Table II
CP T_1 of the Polymorphs of PAIBLA[a] (in s)

	form A	form B
CO	27 (1)	17 (0.5)
$^{\alpha}$CH	20	8.5
$^{\beta}$CH$_2$	28	5
OCH$_2$	0.4	0.3
CH	0.5	0.5
CH$_3$	0.5	0.5

[a] We report in parentheses the estimates for the fast components of the decay.

peak intensities of the main-chain carbons differ significantly in the two spectra, those of form B being the stronger. This is consistent with the conclusion that form B has a higher content of amorphous material than form A. It seems therefore that PAIBLA, even though stereoregular and semicrystalline, enjoys considerable freedom in the amorphous regions.

In an attempt at characterizing the dynamics of the polymer in the two crystalline environments, T_1's were measured at 21 °C for both forms (Table II), using the CPT1 method of Torchia.[5] The decay of the magnetization of the backbone carbons is biexponential, showing short and long time components during the CPT1 experiments. Rough estimates of 1 s and ca. 0.5 s are obtained for the fast time constants in forms A and B, respectively. These values are extracted from the curves corresponding to the carbonyl signals in both forms. The assignment of these short time constants to interfacial or amorphous regions, as has been possible in other cases,[10] is complicated by the overlap of peptide and ester carbonyl resonances. The longer time constants may correspond to main-chain carbons located in the crystalline regions of the material. The T_1's for form A are longer than those for form B. We may conclude from these data that backbone motions are somewhat more restricted in form A than in form B. The side chain, on the other hand, displays essentially the same motional behavior in both phases.

Summarizing our results, we conclude the following: (i) The conformation of the monomer unit, as attested by ^{13}C NMR and infrared spectroscopy,[1a] does not differ significantly in the two crystalline forms. (ii) Some changes in the motional behavior of the main chain do occur in going from one form to the other. These may arise from differences in the morphologies of the two solid forms. (iii) A considerable portion of the polymer is in the amorphous phase and experiences a relatively high degree of mobility at room temperature.

Registry No. PAIBLA (homopolymer), 35239-25-9; PAIBLA (SRU), 37768-91-5.

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	PAIBLA	
	hexagonal (A)	tetragonal (B)
amide A	3292	3298
amide B	3091	3087
CO lateral group	1751	1755
amide I	1660	1661
amide II	1548	1543
amide V	671	668

Another form of PAIBLA, different from the ones we are discussing in this communication, was reported by: (b) Yuki, H.; Okamoto, Y.; Taketani, Y.; Tsubota, T.; Marubayashi, Y. *J. Polym. Sci. Polym. Chem. Ed.* **1978**, *16*, 2237–2251.

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Stereochemical Investigation of the Initiation Step of Propene Polymerization with Differently Activated TiCl$_4$/MgCl$_2$-Supported Catalysts

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In the field of Ziegler–Natta catalysis for α-olefins polymerization, the discovery of MgCl$_2$ as the ideal support for the fixation of TiCl$_4$ marked an exceptional improvement in the industrial polymerization process, and several methods for the preparation of highly active and stereospecific TiCl$_4$/MgCl$_2$-based catalysts are reported in scientific[1] and patent literature.[2] For the preparation of all these catalytic systems, a fundamental stage is the activation of the support MgCl$_2$. In fact, the reaction between anhydrous MgCl$_2$ powder and TiCl$_4$ results in hardly any fixation of titanium. This is probably due to the small surface area of MgCl$_2$ and its high crystallinity. Various procedures are used to decrease MgCl$_2$ crystalline order and to enhance its surface area and number of sites suitable to titanium fixation. The most common among them is a prolonged milling of MgCl$_2$ in the presence or the absence of TiCl$_4$ and/or an electron donor. Many studies have been performed to correlate the structural changes in MgCl$_2$ caused by the activation procedures with the activity and stereospecificity of the corresponding catalytic systems.[1] In the present work, we approach this problem from a different viewpoint, i.e., by the study of the effect of the kind of procedure by which MgCl$_2$ is activated on the steric structure of atactic and isotactic sites of the corresponding catalytic systems. The method we use to obtain structural information on the active sites is the investigation, by ^{13}C NMR, of the initiation step in propene polymerization in the presence of the selectively ^{13}C-enriched cocatalyst Al(^{13}CH$_2$CH$_3$)$_3$. In this case, the initiation step is the insertion of propene into the reactive titanium–ethyl bond resulting after the exchange between the titanium halide and triethylaluminum. In our previous publications,[3-5] we have shown that the stereochemical structure of the ethyl chain end groups, resulting after the initiation, is extremely sensitive to any change of the constitution of the active sites. Therefore, the extent of the first step stereoregularity is a characteristic of each catalytic system and consequently supplies noticeable information on the characteristic steric features of the active sites of the various catalytic systems.

