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A solid state NMR study of polycarbonate oligomer grafted onto the surface of amorphous silica

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Abstract

High resolution solid state ^{13}C and ^{29}Si CP/MAS NMR was used to investigate the grafting mechanism, morphology and interfacial mobility of polycarbonate (PC) oligomer and bisphenol A grafted onto silica surfaces. It was previously shown that interface modification via grafting led to composites with increased hydrolytic stability and interfacial toughness. The NMR experiments were carried out to determine the nature of the bonding of the reactants to the glass surface and to characterize the relaxation properties of the reacted species. The NMR spectra demonstrate differences between the neat and grafted PC oligomer that suggest strong bonding. A model compound, bisphenol A, was used to resolve signal overlaps caused by repeat units and to verify the formation of primary bonding at the silica surface by the existence of a downfield shift of the C_4 resonance peak and other changes in the spectrum. Proton spin-lattice relaxation times in the rotating frame offer secondary evidence of the formation of Si–O–C bonds on the silica surface. The proton spin-lattice relaxation of the grafted molecules were characterized by a bimodal distribution of relaxation times, while unreacted molecules were represented by a single relaxation time. Temperature dependent studies show that the oligomer loses mobility as a result of grafting, and that the transition responses of the material are lost. The grafted material is visualized as a low density monomolecular layer of covalently bonded material. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Solid state ^{13}C and ^{29}Si CP/MAS NMR; Grafting polycarbonate oligomer; Proton spin-lattice relaxation times in the rotating frame $T_{1_\rho H}$

1. Introduction

Polymer/solid composites are widely used as high-performance structural materials. There has been interest in the use of continuous fiber reinforced composites in dental applications, especially as splints, retainers, prosthodontic frameworks and orthodontic wires [1]. Critical factors in their application was the hydrolytic stability and mechanical properties of the composite material when adhesively bonded to the tooth structure. Clinical tests have shown that premature failure of the dental appliance often occurs within the composite because of the hydrolytic deterioration of the fiber–matrix interface [2]. Similar problems exist with silica-filled materials. Silica is used extensively as a filler and reinforcement in polymeric matrices and is surface modified to impart it with various characteristics. The main practical applications of such systems include adhesion-control of biocompatible materials [3], the reinforcement of elasotmers [4], and chromatography [5].

An effort was made to create a hydrolytically stable composite system for dental applications through chemical grafting of the polycarbonate (PC) oligomers on the glass fiber surfaces [6,7]. The grafted PC oligomer fiber reinforced composites showed excellent retention of stress transmission under hydrolytic attack, and improved interfacial shear strength, fracture toughness and hydrolytic stability [7]. However, the grafting mechanism has not yet been elucidated at the molecular level. Clearly, a detailed knowledge of chemical and structural changes that occur in the interphase region is of interest for the optimization of composite properties. Solid state NMR is ideally suited to this task since it is a non-destructive technique that can be used to examine the environments of specific nuclei in the matrix or on the surface of the filler, i.e. in the interfacial region [8,9].

In this article, we report on high resolution CP/MAS solid state NMR experiments that were used to investigate the grafting reaction and the interfacial dynamics of the species grafted on the surface. The relatively small volume of the interfacial region in typical glass fiber reinforced materials,

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however, makes it difficult to separate effects of interface from the spectra emanating from the bulk of the polymer. To increase the interfacial area and facilitate analysis of the NMR signal, high surface area amorphous silica was used to model the glass fiber, while bisphenol A served as a model for and a monomeric equivalent of the PC oligomer. The bisphenol A was used to examine the formation of new Si–O–C bond at the silica surface as a result of the grafting reaction. The high-resolution ^{13}C CP/MAS techniques were used to measure the proton spin lock relaxation time in rotating frame $T_{1_\rho\mathrm{H}}$, as the final evolution of the carbon signal in a cross-polarization experiment tracks the T_{1_ρ} decay of the protons. Rotating frame proton spin-lattice relaxation time $T_{1_\rho\mathrm{H}}$, characterizing chain motions in the kilohertz frequency range, were used to probe the changes in the interfacial dynamics after the oligomer/silica grafting reaction in order to provide secondary evidence concerning the morphology of the organic molecules at the glass surface.

