of poly(vinyl chloride) (PVC) into the analogous hydrocarbon.[1,2] This method of reducing PVC is superior in many respects to the older lithium aluminum hydride procedure,[2a–d] and it has been shown to be a very valuable tool for use in PVC microstructure investigations in which the structure of the starting polymer is deduced from that of the reduction product.[1–3] The $\mathrm{Bu_3SnH}$-reduced polymer has been characterized structurally with a variety of analytical techniques, including ^{13}C[1–3f,g,j–m] and ^{1}H[3k] NMR spectroscopies, IR spectroscopy,[2a,b,3b–e,h,i,n] pyrolysis–gas chromatography,[3a] pyrolysis–hydrogenation–gas chromatography,[3a,g,l] and γ-radiolysis–gas chromatography.[3d,h,n] However, ^{13}C NMR is clearly the method of choice for total structure determinations, since this technique provides the most information with mimimal ambiguity.

The present paper describes the results of ^{13}C NMR studies on polymeric alkanes that were prepared by reducing PVC with tri-*n*-butyltin hydride or tri-*n*-butyltin deuteride. When the latter reagent was used, each chlorine