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Polymer 44 (2003) 2295–2302

polymer

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Supramolecular association of acid-terminated polydimethylsiloxanes. IV. NMR investigation of hydrogen bonding interactions and apparent molecular weight in the bulk state

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Received 30 July 2002; received in revised form 2 December 2002; accepted 23 December 2002

Abstract

Carbon-13 spin-lattice relaxation time measurements were used to probe the existence of hydrogen bonding interactions in bulk for a diacid-terminated oligosiloxane at temperatures well above its glass transition and melting temperatures. The behavior of the corresponding monoacid-terminated oligosiloxane, which can form dimers only, diester-terminated oligosiloxane, which cannot undergo any hydrogen bonding interactions, and two higher molecular weight covalent polymers, which serve as models for the supramolecular polymer, was also studied. The degree of association of the diacid-terminated oligosiloxane was estimated by investigating its transverse relaxation derived from ^{1}H NMR and comparing the results thus obtained with data from a series of polydimethylsiloxane samples with different molecular weights.

Keywords: NMR; Hydrogen bond; Telechelic polydimethylsiloxane

1. Introduction

The concept of self assembly is increasingly applied to the field of polymer science. Supramolecular polymers are defined as arrays of small molecules held together by non-covalent interactions [1]. They offer potential advantages over covalent polymers due to the reversibility of their properties. The interactions used to build supramolecular polymers range from ionic and metal-ligand interactions to dispersive forces. However, hydrogen bonding is particularly favored because of its fixed stoichiometry, directionality and simplicity [2–5].

A way to obtain a supramolecular polymer is to use telechelic polymers bearing self-complementary hydrogen bonding groups at the chain ends. Benzoic acid-terminated polydimethylsiloxanes (PDMS) are typical examples of telechelic oligomers associated through hydrogen bonding interactions at their chain ends. Their synthesis and characterization have been described recently [6]. Their association has been studied in solution by FTIR spectroscopy and viscosimetry [7,8].

Supramolecular polymers are not only employed in solution. They may also be used in bulk. Therefore, the study of hydrogen bonding interactions, as well as the determination of the apparent molecular weight of the supramolecular assemblies in bulk, are of major interest to get a deeper understanding of the bulk organization and properties of acid-terminated PDMS.

In the first part of the present paper, we will employ carbon-13 spin-lattice relaxation to probe the existence of hydrogen bonding interactions in a diacid-terminated oligosiloxane in bulk at temperatures well above its glass transition and melting temperatures. For comparison's sake, we will also study the behavior of a monoacid-terminated oligosiloxane, which can form dimers only, a diester-terminated oligosiloxane, which cannot undergo any hydrogen bonding interactions, and two higher molecular weight covalent polymers, which may serve as models for the supramolecular polymer.

In the second part, we will try to estimate the degree of association of the diacid-terminated oligosiloxane by investigating its transverse relaxation derived from ^{1}H

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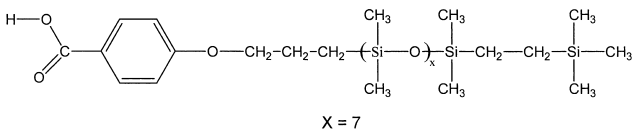
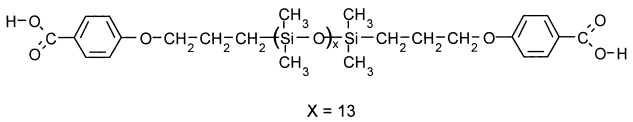
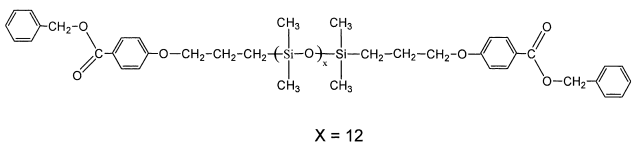
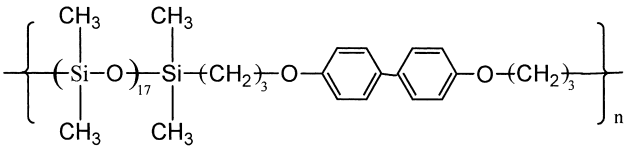
doi:10.1016/S0032-3861(03)00058-2