The dynamic mechanical behavior of high molecular weight PC polymer has been extensively studied and reviewed [10,11] showing that PC undergoes three relaxation processes, alpha (α), beta (β), and gamma (γ). However, there is no reported information about the dynamics and type of motions that cause relaxations in the PC oligomer. In the present study, we have also investigated the temperature dependence of the dynamic motion in kHz range for the neat oligomer and the silica grafted oligomer in the temperature range -100°C to 100°C. The experimental results are used to complement existing ideas in the formulation of a plausible model for the morphological nature of the interfacial region in filled-silica polymer systems.

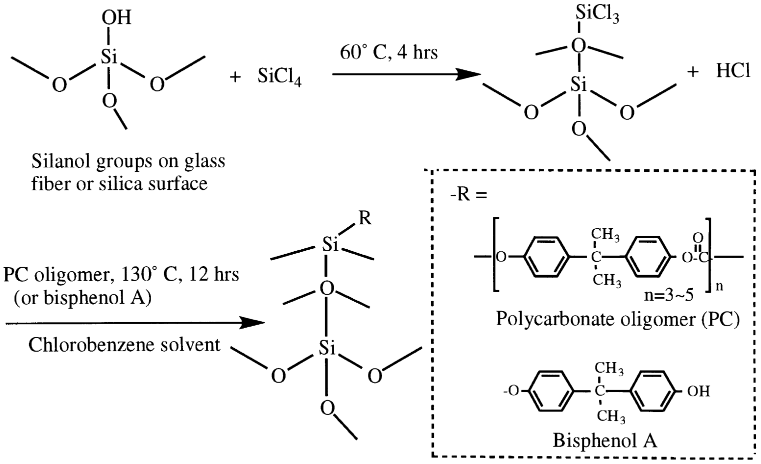
2. Experimental

2.1. Materials

Polycarbonate oligomer with a number average molecular weight of 959 and a weight average of 1197 was supplied by Enichem America. Bisphenol A (4,4′-diydroxy-diphenyl-2,2′-dimethylpropane), silicon tetrachloride and chlorobenzene solvent was purchased from Aldrich Company. The amorphous fumed Silica (Cab-O-Sil, grade M-5, surface area = 200 m^2/g) was supplied by Cabot company.

2.2. Grafting reaction

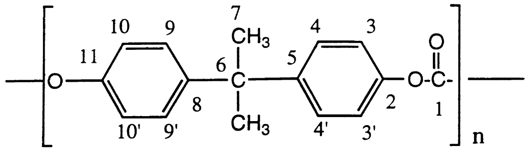
Bisphenol A or PC oligomer was grafted onto silica using $SiCl_4$ according to the following reaction scheme [7].



The silica was dried under vacuum for 24 h at 250°C, transferred to a three-necked flask under a nitrogen purge, and then cooled to about 60°C when an excess of $SiCl_4$ was added. This mixture was allowed to react for 2 h until the excess $SiCl_4$ had boiled off. A solution of bisphenol A in chlorobenzene was then added to the flask and the reaction allowed to proceed for 12 h. The temperature was then raised to 130°C to drive off the chlorobenzene solvent, and the Silica grafted with bisphenol A was Soxhlet extracted, and dried under vacuum at 100°C overnight.

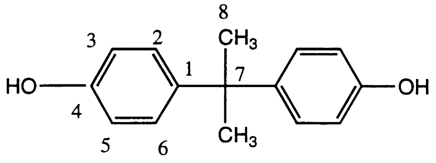
2.3. NMR experiments

Solid state ^{13}C and ^{29}Si CP/MAS NMR spectra were obtained at 75 and 59.6 MHz, respectively, using a Chemagnetics CMX300 NMR spectrometer with a commercial double-bearing 7.5 mm MAS probe. The magic angle was set using the ^{79}Br resonance of KBr. Samples ($\sim$300 mg) were packed in zirconia pencil rotor and spun at the magic angle at 5 kHz. The 90° pulse widths for ^{1}H and ^{13}C were 5 μs. A relaxation time of 2–3 s was used to allow thermal equilibrium, and 1024 or 2048 scans were utilized to achieve a proper signal-to-noise ratio. A 76 kHz proton decoupling field was used during the acquisition of the free induction decay. The Hartman–Hahn match condition for ^{13}C and ^{29}Si were set experimentally using glycine for ^{13}C and TTMS (tetrakis-trimethylsilyl-silane) for ^{29}Si. Chemical shifts are given with respect to TMS for using



