A Study by Solid-State and Solution ^{13}C NMR on Silicon-Containing Polyacetylenes

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ABSTRACT: A preliminary study, both by solid-state and solution ^{13}C NMR, on poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and on the corresponding monosubstituted polymer poly[(trimethylsilyl)acetylene] (PTMSA) is presented here, in order to correlate the properties to the structure of these polymers. According to NMR spectra, PTMSP's obtained by using $TaCl_5$ show a continuous distribution between cis and trans environments, while $NbCl_5$-catalyzed polymers are characterized by a more regular structure. Similar results have been obtained on PTMSA samples: the solution and solid-state spectra of the soluble fraction indicate a highly disordered structure as compared to the insoluble one.

Introduction

A great deal of attention has been devoted in the last few years to substituted polyacetylenes, an interesting class of polymers containing alternating double bonds along the main chain.[1-3]

$$n R_1C{\equiv}CR_2 \longrightarrow -\left(\begin{matrix} C{=}C \\ | \quad | \\ R_1 \quad R_2 \end{matrix}\right)_n-$$

The presence of the substituents seems to prevent the conjugation of adjacent double bonds, conferring to the main chain a remarkably twisted conformation. Thus, unlike polyacetylene, these polymers are electrically insulating, are not paramagnetic, are amorphous, and show some unusual and interesting properties, such as solubility in many organic solvents, good thermal and oxidative stability, and high gas permeability, which make them potentially useful for some practical applications.[4-7]

In this respect, poly[1-(trimethylsilyl)-1-propyne] [PTMSP; $R_1 = CH_3$, $R_2 = Si(CH_3)_3$] is one of the most interesting among these polymers: it can be easily obtained with very high molecular weights in almost quantitative yields and exhibits an extremely high gas permeability.[4,6,7]

The solubility of PTMSP depends on the catalytic system:[8] indeed, polymers obtained with $NbCl_5$ do not dissolve in some aliphatic hydrocarbons, where $TaCl_5$-catalyzed polymers do.

This behavior is not well understood and, in principle, could be ascribed either to differences in the molecular weights due to a different stability of the Nb-based active sites with respect to the Ta-based ones or to some differences in the geometric structure, related to the presence of double bonds along the main chain. The former hypothesis can be ruled out since, on the basis of our results[9] and according to other authors,[8] a straightforward relationship between molecular weight and solubility is not observed for polymers obtained with different catalytic systems. So far, only a few papers devoted to the study of the geometric structure in monosubstituted polyacetylenes have appeared in the literature.[10-13]

In the present paper a preliminary study by solid-state and solution ^{13}C NMR on PTMSP and on the corresponding monosubstituted silicon-containing polyacetylene, poly[(trimethylsilyl)acetylene] [PTMSA; $R_1 = H$, $R_2 = Si(CH_3)_3$], has been carried out in order to correlate the structure to the properties of these polymers. The spectra of PTMSP and PTMSA are compared with the solution spectrum of poly(*tert*-butylacetylene) [PTBA; $R_1 = H$, $R_2 = C(CH_3)_3$], whose geometric structure has been investigated and elucidated.[12,13]

Experimental Section

Monomers. 1-(Trimethylsilyl)-1-propyne (TMSP), (trimethylsilyl)acetylene (TMSA), and *tert*-butylacetylene (TBA) were distilled twice from CaH_2 under nitrogen at atmospheric pressure. All the solvents, analytical grade, were refluxed over $LiAlH_4$ for 2 h and distilled under nitrogen. Catalysts ($TaCl_5$, $NbCl_5$, $MoCl_5$, WCl_6) and cocatalyst (n-Bu_4Sn) from Alfa Products were used without further purification.

Polymers. Polymerization runs were carried out under dry nitrogen in a properly equipped reaction vessel, according to the literature.[1] In a typical example the catalyst was dissolved in the polymerization solvent and aged at the reaction temperature for 15 min. The monomer was mixed with a proper amount of the polymerization solvent and of chlorobenzene (as internal standard for GC) and then added immediately to the catalyst solution. The conversion was followed by gas chromatography, and, after a given time, the polymerization was stopped by adding a mixture of toluene and methanol (4:1 volume ratio). The polymer formed was dissolved in a small amount of solvent, precipitated in a large excess of methanol, filtered and washed with methanol, and dried to a constant weight at 40 °C under vacuum. Polymerization conditions for the different polymers are given in Table I.

