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SILICON-29 NMR STUDIES OF POLYMETHYLHYDROSILOXANES: SPIN-LATTICE RELAXATION TIME (T_1) MEASUREMENTS

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Summary

^{29}Si NMR spectra of polymethylhydrosiloxanes, $Me_3SiO[MeHSiO]_nSiMe_3$ from $n = 3$ to 8 and 35, have been determined. Both chemical shifts and spin-lattice relaxation times (T_1) have been measured. The stereochemistry at the adjacent chiral MeHSiO unit influences the nearest neighbor ^{29}Si chemical shift. The effect of chain length and position of MeHSiO units on T_1 values for $Me_3SiO[MeHSiO]_nSiMe_3$ systems are discussed.

Introduction

The high structural sensitivity of chemical shifts makes silicon-29 NMR a powerful tool for determination of the structure of oligomeric and polymeric siloxanes [1]. Detailed information can be obtained for the characterization of the different structural units [2], for the determination of average chain lengths [3] or for the degree of condensation of the siloxane framework [4].

Both the ^{29}Si chemical shifts as well as the spin-lattice relaxation times (T_1) of the silicon atoms in low molecular weight linear polydimethylsiloxane, $Me_3SiO[Me_2SiO]_nSiMe_3$, (MD_nM) have been determined [5]. In the ^{29}Si NMR spectra of the oligomers MD_nM, $n = 1$ to 8, individual resonance lines can be found for each distinct silicon nucleus. This degree of chemical shift resolution surpasses that observed in the ^{13}C or ^{1}H NMR of the same materials [6]. Spin-lattice relaxation times give information about the mobility at different points in polymer chains [7]. The relatively high values of the ^{29}Si T_1 values found in MD_nM are consistent with high mobility of these polymer chains [8].

In the case of polymethylhydrosiloxanes, $Me_3SiO[MeHSiO]_nSiMe_3$, (MD_n^HM) some of the long range substituent chemical shifts are obscured [9,10]. These complications result from the asymmetry of the CH_3HSiO (D^H) unit. In the ^{29}Si NMR spectra the terminal trimethylsilyl (M) groups and the D^H moieties exhibit resonances in substantially different regions. Tacticity effects are essential in under-

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TABLE 1

^{29}Si CHEMICAL SHIFTS AND T_1 VALUES FOR POLYMETHYLHYDROSILOXANE

δ [a](T_1) [b]					
Compound [c]	M	D_a^H	D_b^H	D_c^H	D_x^H
MD_3^HM	10.00(50)	−35.84(42) −35.87(42)	−35.67 −35.70(30) −35.72		
MD_4^HM	10.22(50)	−35.60(44) −35.65(38)	−35.11(32) −35.15(36) −35.19(41)		
MD_5^HM	10.21(52)	−35.61(43) −35.65(44)	−35.06(44) −35.10(39) −35.20(38)	−34.69(42) −34.76(42) −34.82(41)	
MD_6^HM	10.15(47)	−35.64(44) −35.69(46)	−35.08 −35.12(43) −35.16	−34.72 −34.76(43) −34.81	
MD_7^HM	10.21(48)	−35.60(48) −35.64(43)	−35.02 −35.06(41) −35.10	−34.65(35) −34.66(35) −34.69(32)	
MD_8^HM	10.26(49)	−35.58(46) −35.61(46)	−34.96 −34.99(42) −35.04	−34.56 −34.58(36) −34.60	
MD_{35}^HM	10.07(59)	−35.71 −35.75	−35.15 −35.18 −35.23		−34.66(37) −34.70(37) −34.75(37)

[a] Chemical shifts in ppm from TMS (δ 0.00 ppm ± 0.01 ppm). [b] In seconds; T_1 values where determined are in parentheses. [c] For the definition of the symbols, see the text. The D units are identified as follows: $MD_a^HD_b^HD_c^H\ldots$

standing the stereochemical features of substituted vinyl polymer chains. Tacticity and end group effects were used to interpret the observed fine structure in the proton decoupled spectrum of MD_5^HM: a triplet and a doublet [10]. Analogous features in the ^{29}Si NMR of MD_{50}^HM were explained as resulting from either complete atacticity or from the presence of equal amounts of oligomers of different tacticities. We have investigated in detail both the ^{29}Si chemical shifts and report the first spin-lattice relaxation times [11] of these systems. See Table 1.