Polycarbonate oligomer (PC) n=3~4

site	1,2,5,8	4,9	3,10,	6	7
ppm	149.0	127.5	119.9	42.0	29.8



bisphenol A

site	1	2,6	3,5	4	7	8,9'
ppm	142.3	126.9	113.8	152.4	40.7	30.1

Fig. 1. Structure, chemical shifts and peak assignments of polycarbonate oligomer and bisphenol A.

an external sample of solid glycine (176.03 ppm) for ^{13}C and TTMS (135.26 ppm) for ^{29}Si as the secondary references. High resolution solution NMR spectra were acquired using a Bruker DMX500 NMR spectrometer.

$T_{1_\rho \mathrm{H}}$ (proton spin-lattice relaxation time in rotating frame) values can be measured by two methods through the carbon atom. In one, a variable proton spin-lock period is inserted before contact with the carbons is made. In the other, the contact period itself is varied with time. In this work the former is used, wherein, a normal cross-polarization pulse sequence is utilized while inserting a variable ^{1}H spin-lock time, τ, at the beginning of the contact period. During the time period τ, the rotating-frame ^{1}H spin-lattice relaxation occurs; hence, by observing the ^{13}C intensity at the end of the contact period as a function of τ one can obtain a measure of $T_{1_\rho \mathrm{H}}$ [9]. Experiments to determine the dependence of temperature on the relaxation time ($T_{1_\rho \mathrm{H}}$) values were performed within a temperature range from −100°C to 100°C to study the change of molecular motion in the kHz range after the grafting reaction. Temperature calibrations at the desired rotor frequency, VT flow, and purge gas flow were performed by using lead nitrate, $Pb(NO_3)_2$, mixed with two-third of silica gel to reduce properly the density of lead nitrate and spin, as was reported by Burum and Bielecki [12]. $T_{1_\rho \mathrm{H}}$ values were calculated using curve-fitting analysis of variable proton spin-lock time data with standard deviation less than 8% and a correlation coefficient, $R^2 > 0.9$.

3. Results and discussion

3.1. Characterization of silica-surface bound species

High resolution ^{13}C CP/MAS with dipolar decoupling NMR experiments were carried out to investigate the grafting reaction. Fig. 1 shows the structures and peak assignments for the PC oligomer and bisphenol A. The ^{13}C CP/MAS NMR spectra of neat PC oligomer (Fig. 2(A)), PC–silica reaction without $SiCl_4$ (Fig. 2(B)), and PC–silica reaction with a grafting agent $SiCl_4$ (Fig. 2(C)) are illustrated in Fig. 2. Clearly, $SiCl_4$ as a grafting intermediate enhanced the grafting reaction of PC oligomer onto silica surface, as shown by the good signal intensity (S/N) (Fig. 2(C)), compared to the very poor S/N for the reaction without $SiCl_4$ (Fig. 2(B)). Detailed analysis of the nature of the PC oligomer/silica bonding was hindered because of signal-overlapping from the repeat units of polycarbonate at a distance from the silica surface. Bisphenol A was used as a model compound to obtain an undisturbed spectrum generated by the formation of new Si–O–C bonds at the silica surface as a result of grafting. Fig. 3 shows plots of ^{13}C 75 MHz CP/MAS spectra for the neat bisphenol A (Fig. 3(D),(E)) and the grafted bisphenol A (Fig. 3(B),(C)) at temperatures of 70°C and 20°C, respectively. A ^{13}C 125 MHz NMR spectrum acquired in $CDCl_3$ solution is also shown for comparison (Fig. 3(A)). The chemical shift assignments for the bisphenol A structure, were made on the basis of peak integration and the reported ^{13}C chemical shifts of bisphenol A [13]. As shown in Fig. 3, the magic-angle ^{13}C line shapes of the grafted molecules are distinctly different from those of the corresponding neat ones.

