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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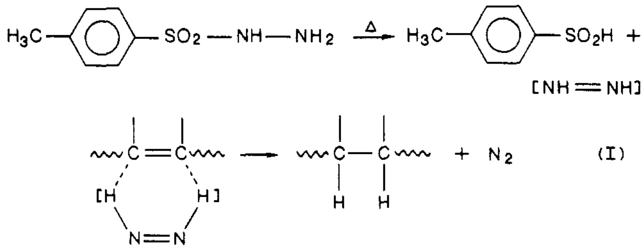
Received October 20, 1988;
Revised Manuscript Received December 14, 1988

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.



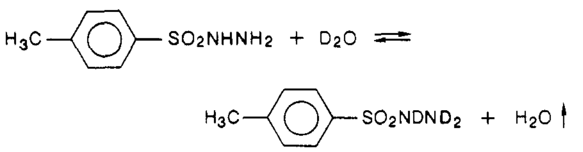
(I)

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 22 600, a

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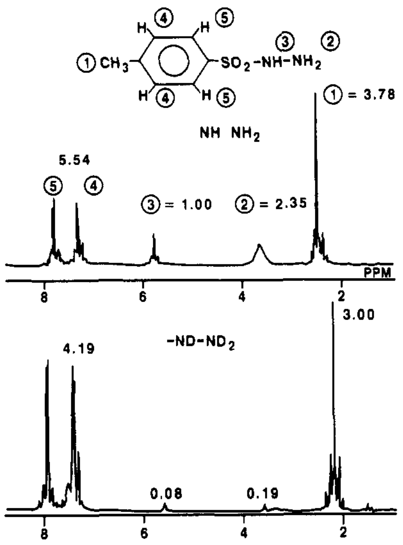


Figure 1. ^{1}H NMR comparison of protio- and deuterio-*p*-toluenesulfonohydrazide.

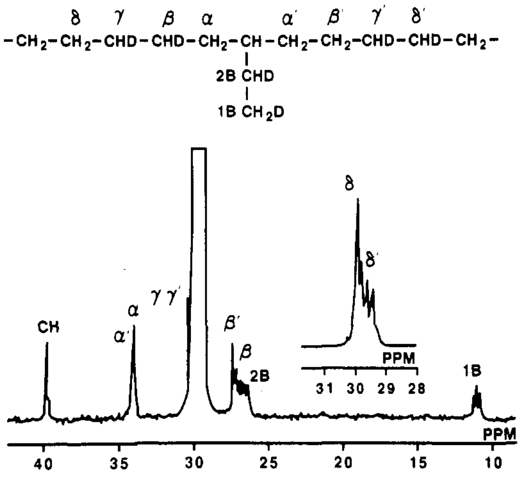


Figure 2. ^{13}C NMR spectrum of deuterated polybutadiene.

molecular weight distribution of 1.04, and a composition of 52% *trans*-1,4, 38% *cis*-1,4, and 10% 1,2 placements (as determined by ^{13}C NMR spectroscopy). To this solution was added 9.7 g of deuterio-PTSH, and the solution was brought to xylene reflux temperature (≈139 °C). After 4 h at reflux, the reactor was cooled, and the product precipitated in methanol. ^{13}C NMR spectroscopy shows that the polybutadiene is completely saturated and that deuterium has been added at all possible sites (Figure 2).

Characterization. NMR spectra were collected on a JEOL GX400 spectrometer. All chemical shifts will be reported relative to TMS at 0 ppm. ^{1}H NMR spectra of H- and D-PTSH were taken at a field of 399.7 MHz. The pulse width was 90°, the pulse delay was 5 s, and the digital resolution was 0.49 Hz/point. Samples were prepared as $CDCl_3$ solutions and were run at 30 °C. ^{13}C NMR spectra (100.4 MHz) of polybutadiene dissolved in $CDCl_3$ were recorded at 55 °C with a pulse width of 90°, a pulse delay of 5 s, with a digital resolution of 0.61 Hz/point, and under complete ^{1}H decoupling. Samples of the deuterated polybutadiene were dissolved in a mixture of *o*-dichlorobenzene-d_4/1,3,5-trichlorobenzene, and ^{13}C NMR spectra were run at 135 °C under complete decoupling. The pulse width was 90°, the pulse delay 15 s, and the digital resolution 0.24 Hz/point.