Table 1
Formulas and code names of the telechelic oligosiloxanes under study

A-PDMS	A-PDMS  X = 7
AA-PDMS	AA-PDMS  X = 13
EE-PDMS	EE-PDMS  X = 12
Polycondensates: PC1 ($n = 7$) and PC2 ($n = 15$)	Polycondensates: PC1 (n=7) and PC2 (n=15) 

NMR and comparing the results thus obtained with data from a series of PDMS samples with different molecular weights. Indeed, in entangled or cross-linked melts, the topological constraints induce a slowing down of the frequency and amplitude of local motions. Therefore, the $^{1}H-^{1}H$ dipole–dipole interactions are not entirely averaged by the motions, which results in a pseudo-solid NMR relaxation behavior [9,10]. The strength of the residual dipolar interactions depends on the molecular weight in entangled polymer melts and on the molecular weight between cross-links in polymer networks [10–13]. In the present work, we will take advantage of the molecular weight dependence of the residual dipole–dipole interactions to derive the apparent degree of association of the acid-terminated PDMS under study. The magnitude of these interactions will be determined by studying the ^{1}H spin–spin relaxation using the Hahn echo pulse sequence [14].

2. Experimental

The telechelic polysiloxanes were prepared according to Ref. [6–8]. Their formulas and code names are given in Table 1. Some of them undergo a phase transition at temperatures which are listed in Table 2, together with the molecular weights of the samples under study. The trimethylsilyl-terminated PDMS samples (PDMS17, PDMS49, PDMS62, PDMS91 and PDMS400) used to determine the molecular weight dependence of the NMR transverse relaxation function were obtained from Petrarch Systems Inc.

The NMR experiments were performed as a function of temperature in the isotropic phase of the bulk compounds. The temperatures were calibrated by using the temperature

Table 2
Molecular weights, polydispersity indices, glass transition temperatures, T_g (°C) and phase transition temperatures, T_m (°C), of the telechelic oligosiloxanes and trimethylsilyl-terminated PDMS samples under study

Sample	M_n	M_w/M_n	T_g (°C)	T_m (°C)
AA-PDMS	1400	1.1	−110	48
A-PDMS	820	1.1	−114	20
EE-PDMS	1500	1.1	−85	
PC1	10,400	1.7	−113	−39
PC2	24,300	1.5	−115	−33
PDMS17	17,000			
PDMS49	49,000			
PDMS62	62,700			
PDMS91	91,700			
PDMS400	4,00,000			