In $CDCl_3$ solution, the inverse gated proton decoupled ^{13}C NMR spectrum (Fig. 3(A)) shows six carbon resonance peaks reflecting a bisphenol A molecule with a fast molecular tumbling. The two peaks at the upfield region (40.7 and 30.1 ppm) are two aliphatic carbons, quaternary C_7 and methyl carbons $C_{8,9}$ of the bisphenol A, respectively. The two most down field peaks correspond to the two non-protonated aromatic carbons, C_1 and C_4. The C_4 carbon (152.4 ppm) is attached to a deshielding hydroxyl group and is located further down field than C_1 (142.3 ppm). Similarly, the peaks with a higher intensity at 126.9 and 113.8 ppm correspond to $C_{2,6}$ and $C_{3,5}$ aromatic carbons in which the C_2 and C_6 and the C_3 and C_5 are equivalent because of fast internal rotation (conformational interchange) in solution.

The ^{13}C solid state NMR spectra of neat bisphenol A in Fig. 3(D),(E) reveal structural information in the crystalline state beyond that available from the solution spectrum. The $C_{2,6}$ and CH_3 resonances are split into two major peaks with a few small shoulders, which indicates a non-equivalent molecular environment in the unit cell and conformational effects in a rigid crystal packed molecule. Such results are consistent with those of the X-ray crystal structure of bisphenol A [14], which has three molecules per unit cell.

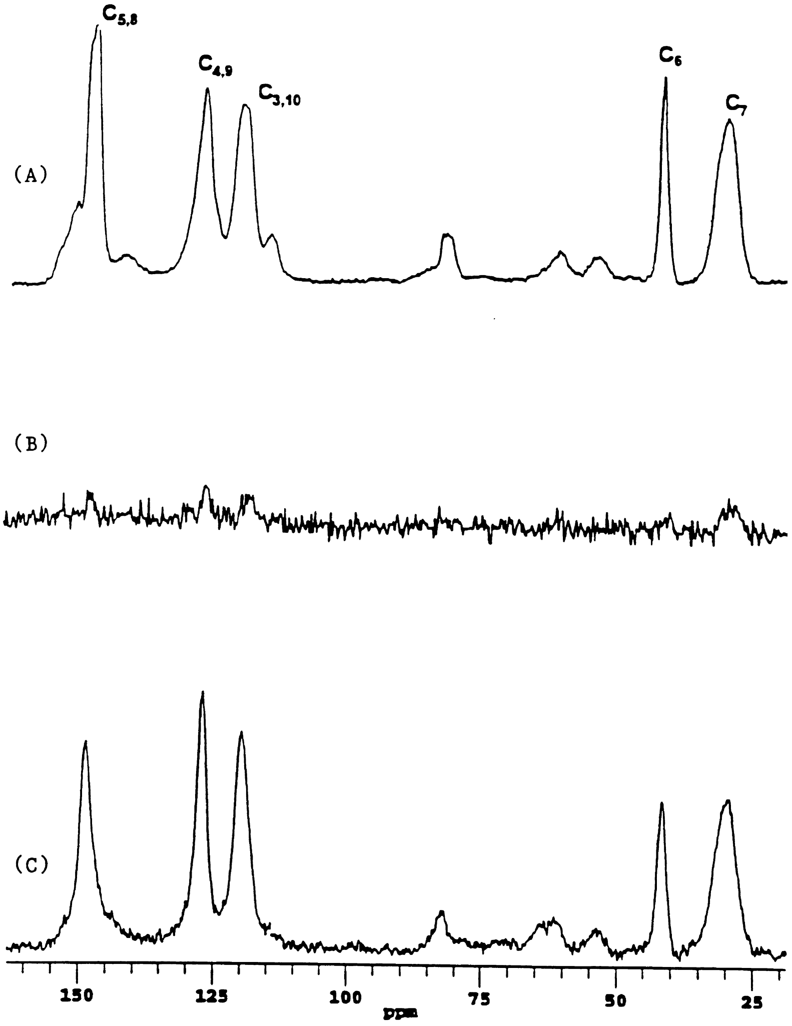


Fig. 2. 75 MHz solid-state ^{13}C CP/MAS NMR spectra of: (A) neat polycarbonate oligomer; (B) oligomer reacted with silica, without $SiCl_4$; (C) oligomer grafted onto silica using $SiCl_4$ as an intermediary. All spectra collected at a spin rate of 5 kHz and with a contact time of 1.5 ms.