Among these polymers only PTMSA is partially insoluble in toluene. The toluene-insoluble fraction (about 50% w/w) was separated by ultracentrifugation at 0 °C and 8000 rpm, washed with toluene several times, and dried under vacuum at 40 °C. The soluble fraction was poured into a large excess of methanol and the precipitate filtered and dried to constant weight at 40 °C under vacuum.

NMR Characterization. The solution experiments were performed on a Bruker AM-270 operating at 67.93 MHz for carbon. Samples were dissolved in $CDCl_3$; concentration ranged from 2 to 5% w/v. All experiments were carried out at room temperature.

The solid-state experiments were performed on a Bruker AC-300 spectrometer with solid-state accessory magic angle spinning

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Table I
Polymerization of TMSP, TMSA, and TBA

sample	catalyst	T, °C	t, h	$[M]_0/[cat.]^e$ molar ratio	$[\eta]$,[c] dL/g
PTMSP[a]	$NbCl_5$	80	1	50	0.9
	$TaCl_5$	80	1	50	5.5
PTMSA[a]	WCl_6–nBu_4Sn[b]	30	24	50	0.2[d]
PTBA[a]	$MoCl_5$	30	24	100	1.6

[a] Polymerized in toluene. [b] $[WCl_6] = [nBu_4Sn]$. [c] Measured in toluene at 30 °C. [d] Soluble fraction. [e] $[M]_0 = 1.0$ M.

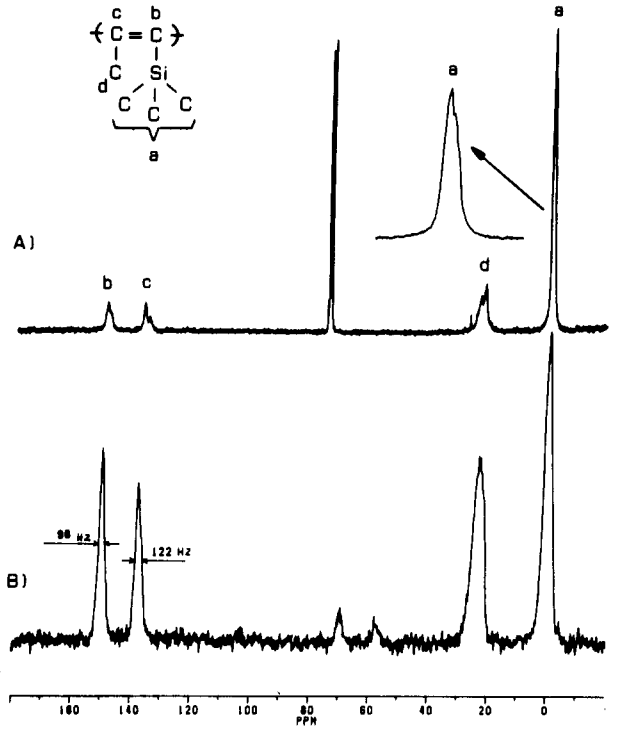

Figure 1. ^{13}C NMR solution- (A) and solid-state (B) spectra of poly[1-(trimethylsilyl)-1-propyne] prepared in the presence of $NbCl_5$.

at spinning speeds ranging from 3 to 5 kHz. Cross-polarization (CP) and proton decoupling were necessary to achieve a good signal to noise and "high" resolution.

All ^{13}C NMR data reported below were measured by using standard pulse sequences.[14,15] The ^{1}H and ^{13}C spin–lattice relaxation times (T_1) were measured by using inversion recovery pulse sequences. The ^{13}C spin–lattice relaxation times in the rotating frame ($T_{1\rho}$) were measured at a spin-lock field of 42.5 G ($\pi/2$ corresponds to 5.5 μs). The rotating-frame relaxation parameters, proton–carbon cross-relaxation time (T_{CH}), and proton relaxation time ($T_{1\rho}$) were obtained by curve-fitting the peak heights as a function of the cross-polarization contact time.

Chemical shifts are given with respect to TMS (tetramethylsilane) with adamantane as intermediate reference in the solid and hexamethyldisiloxane in solution.