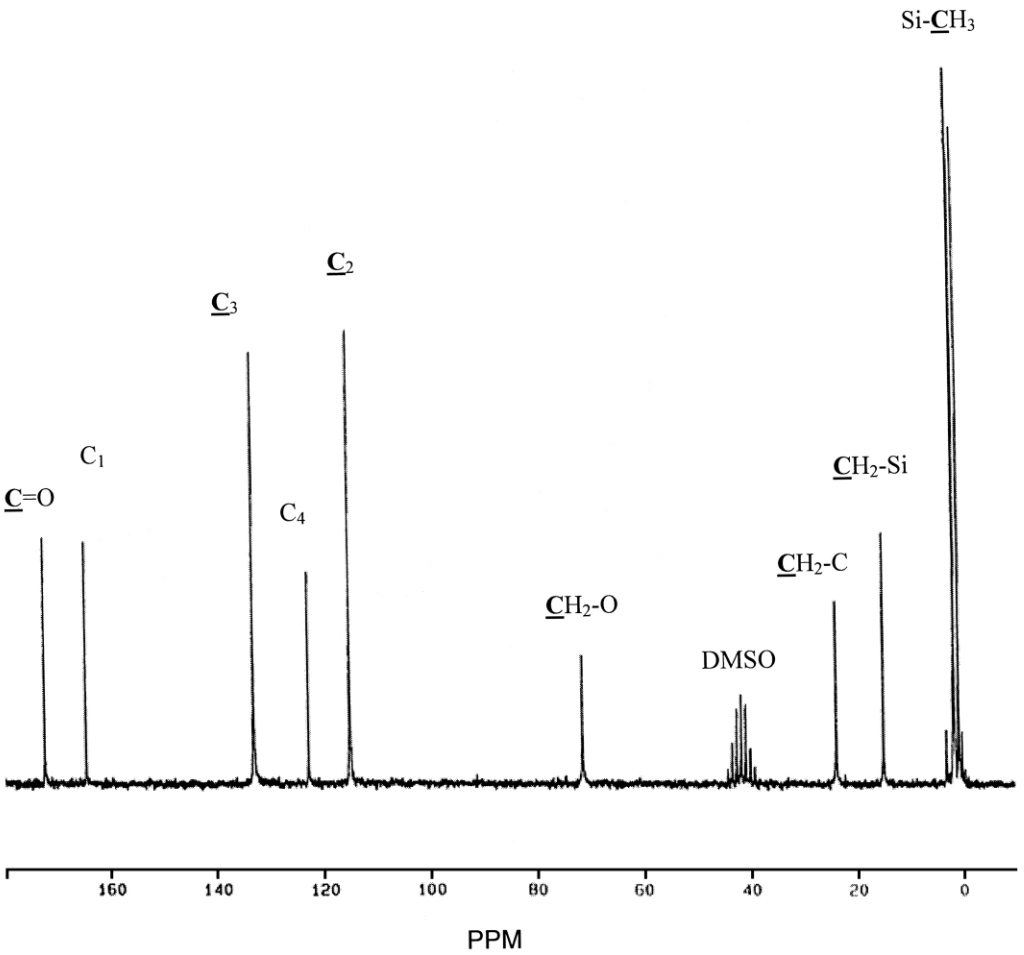


Fig. 1. ^{13}C NMR spectrum of the diacid-terminated oligosiloxane in bulk at 100 °C with DMSO as an external lock.

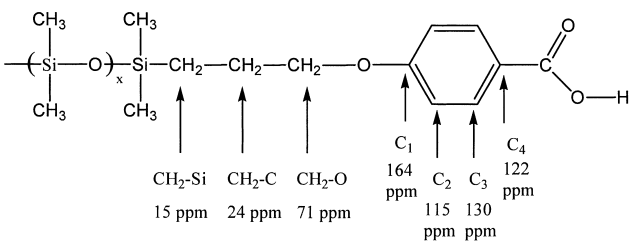
dependence of the resonance frequency difference between the two ^{1}H lines of ethylene glycol. 25.18 MHz ^{13}C NMR spectra were recorded on a Bruker AC100 spectrometer using the technique of proton noise decoupling. The lock signal was obtained from an external DMSO-d_6 tube. ^{13}C spin-lattice relaxation times, T_1, were measured using the standard inversion-recovery (180°, t, 90°) pulse sequence, with repetition times between pulse sequences greater than five times the longest T_1 of the considered nuclei. T_1 values were determined from mono-exponential regression of the carbon-13 magnetization as a function of t. The relative accuracy for each T_1 measurement was estimated to be of the order of 5%.

The Hahn echo experiments were performed at 343 and 353 K using a Bruker ASX100 spectrometer operating at a ^{1}H resonance frequency of 100.15 MHz. Samples were packed as short cylinders of 5 mm diameter placed in the middle of a 6 mm diameter rf coil. The length of the 90°-pulse was 3.1 μs. The delay time between two successive scan sequences was taken as 6 s, long enough to ensure a complete spin-lattice relaxation of the proton spins.

3. Results and discussion

3.1. Hydrogen bonding interactions in monoacid- and diacid-terminated oligomers

As an example, the ^{13}C NMR spectrum of the diacid-terminated oligosiloxane (AA-PDMS) in bulk at 100 °C is shown in Fig. 1. The line assignment is summarized below:



The nT_1 values (where n is the number of protons directly attached to the carbon of interest) determined for the different carbons of the diester-terminated oligosiloxane are plotted as a function of the reciprocal temperature in Fig. 2. In the temperature range investigated, the nT_1 values are an

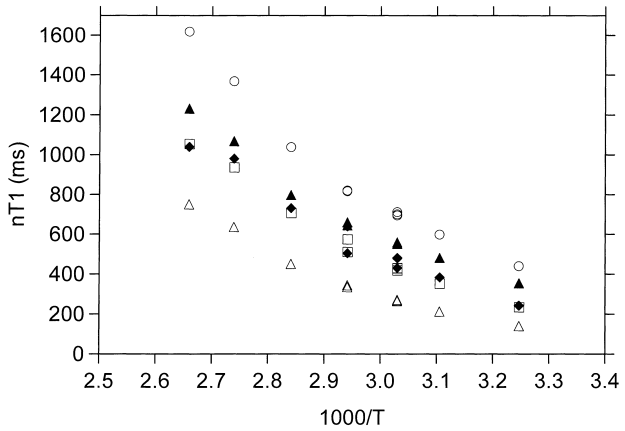


Fig. 2. nT_1 values vs $1/T$ for the different carbons of bulk diester-terminated oligosiloxane. (○ CH_2–Si, ▲ CH_2–C, □ CH_2–O, ◆ benzyl group CH_2, △ C_2 and C_3 aromatic carbons).