The major splitting can be explained by non-equivalence of the methyl groups in the crystalline bisphenol A, while the C_2 and C_6 resonances are split for the three rotations within each molecule. The minor splitting, or shoulders, may arise from differentiation between rings in each molecule or among the three molecules in each unit cell [13].

The observed broad spectra for the silica grafted bisphenol A (Fig. 3(B),(C)) indicated non-crystalline packing and a higher degree of internal mobility (such as ring flipping) in the interfacial zone. The inhomogeneous broadening observed also suggests a distribution of molecular environments. A significant upfield shifting of the C_4 resonance (149.4 ppm) was observed for the grafted molecule in comparison to that before grafting (152.3 ppm). This is attributed to the electron shielding effect of the Si atom from the formation of the Si–O–C_4 bond between silica and bisphenol A. As a result of the bonding, the adjacent conjugated phenolic carbons C_3 and C_5 were shifted downfield. A shoulder peak at 114.2 ppm may be attributed to a small amount of remaining unbounded bisphenol A, which may not have been removed by solvent extraction. The C_1, $C_{2,6}$, C_7, and $C_{8,9}$ carbons have no observable chemical shift changes. However, the doublet aromatic carbons $C_{2,6}$ and the methyl carbon have collapsed into the broad singlets, 126.6 and 30.0 ppm, respectively, indicating an equivalence of the carbon nuclei in the non-crystalline packing.

3.2. Characterization of the mobility of tethered molecules

The chemical shift changes of bisphenol A molecule reflect the formation of the Si–O–C_4 linkage as a result of successful grafting reaction. The dynamic properties of the surface bound molecules are obtained from NMR spin-lattice relaxation time studies.

The behavior of molecular motion in the kHz range for the neat and grafted PC oligomers can be described by the ^1H and ^{13}C spin-lattice relaxation times in the rotating frame, $T_{1_\rho H}$ and $T_{1_\rho C}$. As $T_{1_\rho C}$ values may be strongly