Results and Discussion

The ^{1}H NMR spectra for the deuterio- and protio-PTSH are given in Figure 1, and the integrated peak areas clearly show that approximately 90% of the hydrogens attached to the hydrazide group have been replaced by deuterium (>NH at 5.8 ppm and $-NH_2$ at 2.6 ppm). A higher percentage of the protons might be replaced by increasing the number of D_2O exchanges beyond the four that were used to synthesize the D-PTSH.

The ^{13}C NMR spectra of the base polybutadiene (PBd) and the hydrogenated version of the same material are given in Figures 3 and 4, respectively. Comparison of Figure 3 with Figure 2 (D-PBd) and Figure 4 (H-PBd) shows that the resulting material is completely saturated.

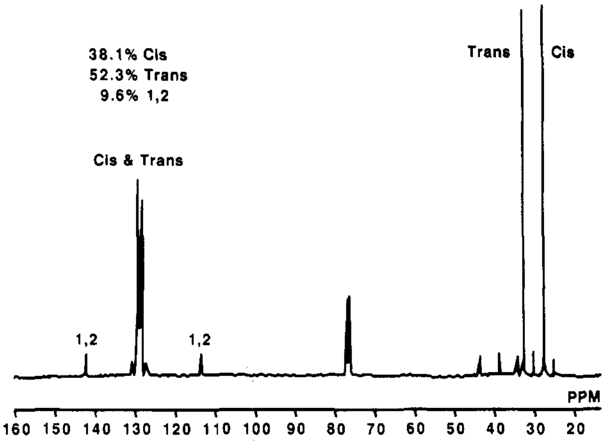


Figure 3. ^{13}C NMR spectrum of polybutadiene.

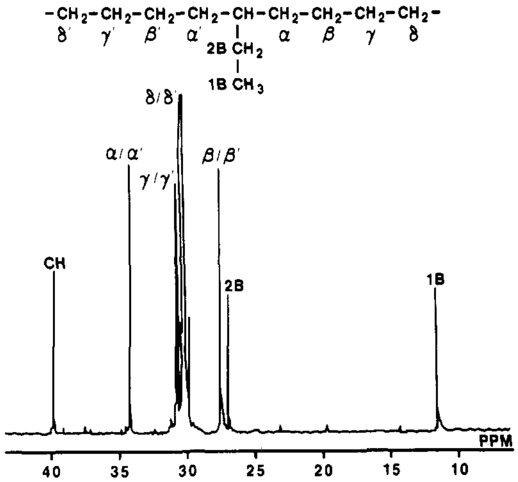
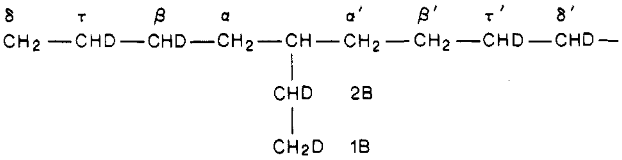


Figure 4. ^{13}C NMR spectrum of hydrogenated polybutadiene.

Table I
Observed Shifts and Couplings for D-PBd



$$\overset{\delta}{-CH_2}-\overset{\tau}{CHD}-\overset{\beta}{CHD}-\overset{\alpha}{CH_2}-\underset{\underset{CH_2D\ \ 1B}{|}}{\underset{CHD\ \ 2B}{\underset{|}{CH}}}-\overset{\alpha'}{CH_2}-\overset{\beta'}{CH_2}-\overset{\tau'}{CHD}-\overset{\delta'}{CHD}-$$

carbon	δ(HPBd), ppm obsd	δ(DPBd), ppm calcd	δ(DPBd), ppm obsd	J_{CD}, Hz
1B	11.20	10.85	10.85	19.0
2B	26.80	26.45	26.35	19.5
CH	39.75	39.65	39.67	
α	34.14	34.04	34.04	
α′	34.14	34.14	34.14	
β	27.35	27.00	26.89	19.5
β′	27.35	27.25	27.28	
τ	30.49	30.14	*a*	*a*
τ′	30.49	30.14	*a*	*a*
δ	30.00	29.90	29.90	
δ′	30.00	29.65	29.55	19.5

[a] Not completely resolved.

Table I summarizes the chemical shift and scalar coupling data for Figures 2 (D-PBd) and 4 (H-PBd). The expected chemical shifts for the D-PBd were calculated on the basis of upfield shifts for the upfield shifts which result from deuteration. These slight decreases in chemical shift are typically ≈–0.25 ppm for an ipso-deuteron and ≈–0.10 ppm for the α-deuteron.[10] The calculated and observed shifts for the D-PBd agree quite well with the largest deviations occurring in the poorly resolved peaks. The observed J splittings result from carbon–deuterium coupling which is not removed by ^{1}H irradiation. Because the spin of the ^{2}H nucleus is one, a C–D bond appears as a triplet. The coupling constant J^1_{CD} is expected to be about 20 Hz.[10] As Table I shows, J^1_{CD} is found to be 19.0–19.5 Hz.