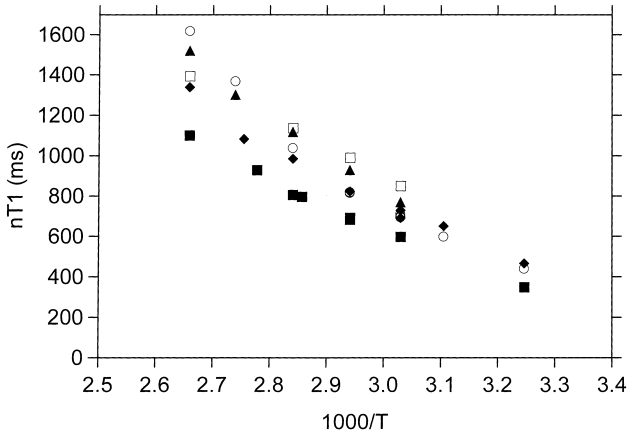


Fig. 3. nT_1 values vs $1/T$ for the CH_2–Si carbons of the monoacid-, diacid-terminated oligosiloxanes and covalent polymers. (○ EE-PDMS, ◆ A-PDMS, ■ AA-PDMS, ▲ PC1, □ PC2).

increasing function of temperature. The nT_1 minimum is not observed in the temperature range of interest, even at the lowest temperature investigated (35 °C), which indicates that, at high temperatures, the nT_1 values are within or close to the extreme narrowing region where T_1 is proportional to the reciprocal of the mean correlation time, τ_c.

Whatever the temperature, the nT_1 values obtained for the CH_2–Si carbon are significantly higher than the nT_1 values measured for the CH_2–C carbons, which themselves are higher than the nT_1 values of the CH_2–O and C_2 and C_3 aromatic carbons. Since, in the temperature domain investigated, T_1 is an increasing function of temperature and, therefore of mobility, this T_1 comparison shows that the local chain dynamics is slower at the chain extremities. Such a result can be understood in terms of the flexibility of the PDMS chain, which is higher than the flexibility of the methylene sequences that are close to the bulky aromatic end-group. Therefore, the presence of the aromatic units at the chain ends induces a progressive slowing down of the local dynamics from the PDMS units in the center of the chain to the oligomer chain ends.

The nT_1 values determined for the CH_2–Si, CH_2–C, CH_2–O and aromatic C_2 and C_3 carbons of the monoacid- and diacid-terminated oligosiloxanes as well as for the two covalent polymers are shown in Figs. 3–6, respectively. They qualitatively show the trends observed for the diester-terminated oligosiloxane: nT_1 is an increasing function of temperature. Moreover, nT_1 decreases from the oligomer center to the extremities. For all the samples, the shortest nT_1 values are obtained for the aromatic carbons.

The temperature dependence of the nT_1 value determined for the CH_2–Si carbons in the different samples is shown in Fig. 3. At a given temperature, the nT_1 values and, therefore, the mobility, are higher in the diester- than in the monoacid- and the diacid-terminated oligosiloxanes. As shown in Figs. 4–6, similar results are observed for the CH_2–C, CH_2–O and C_2 and C_3 aromatic carbons in all the samples.

Motions that are responsible for the T_1 relaxation in a polymer chain are mainly segmental motions, which involve only a limited number of monomer units, and librations [15]. As indicated by the above results, the Si–O links, which are common to all the samples, exhibit a rapid segmental dynamics. Among the different T_1 data, the T_1 measured for the CH_2–Si carbon is the most representative of the dynamics of the central units of the PDMS oligomers. Librations are very fast localized modes whose amplitude is determined by the steric hindrance at the site of the considered carbon. For a given CH or CH_2 carbon such as the methylene carbons in the compounds under study, the libration amplitude is not expected to depend on the chemical nature of the chain extremities [16,17]. Besides, since we are dealing with oligomers, the relaxation should also contain a contribution from the overall rotational diffusion. The shorter is the oligomer chain, the faster the overall diffusion. Therefore, if there were no interactions or associations between individual chains, the relative T_1 order for the CH_2–Si carbons should only depend on the