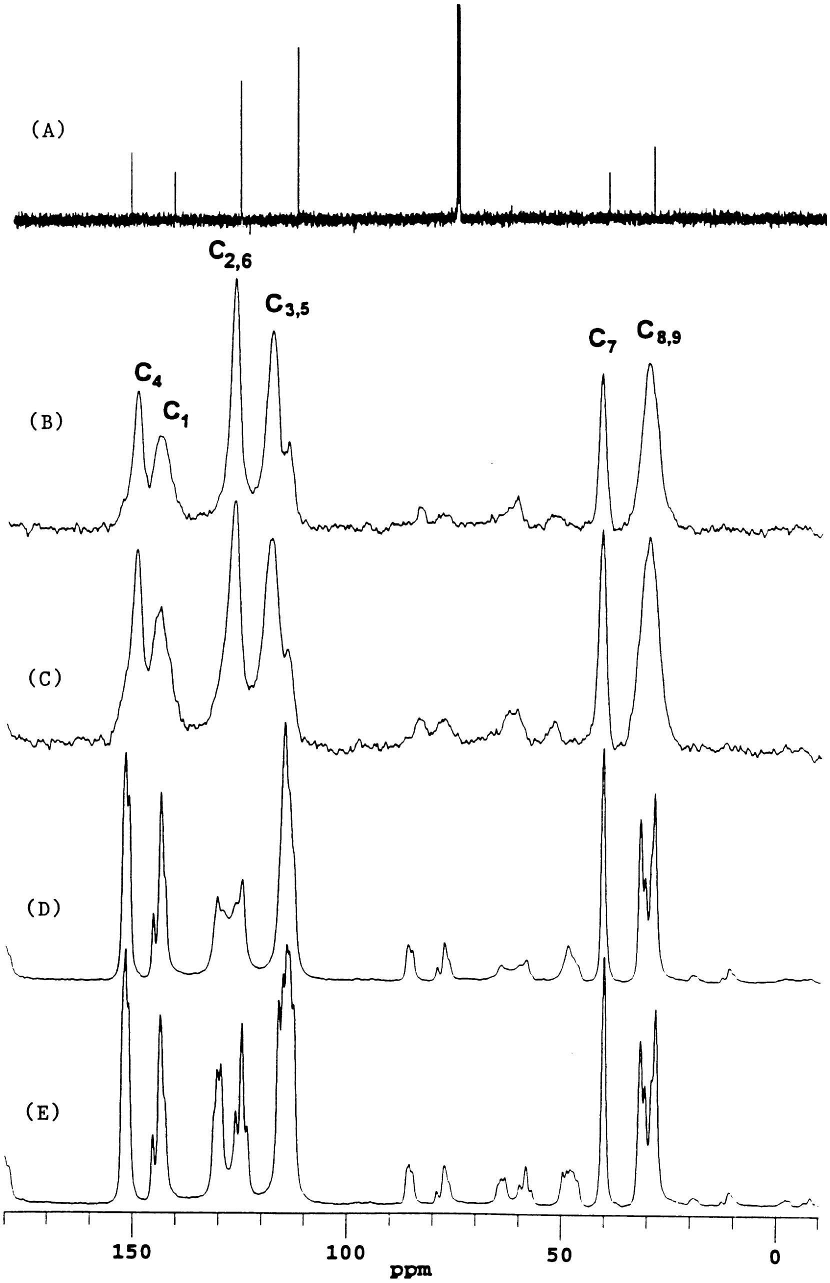


Fig. 3. ^{13}C NMR spectra of: (A) neat bisphenol A in $CDCl_3$ solution (solution NMR); (B) grafted bisphenol A at 70°C; (C) grafted bisphenol A at 20°C; (D) neat bisphenol A at 70°C; (E) neat bisphenol A at 20°C.

influenced by spin–spin interactions [14], with resulting ambiguous interpretation, proton $T_{1_\rho H}$ is more useful in probing the local dynamics of surface-bonded species [15]. $T_{1_\rho H}$ was measured via ^{13}C detection in order to retain the spectral resolution offered by ^{13}C CP/MAS NMR. We then correlate the information on chemical structure from ^{13}C NMR with the phase properties of $T_{1_\rho H}$ [16,17].

Fig. 4(A),(B) show the stacked plot of ^{13}C-detected proton spinlock time in rotating frame ($T_{1_\rho H}$) for the neat and the grafted PC oligomer respectively, and individual $T_{1_\rho H}$ values are also shown. The intensities of carbon resonances for neat PC oligomer decrease exponentially as the spin lock time increases from 0.5 to 22 ms, while the peak intensities for the grafted PC oligomer decrease non-exponentially and level out as spin lock time increases beyond 10 ms. The log of the ^{13}C resonance intensity for the protonated aromatic carbon signals at 127 and 120 ppm versus the spin lock time for the two systems are shown in Fig. 5. The exponential decay of the pure PC oligomer can be represented by a single relaxation time, indicating a homogeneous system, with $T_{1_\rho H}$ of 5.2 ms, while for the grafted oligomer, the relaxation time data represent a