Figure 1 shows the ^{13}C NMR spectra of the isotactic (heptane insoluble) fractions of polypropene samples obtained respectively in the presence of the conventional δ-TiCl$_3$-based catalyst and of a TiCl$_4$ supported on MgCl$_2$ catalyst, using selectively enriched Al(^{13}CH$_2$CH$_3$)$_3$ as co-

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Table I

	catalyst	Ti %	*Y*	polymer fractions no.[c]	polymer fractions wt %	mm[d]	I_e/I_t[e]
	δ-$TiCl_3/Al(^{13}CH_2CH_3)_3$		8[a]	F.5	5	0.48	1.1
				F.7	8	0.82	2.9
				R.7	87	0.98	3.4
a	$MgCl_2/TiCl_4/Al(^{13}CH_2CH_3)_3$[f]	0.22	11[b]	F.5	30	0.31	0.6
				F.7	35	0.76	1.2
				R.7	35	0.97	2.2
b	$MgCl_2/TiCl_4/Al(^{13}CH_2CH_3)_3$[g]	0.34	21[b]	F.5	26	0.31	0.7
				F.7	25	0.77	1.2
				R.7	49	0.96	2.2
c	$MgCl_2/TiCl_4/Al(^{13}CH_2CH_3)_3$[h]	2.43	61[b]	F.5	25	0.32	0.7
				F.7	33	0.75	1.2
				R.7	42	0.95	1.9

[a] *Y* = yield in grams of polymer/(grams of $TiCl_3$·48 h). [b] *Y* = yield in grams of polymer/(grams of catalyst·hour). [c] F.5 = diethyl ether soluble; F.7 = diethyl ether insoluble–heptane soluble; R.7 = heptane insoluble. [d] mm = molar fraction of isotactic triads by NMR. [e] I_e/I_t = intensity ratio (integrated peak area) of resonances related to the isotactic (e) and syndiotactic (t) placement of the first propene unit. [f] $MgCl_2$ (type A), by 7 days of milling. [g] $MgCl_2$ (type B), by 10 days of milling. [h] $MgCl_2$ (type C), by Grignard.

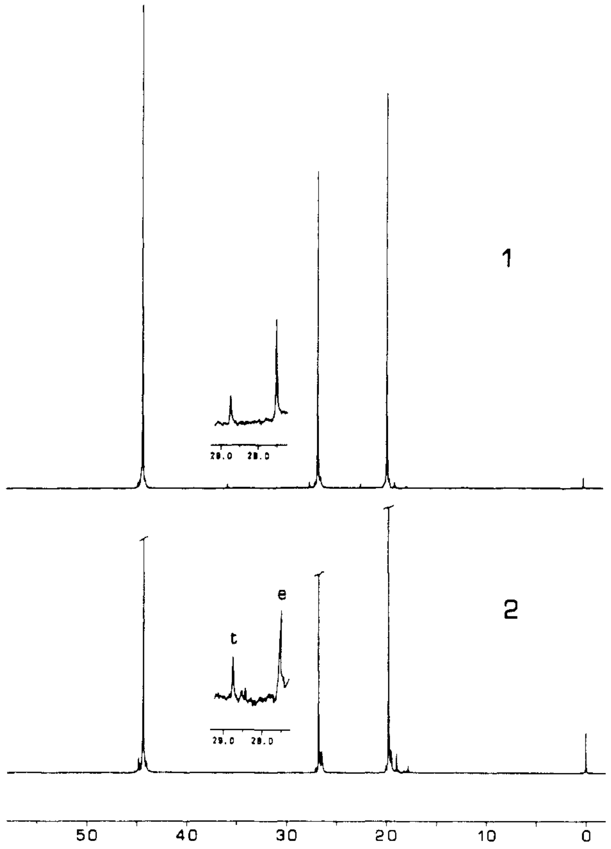


Figure 1. ^{13}C NMR spectra of heptane-insoluble fractions of polypropene samples prepared with (1) δ-$TiCl_3/Al(^{13}CH_2CH_3)_3$ and (2) $MgCl_2(A)/TiCl_4/Al(^{13}CH_2CH_3)_3$.