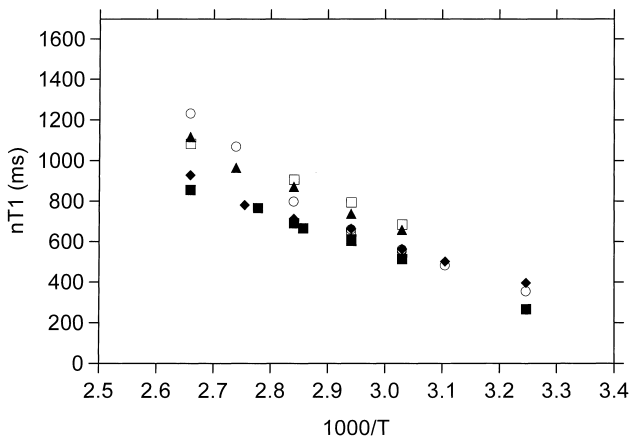


Fig. 4. nT_1 values vs $1/T$ for the CH_2–C carbons of the monoacid-, diacid-terminated oligosiloxanes and covalent polymers. (○ EE-PDMS, ◆ A-PDMS, ■ AA-PDMS, ▲ PC1, □ PC2).

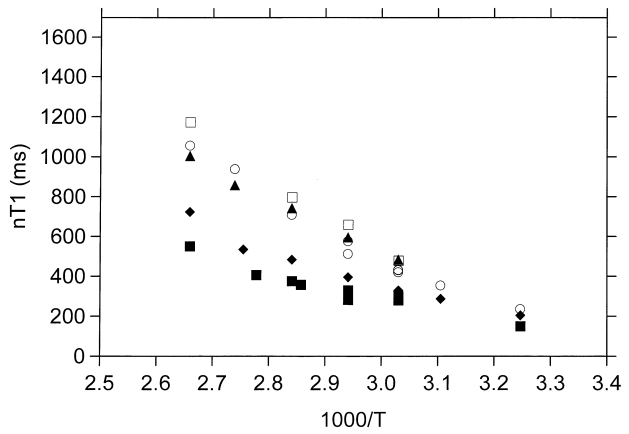


Fig. 5. nT_1 values vs $1/T$ for the CH_2-O carbons of the monoacid-, diacid-terminated oligosiloxanes and covalent polymers. (○ EE-PDMS, ◆ A-PDMS, ■ AA-PDMS, ▲ PC1, □ PC2).

oligomer size:

nT_1 CH_2-Si (monoacid) > nT_1 CH_2-Si (diacid)

> nT_1 CH_2-Si (diester)

Therefore, the fact that the nT_1 value measured for the CH_2-Si carbon is higher for the diester than for the monoacid derivative shows that the local dynamics of the monoacid-terminated oligosiloxane is the dynamics of a chain longer than the chain of the diester-terminated oligosiloxane. This result is a first indication that the monoacid-terminated oligosiloxane is associated through hydrogen-bond interactions, yielding dimers. In the same way, the higher nT_1 value observed for the monoacid-terminated oligosiloxane than for the diacid-terminated oligosiloxane points out the slowing down of the chain dynamics in the diacid derivative. It is consistent with the existence of two association sites per molecule, in agreement with data obtained from FTIR spectroscopy that show that in this temperature range, the acid functions are mostly dimerized [18].

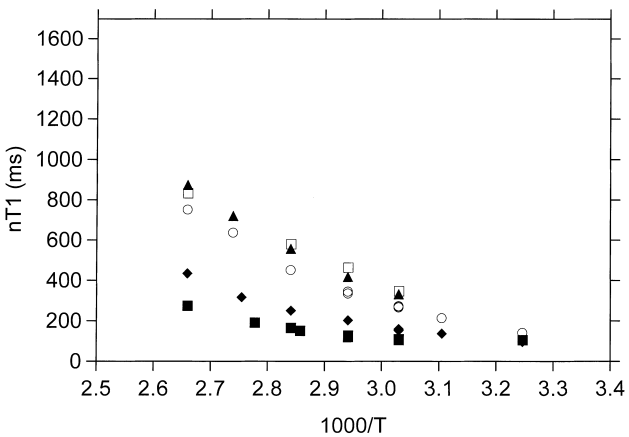


Fig. 6. nT_1 values vs $1/T$ for the C_2 and C_3 aromatic carbons of the monoacid-, diacid-terminated oligosiloxanes and covalent polymers. (○ EE-PDMS, ◆ A-PDMS, ■ AA-PDMS, ▲ PC1, □ PC2).