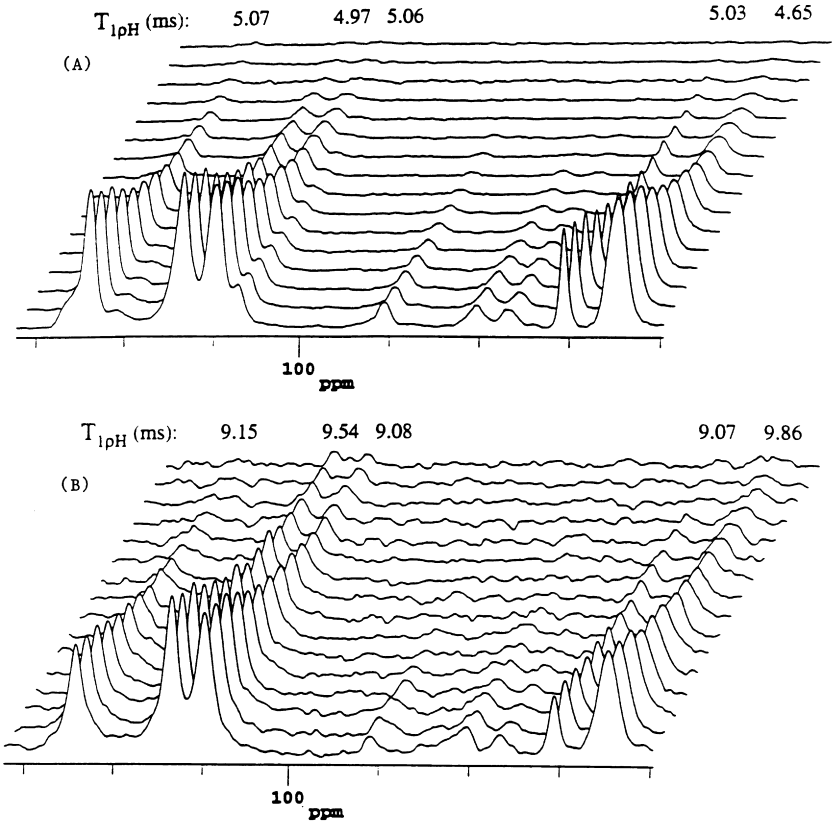


Fig. 4. Stacked plot of ^{13}C-observed proton spin-lock relaxation time in rotating frame ($T_{1_\rho \mathrm{H}}$) data for: (A) neat polycarbonate oligomer, and (B) oligomer grafted onto silica. Each spectrum is a result of 512 acquisitions, with a pulse delay of 2 s, contact time of 0.5 ms and 50 Hz line broadening. The spin-lock time was varied from 0.5 to 22 ms.

broad range of relaxation times that perhaps could be represented by a distribution of exponential decays. One can argue that within the precision of the measurement the data may be adequately described by a double-exponential decay with values of $T_{1_\rho \mathrm{H}}$, 6 ms (60%) and 11 ms (40%). This seems to suggest a heterogeneous phase which consists of two portions: one close to the bonded silica surface, and the other further away from it. Although the use of two relaxation times is a rather crude estimate of what is more likely a continuous distribution of relaxation times, nevertheless these data provide a strong indication that the PC oligomer was tethered to the silica surface. When comparing within a single grafted chain, the higher $T_{1_\rho \mathrm{H}}$ value (11 ms) for the grafted oligomer represents restricted motions of the oligomer chain nearer to the chemically bonded end, while the shorter $T_{1_\rho \mathrm{H}}$ values (6 ms) correspond to the parts of the oligomer away from the bonded surface. When comparing a grafted chain (~9.3 ms) to a neat one (~4.9 ms), the increase of $T_{1_\rho \mathrm{H}}$ values (Fig. 4) reflect that the grafting of PC onto a silica surface leads to greater interchain spacing of the oligomer molecules relative to that of the neat material and, thus, a higher mobility of portions of the grafted material.

Further experiments were conducted to investigate the temperature effects on the grafted PC oligomers. Fig. 6 is a stacked plot of three selected spectra of the neat oligomer PC (Fig. 6(A)) and the grafted PC (Fig. 6(B)) measured at temperatures of 100°C, 20°C and −100°C. At the low temperature, the signals for the protonated aromatic carbon resonances C-4 and C-4′ are broadened and split into two or more peaks. Such spectral features of the phenylene carbons indicate that the aromatic ring flipping process is much slower at −100°C, which leads to non-equivalent local environments for the protonated carbon C-4 and C-4′. Fig. 6 shows that the protonated aromatic carbons C-3 and C-3′ are less sensitive to the ring flipping effect, showing slight broadening, which is consistent with data reported by Kenrichs and Nicely [18]. We interpret this to show that the C-3 and C-3′ carbons are further away from the methyl groups and adjacent aromatic rings, and the planar carbonate group is oriented close to the perpendicular with respect to the aromatic rings, which affects the environment for the C-3 and C-3′ carbons equally [18]. A low temperature transition is also observed for PC oligomer ($n = 3$–4) using differential scanning calorimetry (DSC). Such aromatic ring flipping motion is attributed to that of the phenyl group rotating and wiggling about its 1–4 axis, allowing the C-3 and C-4 carbons to exchange position