catalyst. As previously reported,[3-5] the resonances at 27.5_9 and 28.7_8 ppm are due to the ^{13}C-enriched methylene of the 2,4-dimethylhexyl chain end groups formed according to the following reactions

$$Ti^{13}CH_2CH_3 + CH_2{=}CH(CH_3) \rightarrow TiCH_2CH(CH_3)^{13}CH_2CH_3$$

$$TiCH_2CH(CH_3)^{13}CH_2CH_3 + CH_2{=}CH(CH_3) \rightarrow TiCH_2CH(CH_3)CH_2CH(CH_3)^{13}CH_2CH_3$$

and are related respectively to the e (or isotactic) and t (or syndiotactic) placements of the first propene unit with respect to the second one (see Figure 2). The intensity ratio I_e/I_t (integrated peak area) of the e and t ^{13}C NMR methylene resonances can be considered the extent of the first step stereoregularity.

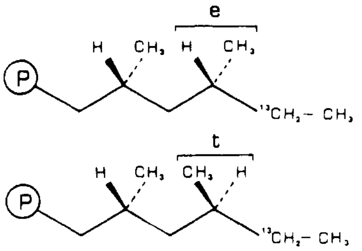


Figure 2. Stereochemical placement of ^{13}C-enriched end groups resulting after the insertion of two monomer units on the Ti–$^{13}CH_2CH_3$ bond. The end groups are labeled e (or isotactic) and t (or syndiotactic) depending on the steric relationship between the methyl substituents of the first two propene units.

Scheme I

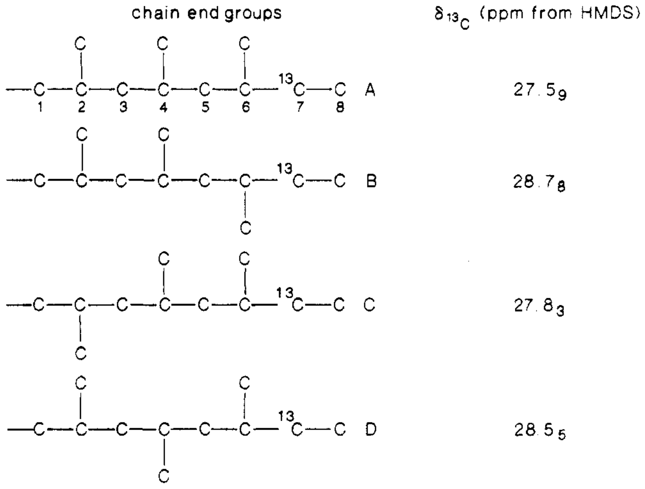


Figure 3 shows the ^{13}C NMR spectra of the atactic (boiling diethyl ether soluble) fractions of the same samples. A further splitting of the resonances of the enriched carbons of the end groups is observed here, due to the stereochemical effect on the chemical shift of the enriched carbons, by the substituent of the third monomer unit incorporated into the growing polymer chain. Actually, when, e.g., propene is polymerized in the presence of the moderately stereospecific system $VCl_4/Al(^{13}CH_2CH_3)_2Cl$,[6] four resonances are detected for the diastereomeric-enriched 7-^{13}C 2,4,6-trimethyloctyl end groups reported in Scheme I.

Only the A and B resonances are detected in the spectra of the highly isotactic fractions (Figure 1), while all four resonances are detected in the spectra of the atactic fractions (Figure 3). In the latter case, I_e is the sum of the intensities of the resonances centered at 27.7_1 ppm and I_t