Results

Poly[1-(trimethylsilyl)-1-propyne]. Figures 1 and 2 show the solution- (A) and solid-state (B) spectra, of sample 1 (Nb-based catalyst) and sample 2 (Ta-based catalyst), respectively. In the solution spectra the two methyl resonances have been assigned on the basis of chemical shifts and relative intensities. In the solid state the same assignment has been made by considering relative intensities and proton–carbon cross-relaxation times.

The assignment of the olefinic carbons is more subtle, but considering that the cross-relaxation time (see Table II) for the resonance at 152.5 ppm is shorter than the one for the resonance at 140.4 ppm, we tentatively assign the

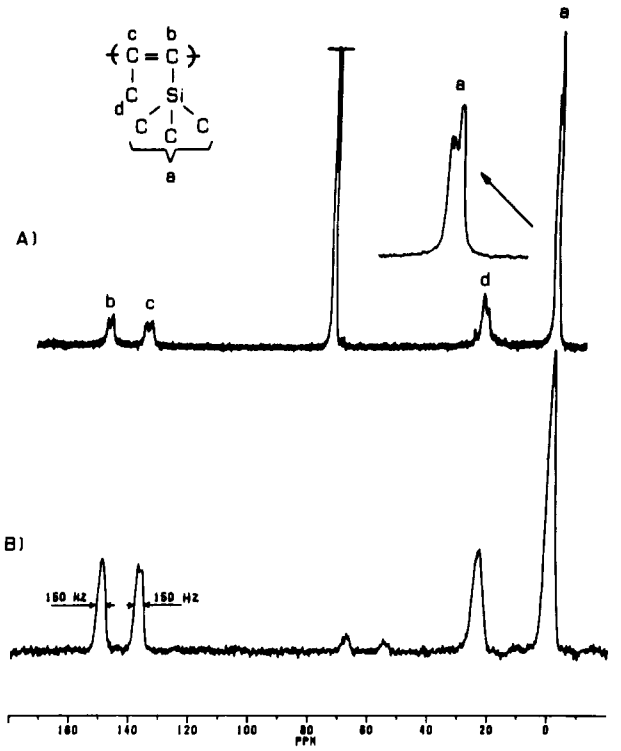

Figure 2. ^{13}C NMR solution- (A) and solid-state (B) spectra of poly[1-(trimethylsilyl)-1-propyne] prepared in the presence of $TaCl_5$.

Table II
Carbon Spin–Lattice Relaxation Time (T_1), Relaxation Time in the Rotating Frame ($T_{1\rho}$), and Proton–Carbon Cross-Relaxation Time in the Rotating Frame (T_{CH}) for the Different Carbon Sites in PTMSA and PTMSP

		C_b	C_c–C_c[a]	C_d	C_a
PTMSP	T_1, s	16	16	4	1.6
	$T_{1\rho}$, ms	25	25	25	25
	T_{CH}, ms	0.50	0.73	0.14	0.47
PTMSA	T_1, s	21	10–16		1.26
	$T_{1\rho}$, ms	20	20–100		100
	T_{CH}, ms	0.18	0.27–0.45		0.59

[a] Labels c and c′ for PTMSA refer to the relaxation times of the two peaks observed for C_c in Figure 5.

former to C_b and the latter to C_c. The assignment of the olefinic carbons is not in agreement with the assignment performed by other authors in the solution spectrum[8] but in agreement with the assignment in PTBA,[12,13] taking into account substituent effects.

Inspection of Figures 1 and 2 shows a strong matching between the main resonances of the solution- and solid-state spectra. Since conformational changes generally induce shifts on the order of a few parts per million, this comparison suggests that PTMSP has a similar conformational structure both in solution and in the solid state. However, substantial differences can be observed between the solution and the corresponding solid-state spectra. The solution spectra (Figures 1A and 2A) show a splitting of all the resonances, and the splitting depends on the catalyst, as does the relative amplitude within the doublet. The solid-state spectra show no well-resolved resonances, but the effect of the catalyst is visible in the olefinic region. Indeed in the spectrum of the sample prepared with the Ta-based catalyst (Figure 2B) a significant broadening of the resonances of both olefinic carbons is observed with respect to the spectrum of the other sample (Figure 1B), accompanied by a poorly resolved splitting of the resonance assigned to C_c. Since both samples are completely