Experimental section

Materials

Polymethylhydrosiloxane, MD_{35}^HM, was obtained from Alfa Products and was used as received. MD_n^HM oligomeric mixtures were prepared by cohydrolysis of trimethylchlorosilane and dichloromethylsilane [12]. Each MD_n^HM (n = 3–8) oligomer was purified by GLPC (5.5 ft column, 10% SE-30 on Chromosorb W). Their properties were in agreement with literature values [12].

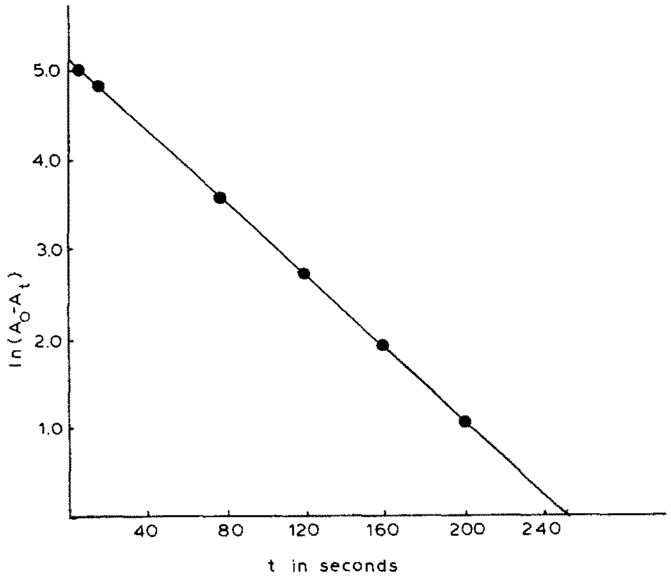

Fig. 1. A plot of $\ln(A_0 - A_t)$ vs. t for the determination of the T_1 for "M" silicon of MD_7^HM by inversion recovery techniques.

NMR measurements

All ^{29}Si NMR spectra were recorded on an IBM WP-270SY NMR spectrometer (63.51 MHz for ^{29}Si) equipped with an Aspect 2000 computer. All samples were run as 80% solutions in acetone-d_6 in 10 mm o.d. NMR tubes. Nitrogen was bubbled through the solution for at least 30 minutes in order to remove dissolved oxygen. The ^{2}H signal of the solvent was used as an internal lock. Chemical shifts were calculated from the line positions in proton noise-decoupled spectra at ambient probe temperature (37°C). Tetramethylsilane was used as an internal standard. For the ^{1}H decoupled ^{29}Si spectra, the experiments were performed by using the "gated decoupling without NOE effect" technique [13]. In this technique, the decoupling rf power is switched on at the same time as the measuring rf pulse, and the decoupler is switched off when data acquisition stops. The following parameters were used: time pulse 9 μs (α 45°), delay time 100 sec.

Spin-lattice relaxation measurements

The spin-lattice relaxation time (T_1) for all ^{29}Si nuclei were measured simultaneously by the inversion-recovery pulse method under conditions of proton noise decoupling [8]. The pulse sequence utilized in these measurements was $(180°\text{-}t\text{-}90°\text{-}T)_n$ where the pulse interval time (t) is experimentally varied and T is set to at least five times the longest T_1 measured [14]. In this sequence, a semilog plot of $(A_\infty - A_t)$ vs. t results in a straight line with a slope equal to $-1/T_1$ where A_∞ and A_t were the transformed signals intensities from the 90° and $90°_t$ pulses. For each determination 8–12 sets of measurements were taken. The delay between pulse sequence (T) was set at 300 sec [8]. This delay time was shown to be sufficient to make accurate T_1 measurements. See Fig. 1.