As can be seen from the above results, a novel deuterating agent for adding deuterium to olefinic bonds can easily be synthesized by replacing the protons of the hydride group of PTSH with deuterium by using a simple D_2O exchange.

Registry No. PTSH, 1576-35-8; D-PTSH, 109333-73-5; polybutadiene, 9003-17-2.

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Interpolymer Association of Polymers in Extremely Dilute Solution Studied by Normal Pulse Polarography

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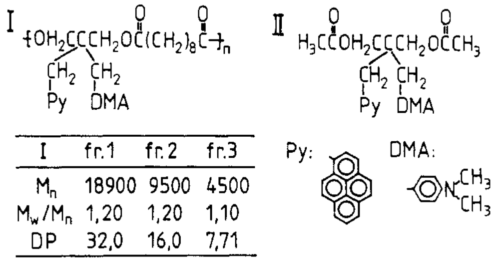
Received June 16, 1988;
Revised Manuscript Received August 26, 1988

Introduction

Interpolymer association of neutral synthetic polymers, unexpected from conventional solution theory, has been reported for a number of exciplex-forming polymers.[1] Extensive spectroscopic investigation on polymer structural, concentration, and molecular weight effects on intra- and interpolymer exciplex formation revealed that weak interchromophore interactions, typically between aromatic hydrocarbons such as anthracene or pyrene (Py) and N,N-dimethylaniline (DMA) groups, both bonded to polymers, were responsible for polymer association.[2] This behavior seems to be common for polymers containing weak electron-donor and -acceptor groups which exhibit donor–acceptor interaction only in the excited state. The ground-state interaction is so weak that the ground-state electronic state is hardly affected and the origin of interaction is believed to be dipole–dipole interaction. Since no such interaction was detected in small molecular model systems, cumulative interactions in polymers in which weak donors and acceptors are regularly arranged were believed to be the essential requirement.



I	fr.1	fr.2	fr.3
M_n	18900	9500	4500
M_w/M_n	1,20	1,20	1,10
DP	32,0	16,0	7,71

Figure 1. Structures of exciplex-forming polymer and its monomer model compound.

This kind of interpolymer association occurs in extremely dilute solution where the chromophore concentration is as low as 10^{-5} M or less and can be evidenced only by the concentration dependence of I^{EX}/I^{LE}, where I^{EX} and I^{LE} are the fluorescence intensities of the exciplex and of the locally excited state of the photoabsorbing species, respectively. Under the condition of high dilution, it is difficult to prove polymer association by methods other than fluorescence spectroscopy since (i) the interaction is too weak to be detected by absorption spectroscopy and (ii) conventional methods for the study of solution properties such as viscometry, osmometry, small-angle light scattering, vapor pressure osmometry, etc., cannot be applied to this highly dilute system. We have been searching for other techniques to demonstrate this interesting polymer association phenomenon.

Electrochemical measurement of the diffusion constant (D) is a candidate method for determining molecular aggregation under extremely dilute conditions. Since D for molecular aggregates decreases with increasing extent of aggregation, the concentration dependence of D provides unequivocal evidence for intermolecular association. This principle has been used for the determination of the association number (AN) of various dye molecules in both aqueous and organic solutions.[3] In this note, we describe spectroscopic and electrochemical studies on the association of exciplex-forming polymers, shown in Figure 1, and of the monomeric model system.

Experimental Section

Both spectroscopic (Hitachi MPF-4 spectrofluorometer) and electrochemical (Fuso polarograph, Model 312) measurements were carried out in N,N-dimethylformamide (DMF) at 25 °C. In order to adjust the experimental conditions, both measurements were conducted in the presence of 0.1 M tetra-n-butylammonium perchlorate (TBAP). Polymer I and its monomer model compound (II) were prepared according to the literature.[2f] Polymer I was fractionated into three samples by means of gel permeation chromatography (Toyo Soda) (Table I). DMF was refluxed over calcium hydride and then fractionally distilled twice. TBAP as a supporting electrolyte was prepared from the corresponding bromide salt with perchloric acid in water and was recrystallized 3 times from an n-hexane–ethyl acetate mixture.

Results and Discussion

Concentration Dependence of Exciplex Formation. The concentration dependence of I^{EX}/I^{LE} by I and II is

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