In order to show the relative immobilization of the chain extremities in the associated oligomers, we have compared the nT_1 relaxation times of the CH_2-C, CH_2-O and C_2 and C_3 aromatic carbons of the different derivatives for a given main-chain dynamics. For example, for a nT_1 (CH_2-Si) of 1 s, the nT_1 values determined for the CH_2-C, CH_2-O and C_2 and C_3 aromatic carbons are given in Table 3.

For a given dynamics of the main chain, the nT_1 measured for the CH_2-C carbons are very close to each other. On the opposite, for the CH_2-O carbons, the nT_1 values are much smaller in the monoacid and in the diacid than in the diester derivative. The differences observed between the T_1 values are higher for the aromatic carbons. In the monoacid and diacid-terminated derivatives, the slowing down of the chain-end mobility can be explained by the existence of hydrogen bonding interactions between oligomers. Of course, the diester-terminated oligomer cannot undergo such interactions.

In a very similar way, the slowing down of the ring motion due to the presence of hydrogen bonding interactions can be demonstrated by comparing the nT_1 values of the C_2 and C_3 aromatic carbons obtained for a given value of the nT_1 relaxation time of the CH_2-O carbon. Results obtained for nT_1 (CH_2-O) equal to 0.5 s are shown in Table 4. As shown in this table, for a given dynamics of the CH_2-O units, the nT_1 observed for the aromatic carbons are shorter in the monoacid and diacid derivatives than in the diester-terminated oligomer. In agreement with results observed for the CH_2-O carbon, the relatively slow dynamics of the ring carbon can be interpreted in terms of association between the acid-terminated oligomers, the monoacid derivative leading to dimers, the diacid derivative yielding longer chains. Besides, it may also be an indication that the rotational motion of the ring about its symmetry axis is strongly hindered by a close packing of aromatic rings belonging to different chains.

The apparent activation energies associated with the motions of the different carbons have been derived from the high temperature data, in the range from 70–110 °C, under the assumption of the extreme narrowing limit. The values thus obtained are listed in Table 5. They are quite similar for the monoacid and diacid derivatives and for the PC1 and PC2 higher molecular weight compounds. Only the diester-terminated derivative exhibits a different behavior. A likely interpretation of these data is that, in the former series of

Table 3
nT_1 values of the CH_2-C, CH_2-O and C_2 and C_3 aromatic carbons obtained for a nT_1 value of the CH_2-Si carbon of 1 s

	nT_1 CH_2-C (ms)	nT_1 CH_2-O (ms)	nT_1 C_2 and C_3 (ms)
AA-PDMS	795	463	229
A-PDMS	755	505	270
EE-PDMS	790	680	434
PC1	784	653	479
PC2	795	658	474

Table 4
nT_1 values of the C_2 and C_3 aromatic carbons obtained for a nT_1 value of the CH_2–O carbon of 0.5 s

	nT_1 C_2 and C_3 (ms)
AA-PDMS	226
A-PDMS	265
EE-PDMS	313
PC1	347
PC2	337

compounds, the relaxation is mainly controlled by segmental motions, in agreement with the fact that chains are quite long due to hydrogen bonding interactions or synthesis whereas, in the short diester-terminated oligomer which cannot undergo hydrogen bonding interactions, the contribution of the overall rotational diffusion to the spin-lattice relaxation is more significant.

3.2. Estimation of the apparent molecular weight of the associated diacid-terminated oligosiloxane

Transverse relaxation functions of PDMS samples as obtained from the Hahn echo pulse sequence at 80 °C are plotted for the PDMS samples with different molecular weights, M_n, in Fig. 7. At short times, the transverse relaxation functions exhibit a quasi-exponential decay whose relaxation time is a decreasing function of molecular weight and an increasing function of temperature. At longer times, a second component appears in the transverse relaxation function of PDMS samples with a high molecular weight. Whereas the first part of the decay can be assigned to protons in the neighborhood of entanglements, the second part of the decay corresponds to protons far from these topological constraints.