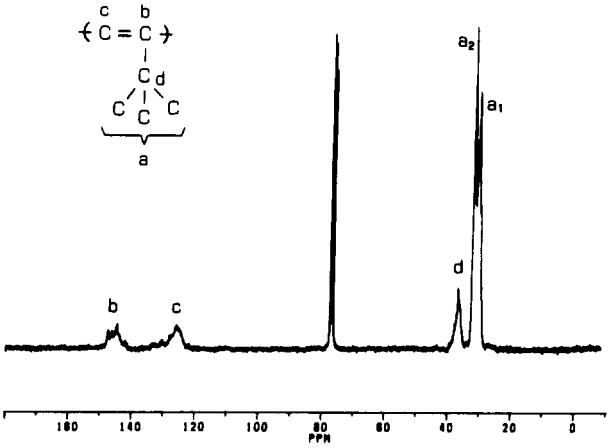

Figure 3. ^{13}C NMR solution spectra of poly(*tert*-butylacetylene). Peaks a_1 and a_2 are attributed to cis and trans units, respectively.[12]

Table III
Proton Relaxation Time (T_1) and Relaxation Time in the Rotating Frame ($T_{1\rho}$) for PTMSP and PTMSA

	PTMSP	PTMSA
T_1, s	0.65	0.70
$T_{1\rho}$, ms	5	37

amorphous, according to X-ray analysis,[8] this line broadening should not arise from the presence of amorphous regions in sample 2. Moreover, several spectra of sample 2 have been run with different cross-polarization contact times, and essentially no changes in the shape of the peak at 140.4 ppm have been observed. Normally we would expect different CP dynamics for different morphological regions, so this possibility can be ruled out. Therefore, we can interpret the differences in the solid-state spectra of the two samples as due to differences in the chain microstructure rather than to intermolecular, solid-state effects.

In order to identify the microstructure, we compared the solution spectra of PTMSP with that of PTBA in which, according to the literature, the splitting of the methyl resonances has been assigned to the presence of cis and trans units (Figure 3).

The carbon relaxation times of sample 2 are summarized in Table II. The proton relaxation times are given in Table III and, as expected, are independent of the carbon site. The methyl group resonance has a unique carbon T_1.

Poly[(trimethylsilyl)acetylene]. Figure 4 shows the solution (A) and solid-state (B) spectra of the soluble component of a sample of poly[(trimethylsilyl)acetylene]. In the solid-state spectrum (Figure 4B), no resolved resonances appear in the olefinic region, but instead one broad line with a shoulder appears. This is an indication of a highly disordered local environment for these carbons. No such effect is visible for the methyl carbon. The effect of the disordered environment is also visible in the solution spectrum (Figure 4A) on the methyl carbon where several resonances are observed.

The solid-state spectrum of the insoluble component (Figure 5) shows more structure. The peaks in the olefinic region are better resolved even if not sufficiently to make it possible to determine the individual carbon–proton cross-relaxation times. It is clear though that the carbon–proton cross relaxation times, for the rightmost peak, is shorter than those for the other peaks.

The methyl group resonance appears as a single peak: however, a relaxation time experiment has shown that the methyl group resonance does not exhibit one unique carbon

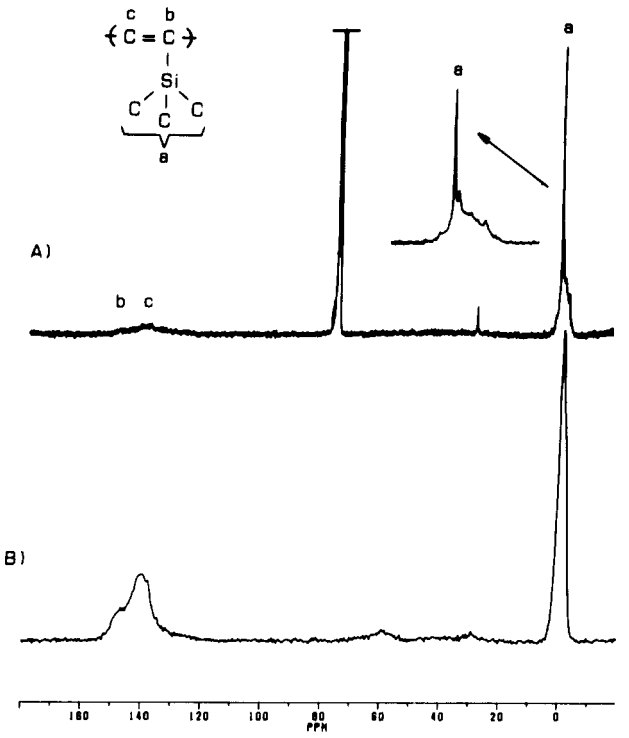

Figure 4. ^{13}C NMR solution- (A) and solid-state (B) spectra of the soluble component of poly[(trimethylsilyl)acetylene].