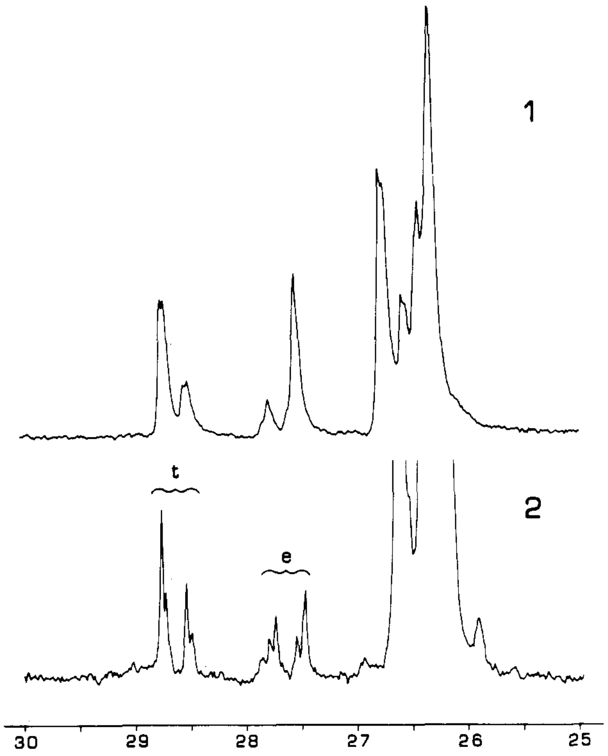


Figure 3. ^{13}C NMR spectra of enriched methylene chain end groups of diethyl ether soluble fractions of polypropene prepared with (1) δ-$TiCl_3/Al(^{13}CH_2CH_3)_3$ and (2) $MgCl_2(A)/TiCl_4/Al(^{13}CH_2CH_3)_3$.

is the sum of the intensities of the resonances centered at 28.6_6 ppm.

Table I collects the I_e/I_t values of all the fractions of the sample prepared with the $TiCl_3$-based catalyst and of three samples prepared with catalytic systems supported on $MgCl_2$ activated by using different procedures, together with the activities, the fraction distributions, and the stereochemical compositions. As is apparent from the given results, the $MgCl_2/TiCl_4$-based catalysts are highly active and have low stereospecificity in comparison with the $TiCl_3$-based catalyst, and this is in agreement with the fact that $MgCl_2$-supported catalysts do not contain any electron donor as stereoregulating agent. In addition, Table I shows that, though all the heptane-insoluble fractions have nearly the same stereochemical composition, insertion of propene into the Ti–ethyl bond appears to be noticeably less stereoselective ($I_e/I_t \simeq 2$) in the supported catalysts than in the conventional catalyst ($I_e/I_t = 3.4$). In our previous papers, we have shown that the extent of the first step stereoregularity is affected by the steric hindrance of the titanium ligands[4,5] as well as by the more or less exposed position of the active titanium on the catalyst surface.[7,8] Since in the supported catalysts the titanium atoms are preferentially located on the corners and edges of the surface of the activated $MgCl_2$,[9,10] the more exposed location of the resulting active sites should account for the low I_e/I_t value observed. On the other hand, in the supported catalysts, the active sites of the atactic fractions show a prevailingly syndiotactic steric control ($I_e/I_t < 1$) on the first monomer insertion and therefore are different from the atactic sites in the $TiCl_3$-based catalyst ($I_e/I_t = 1$) (see Figure 3 and Table I). The most plausible interpretation of this fact is that at least some atactic sites in $MgCl_2$-based catalysts are completely lacking in intrinsic chirality; as a consequence, after the first random propene insertion, the second one is partially controlled by the configuration of the chiral carbon of the 2-methylbutyl end group:

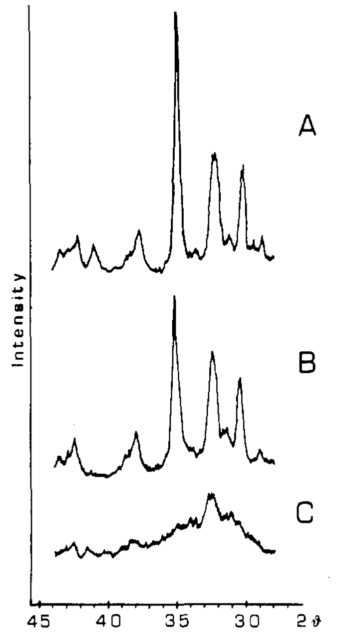
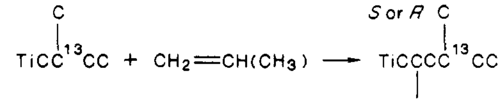


Figure 4. X-ray powder spectra of $MgCl_2$ samples: A, 7 days of ball milled; B, 10 days of ball milled; C, prepared by Grignard.



$$\underset{R\text{ or }S}{\mathrm{Ti\overset{C}{\overset{|}{C}}{}^{13}CC}} + \mathrm{CH_2{=}CH(CH_3)} \longrightarrow \mathrm{TiC\overset{S\text{ or }R}{C}\underset{\underset{C}{|}}{C}\overset{C}{\overset{|}{C}}{}^{13}CC}\ \ R\text{ or }S$$

Therefore, of the four diastereomeric end groups detected in atactic polypropene (see Scheme I), those in which the second inserted unit has the opposite configuration with respect to the first one (B and D) are present to a major extent.