Data measured at 80 °C for the oligosiloxanes are also given in Fig. 7. In the monoacid-, diacid- and diester-terminated oligomers, the transverse magnetization exhibits monoexponential decay. As observed for the PDMS samples, only the two higher molecular weight compounds (PC1, PC2) have biexponential decay. In the following, we will consider the first part of the decay only. The diacid-terminated oligomer, which can form rather long chains by hydrogen bonding, has the fastest decay and, therefore, the shortest T_2. The PC1 and PC2 covalent polymers have longer T_2's, the PC1 T_2 being longer than the PC2 T_2, in agreement with the relative

Table 5
Apparent activation energies determined from the temperature dependence of T_1

	AA-PDMS	A-PDMS	EE-PDMS	PC1	PC2
Ea CH_2–Si (kJ mol^{-1})	13.8	13.5	20	14	12.4
Ea CH_2–C (kJ mol^{-1})	10.2	10.2	19.7	11.6	12
Ea CH_2–O (kJ mol^{-1})	16.7	16.6	18.2	14.7	21.7
Ea CH_2–Es (kJ mol^{-1})			16.1		
Ea C_2 (kJ mol^{-1})	22.9	22	23.2	21.4	22
Ea C_3 (kJ mol^{-1})	23	22.3	23.4	20.8	22

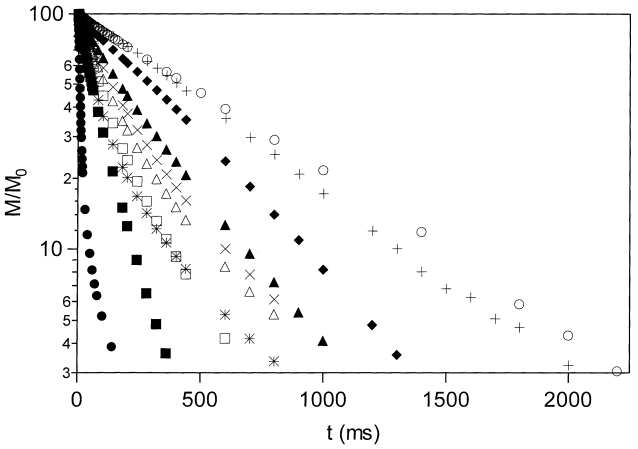


Fig. 7. Transverse relaxation functions of PDMS and telechelic oligosiloxane samples as obtained from the Hahn echo pulse sequence at 80 °C. (+ PDMS17, × PDMS49, △ PDMS62, ∗ PDMS91, ● PDMS400, ◆ A-PDMS, ■ AA-PDMS, ○ EE-PDMS, ▲ PC1, □ PC2). As a first approximation, the AA-, EE-, A-PDMS and PDMS17 samples exhibit a mono-exponential decay, the other samples exhibit a bi-exponential decay.

values of their molecular weight. The monoacid- and diester-terminated oligosiloxanes, which have the smallest molecular weight, have longer T_2's, the longest T_2 belonging to the diester derivative which cannot undergo any chain association. All these results indicate that the telechelic oligosiloxanes have a molecular weight dependence, which qualitatively resembles the molecular weight dependence of the PDMS samples. Besides, they are in very good agreement with the above conclusions derived from the investigation of T_1 spin-lattice relaxation.

In order to perform a more precise analysis of the transverse relaxation function and to compare the strength of the residual dipolar interaction in different samples, several parameters have been proposed. The first parameter, χ_c, was defined by Cohen-Addad et al. [19]:

$$\chi_c = \psi_3/\psi_1 \tag{1}$$

where ψ_1 and ψ_3 are obtained from the transverse magnetization $Mx(t)$:

$$\psi_1 = \int t^{-1/2} Mx(t) \mathrm{d}t \tag{2}$$

and:

$$\psi_3 = \int t^{-1/2} \mathrm{d}Mx(t)/\mathrm{d}t \; \mathrm{d}t \tag{3}$$

with $Mx(0) = 1$.

Sotta et al. [12] used the parameter α_{CT} to describe the influence of topological constraints, i.e. cross-links and entanglements. α_{CT} is determined in such a way that a series of given NMR data obtained as a function of time, t, yields a single master curve when plotted as a function of t/α_{CT}.