Results and discussion

The ^{29}Si chemical shifts for the series $\mathrm{MD}_n^{\mathrm{H}}\mathrm{M}$ (n = 3–8, 35) reported in Table 1 were obtained by gated decoupling in order to eliminate the NOE [13]. The values are reported relative to TMS, with positive values when the sample resonates at higher frequency than the reference. The group multiplicities which can be seen in each spectrum must be caused by asymmetry effects. These results are consistent with those values previously reported for $\mathrm{MD}_n^{\mathrm{H}}\mathrm{M}$ oligomers [9,10]. The number of peaks indicates that only the stereochemistry at the nearest-neighbor D^{H} influences the adjacent ^{29}Si resonance frequencies in the D^{H} region. The D^{H} units are identified as follows: $\mathrm{MD}_a^{\mathrm{H}}\mathrm{D}_b^{\mathrm{H}}\mathrm{D}_c^{\mathrm{H}}\ldots$ The spectrum appears as a doublet and a triplet for either $\mathrm{MD}_3^{\mathrm{H}}\mathrm{M}$ or $\mathrm{MD}_4^{\mathrm{H}}\mathrm{M}$. Since $\mathrm{MD}_3\mathrm{M}$ and $\mathrm{MD}_4\mathrm{M}$ are atactic, the sequences $ddd = lll$, $ddl = ldd = lld = dll$, and $ldl = dld$ are equally probable for the D^{H} unit. This gives a 1 : 2 : 1 triplet for $\mathrm{D}_b^{\mathrm{H}}$ position in $\mathrm{MD}_3^{\mathrm{H}}\mathrm{M}$ and $\mathrm{MD}_4^{\mathrm{H}}\mathrm{M}$. For the $\mathrm{D}_a^{\mathrm{H}}$ position, the sequences $\mathrm{M}dd = \mathrm{M}ll$ and $\mathrm{M}dl = \mathrm{M}ld$ are equally probable. The result is a doublet for the $\mathrm{D}_a^{\mathrm{H}}$ position in $\mathrm{MD}_3^{\mathrm{H}}\mathrm{M}$ and $\mathrm{MD}_4^{\mathrm{H}}\mathrm{M}$.

The ^{29}Si spectrum of $\mathrm{MD}_n^{\mathrm{H}}\mathrm{M}$ (n = 5–8, 35) oligomers show four distinct regions of absorption, M at 10.00 to 10.26 ppm, $\mathrm{D}_a^{\mathrm{H}}$ from −35.58 to −35.84 ppm, $\mathrm{D}_b^{\mathrm{H}}$ from −34.96 to −35.72 ppm, and $\mathrm{D}_x^{\mathrm{H}}$ ($x = 3$ to $n - 2$) from −34.56 to −34.82. The predominant feature, a triplet at −34.66 to −34.75 ppm, can be assigned to the D^{H} groups which are three or more D^{H} groups away from the terminal M group of the oligomer. These coalesce to a triplet structure. Hence there is no detectable

Fig. 2. ^{29}Si {^{1}H} NMR of the D^{H} region of $\mathrm{MD}_5^{\mathrm{H}}\mathrm{M}$ (upper) and $\mathrm{MD}_7^{\mathrm{H}}\mathrm{M}$ (lower) oligomers.

change in these chemical shifts and no new stereochemical effects for oligomers MD_n^HM beyond $n = 5$. (See Fig. 2)

Once the spectra were fully assigned, it became feasible to investigate the ^{29}Si spin-lattice relaxation times of these polymethylhydrosiloxanes in order to provide information about their molecular motion. The general trends in T_1 values can be seen in Table 1. The T_1 for the M end groups are longest. The D_a^H units have longer relaxation times than those of more internal D^H units. It is reasonable that M has the longest T_1 because M units are able to spin freely at the ends of the chain while D^H units may only rotate through a restricted angle which obviously decreases their T_1 values. These values decrease gradually as the D^H units approach the middle of the chain. All D^H units have comparable relaxation times. This implies that the motional process along the chains are similar. The relatively long values of T_1 make it clear that these systems are quite mobile. This is to be expected in the absence of crosslinking of linear MD_n^HM chains. Finally, the T_1 values of the different stereoisomers do not change significantly in oligomers and polymer systems. This implies that tacticity and chain length have little effect on the motion occurring in these systems. The ^{29}Si T_1 measurements on the series of MD_n^HM oligomers demonstrate that localized motions along segments of the oligomer backbone result in ^{29}Si relaxation that rapidly becomes independent of chain length. For comparison, the T_1 values for the D^H groups in the MD_n^HM oligomers are consistently shorter than the T_1 values for the D groups in MD_nM oligomers. The Si–H groups present in the MD_n^HM oligomers provide a dipolar contribution to the relaxation mechanism which shortens the ^{29}Si T_1 relaxation times.

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