The data of Table I allow us to infer some information concerning the effect of the kind of $MgCl_2$ activation on the performance of the supported catalysts. Catalysts a and b were supported on $MgCl_2$ activated by ball milling for different milling times, while catalyst c was supported on an active $MgCl_2$ obtained by chlorination of a Grignard compound. Figure 4 shows the X-ray powder spectra of the differently activated $MgCl_2$ samples. Looking at the spectra and considering the data of Table I, one can observe that the decrease of the crystalline order by the prolonged grinding of the support (catalysts a and b) produces an increase in titanium content and in activity. Both effects are definitely more evident in catalyst c: the activation procedure via Grignard compound allows us to obtain a clearly more disordered form of $MgCl_2$ and an increased number of specific sites suitable for titanium fixation than even prolonged mechanical treatment. Besides titanium content and activity, polymer fraction distribution also varies by varying the procedure of support activation. However, the nearly identical values of the I_e/I_t ratios of all the corresponding fractions of the samples show that the steric features of the isotactic and atactic active sites are the same in the three different systems. Therefore, we can conclude that the activation process affects the structural disorder, the titanium content, and the activity of the $TiCl_4/MgCl_2$-based catalysts as well as active site distribution; however, the steric structure of both isotactic and atactic sites is independent of the activation procedure.

Experimental Section

Activation of $MgCl_2$. $MgCl_2$ (A). Three hundred and seventy grams of stainless steel balls (8 mm in diameter) was put into a

350-mL pot. The inside was purged with N_2, then $MgCl_2$ (50 g) was added, and the pot was placed on a roller-type milling machine. After 7 days, the milled $MgCl_2$ was transferred with heptane into a flask and dried under vacuum. **$MgCl_2$ (B).** It was activated following the same procedure by 10 days of ball milling. **$MgCl_2$ (C).** It was obtained by chlorination of the Grignard compound n-C_4H_9MgCl as described in the patent literature.[2] **Preparation of Supported Catalysts.** Fifty milliliters of $TiCl_4$ was added to 25 g of activated $MgCl_2$ and refluxed for 1 h, the excess $TiCl_4$ was filtered at 90 °C, and the solids were washed twice at the same temperature with heptane and dried under vacuum.

Polymerizations. All the samples were prepared at 20 °C, at an atmospheric pressure of C_3H_6, in a glass reactor containing 50 mL of heptane in the presence of 0.2 g of solid catalyst and 0.15 mL of $Al(^{13}CH_2CH_3)_3$.

$Al(^{13}CH_2CH_3)_3$ was prepared by reaction of $CH_3{}^{13}CH_2Li$ with $AlCl_3$ according to the literature.[11] All the polymers were fractioned with boiling solvents by conventional methods.

NMR Analysis. The NMR samples were prepared by dissolving ca. 100 mg of polymer in 1 mL of 1,2,4-trichlorobenzene in a 10-mm-o.d. tube. One-half milliliter of $C_2D_2Cl_4$ was added as a lock solvent, and 1% hexamethyldisiloxane was used as an internal chemical shift reference. All the spectra were obtained by using a Bruker AM-270 spectrometer operating at 67.89 MHz in PFT mode, at a temperature of 115 °C. A standard pulse sequence (INEPT)[12] was employed: for ^1H, RD–90–τ_1–180–τ_1–90–τ_2–180–τ_2–decouple; for ^{13}C, 180–τ_1–90–τ_2–180–detect. In this sequence, the recycle time of 5 s ensures that the system is fully relaxed. A total of 16 K data points were accumulated over a sweep width of 7.5 kHz. Delay times t_1 and t_2 were 1.9 and 1 ms, respectively; ^{13}C pulse widths were 8.4 (90°) and 16.8 s (180°).