The χ_c values obtained for the different PDMS and telechelic oligosiloxane samples whose molecular weight is known are plotted in Fig. 8 at 80 °C. The α_{CT} values derived

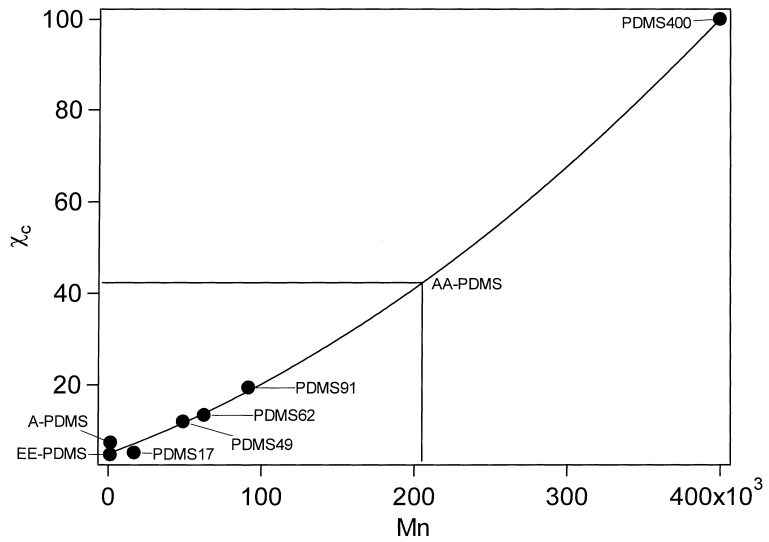


Fig. 8. χ_c values, obtained at 80 °C for the trimethylsilyl-terminated PDMS and telechelic oligosiloxane samples, vs molecular weight, M_n.

at 80 °C are given in Fig. 9. Both χ_c and α_{CT} parameters are increasing functions of molecular weight. Using these χ_c and α_{CT} dependences on molecular weight as calibration curves, the apparent average molecular weight of the diacid-terminated oligosiloxane can be estimated. Interpolation of the α_{CT} parameter leads to an apparent average molecular weight of 1,36,200, at 80 °C, which corresponds to the association of about 90 chains. Apparent average molecular weight derived by using the χ parameter is somewhat higher. It is equal to 2,05,700 at 80 °C. However, whatever the precise value of the apparent molecular weight of the supramolecular assembly, the above results indicate that, in bulk, and thanks to the intermolecular association through hydrogen bonding interactions, the diacid-terminated oligosiloxane exhibits the behavior of long covalent chains.

4. Conclusion

Measurements of carbon-13 spin-lattice relaxation times in a series of oligosiloxanes which exhibit progressive variations in their chemical structure have shown, that in the bulk state, whereas the monoacid-terminated oligosiloxanes form dimers only, the diacid-terminated oligosiloxane associates through hydrogen bonding to yield long supramolecular polymers. The apparent molecular weight of the assembly has been derived from the determination of the transverse relaxation function obtained from ^{1}H NMR. It has been estimated to be of the order of 1,30,000 or 2,00,000 depending on the parameter used for this determination.

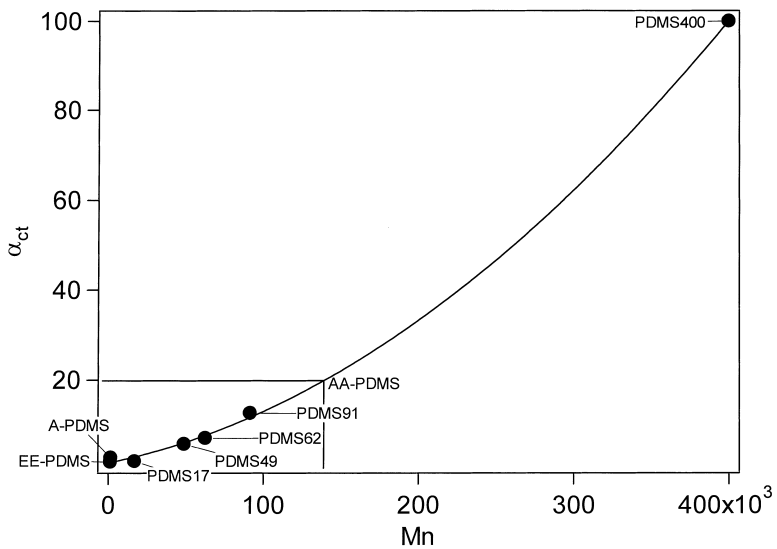


Fig. 9. α_{CT} values obtained at 80 °C for the trimethylsilyl-terminated PDMS and telechelic oligosiloxane samples, vs molecular weight, M_n.

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