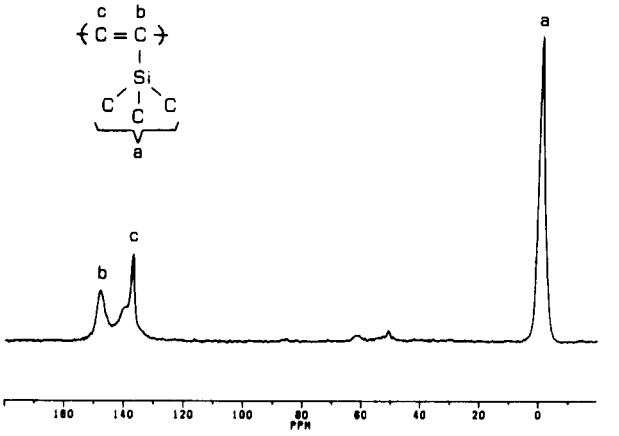

Figure 5. ^{13}C NMR solid-state spectrum of the insoluble component of poly[(trimethylsilyl)acetylene].

relaxation time but shows instead that the T_1 values depend on the position within the line. This is an indication that in the insoluble component of this sample the local environment consists of at least two distinct possibilities and not of a continuous distribution of local environments as in the soluble component.

Discussion

As shown above, the two differently prepared samples of PTMSP have different solution and solid-state spectra. According to Masuda et al.,[8] there is no evidence for monomer isomerization before polymerization and head to head addition is unlikely because of the steric hindrance of the trimethylsilyl group. Therefore, the differences between the two samples must depend on the geometric structure of the double bonds along the chain.

By comparing PTBA (Figure 3) and PTMSP solution spectra (Figures 1A and 2A), we can interpret the doubling of the resonances of the PTMSP samples and the relative intensities within the doublets in terms of cis/trans content. Therefore, though we cannot assign the cis and

trans resonances only on the basis of this comparison, we can state that the sample prepared with $NbCl_5$ has a higher content of long cis or trans sequences, while the sample prepared with $TaCl_5$ has a more or less continuous distribution between cis and trans environments.

The situation in the solid is less clear since, owing to the broad lines, it is impossible to resolve the cis and trans contributions. However, the broadening of the resonances of the olefinic carbons of sample 2, the slightly resolved splitting of C_c, and the single relaxation times of the $Si(CH_3)_3$ group, indicating a continuous distribution of local environments, confirm that the amount of cis/trans order is smaller in this sample than in the sample prepared with $NbCl_5$. As to the splitting of the C_c resonance, it is much smaller than the shift observed between cis and trans polyacetylene (about 9 ppm)[16] but of the same order as the one observed in PTBA.[17]

As far as PTMSA is concerned, we can reasonably say that in this polymer too the solubility depends on the geometrical structure. Indeed, inspection of the solution and solid-state spectra of the soluble fraction indicates a highly disordered geometrical structure. Such disorder is clearly visible in the methyl region of the solution spectrum, where a splitting is observed similar to the one in PTBA (see Figure 3) and in the olefinic region of the solid-state spectrum. A larger amount of order is present in the insoluble fraction of the sample. However, on the whole the results suggest a large amount of short range order rather than a prevailing ordered structure, as in the more regular sample of PTMSP. Indeed, the broad lines of the olefinic carbons and the observation of distinct carbon T_1's within the resonance of the methyl carbon indicate the presence of large segments of the polymer being either cis or trans.

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Registry No. PTMSP, 87842-32-8; PTMSA, 30553-41-4; PTBA, 51730-68-8; $NbCl_5$, 10026-12-7; $TaCl_5$, 7721-01-9; WCl_6, 13283-01-7; $MoCl_5$, 10241-05-1; n-Bu_4Sn, 1461-25-2.