Acknowledgment. We sincerely thank Dr. William Porzio for X-ray analysis.

Registry No. $TiCl_4$, 7550-45-0; $MgCl_2$, 7783-40-6; $Al(^{13}CH_2CH_3)_3$, 80480-36-0; propene, 115-07-1; polypropylene, 9003-07-0.

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Novel Deuterating Agent for Unsaturated Hydrocarbons

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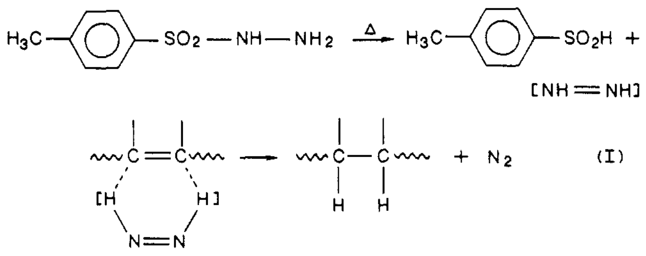
Introduction

One of the oldest polymer modification reactions is the hydrogenation of polymers containing olefinic groups.[1] This has traditionally been done through the use of heterogeneous catalysts like nickel on Kieselguhr at high pressures and temperatures.[2] In addition to requiring reactors capable of high pressures (40 atm), the method can cause chain cleavage under severe hydrogenation conditions. Homogeneous catalyst systems, like nickel octanoate/aluminum triethyl, can operate at atmospheric pressure and moderate temperatures but present considerable problems in the separation of the polymer from the catalyst.[3] Recently, diimide has been shown to be an extremely useful material for hydrogenation of unsaturated, nonpolar polymers such as polydienes.[4,5] Compounds such as p-toluenesulfonohydrazide (PTSH) decompose at moderate temperature (105 °C) to give a transitory species, diimide (N_2H_2), which readily adds hydrogen to olefinic groups. The proposed mechanism is shown below in eq I.



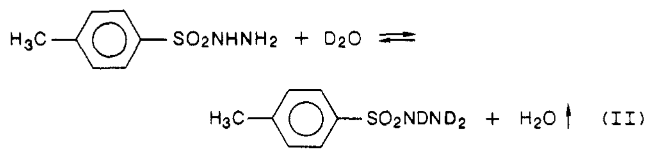
(I)

This method can be carried out at atmospheric pressure under moderate temperatures with easy isolation of the product.

Similar problems exist when deuterium (D_2) is substituted for hydrogen (H_2) in the heterogeneous and homogeneous systems. Deuterated polymers have found considerable use in recent years as tagged components in solid-state studies of chain conformation using small-angle neutron scattering[6,7] and ^2H NMR[8,9] methods. This paper discusses the preparation and use of a deuterium-modified PTSH, which can be used as a convenient and simple way to add deuterium to olefinic groups.

Experimental Section

Synthesis of Deuterating Agent. The deuterating agent was prepared by replacing the labile hydrogens of the hydrazide groups of p-toluenesulfonylohydrazide according to the following equation:



(II)

This was accomplished by dissolving 10 g of PTSH (Aldrich Chemical Co.) in 200 mL of benzene in a reactor equipped with a condenser and a Dean–Stark trap. To the solution was added 2 mL (d_{20} = 1.107 g/m^3) of D_2O, and the mixture heated to reflux. After about 2 mL of water was collected in the trap (azeotrope temperature was 69.4 °C), another 2 mL of D_2O was added, and the process was repeated until about 8 mL of D_2O was used. About 9 mL of an aqueous phase was collected in the trap (theoretical should be 8.8 mL of H_2O). The reactor was cooled to room temperature, whereupon the product crystallized out. Recrystallization from petroleum ether gave a yield of 9.7 g of final product (theoretical = 10.2 g). Analysis of the deuterated product by ^1H NMR spectroscopy showed that over 90% of the hydrazide protons had been replaced by deuterium (Figure 1).

Deuteration of Unsaturated Polymers. The deuteration of polybutadiene was carried out according to the method used by Harwood.[4] This was accomplished by dissolving 1.5 g of a polybutadiene, which had been prepared by anionic polymerization, in 150 mL of dried xylene (molecular sieves) in a reactor. The polybutadiene had a molecular weight (M_n) of 22600, a

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