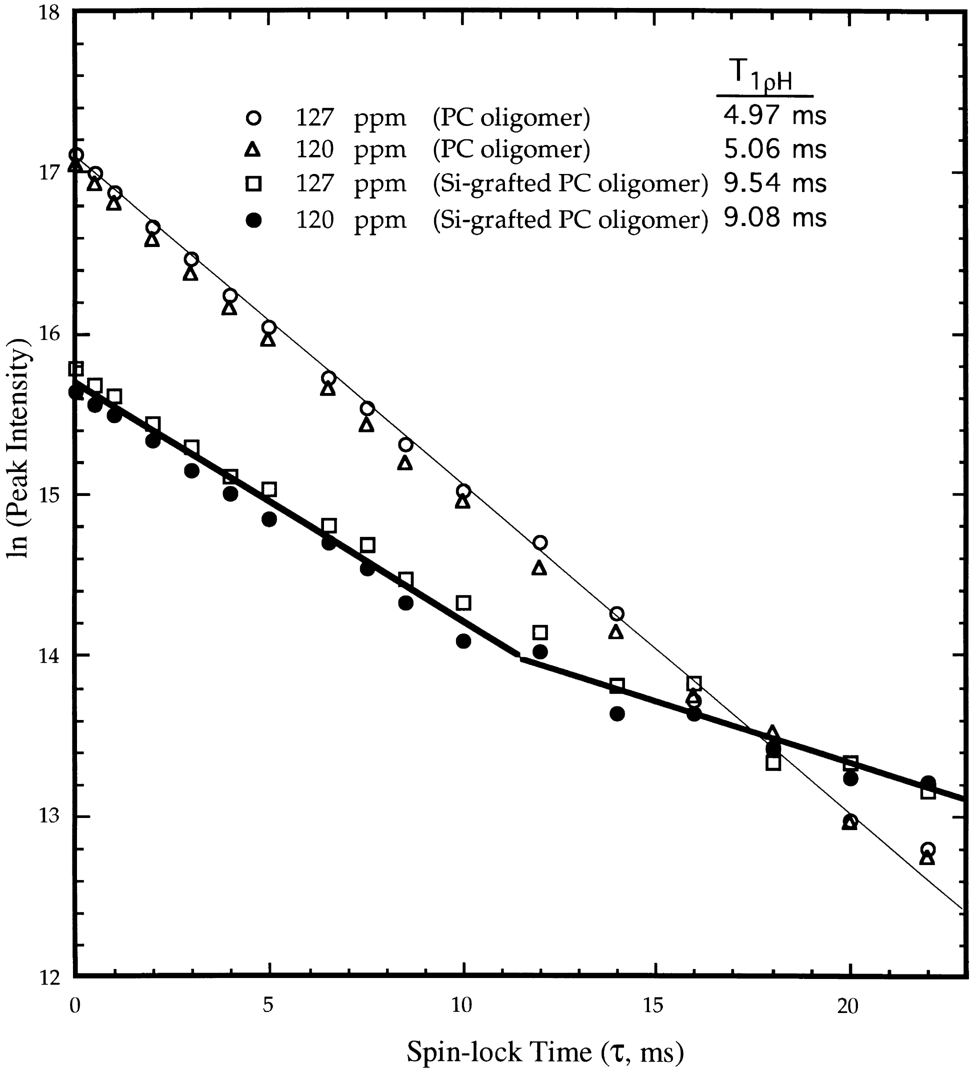


Fig. 5. Proton $T_{1_\rho \mathrm{H}}$ plot of the protonated aromatic carbon intensities as a function of spin-lock times (ms) for the neat and grafted oligomers.

with the C-3′ and 4′carbons. Above room temperature, rapid ring flipping averages the two signals of the C-4 and 4′ carbons into a single resonance. This finding correlates well with the γ relaxation of high molecular weight PC, which is thought to be the result of an oscillatory motion and aromatic ring flipping of the phenylene groups in the bisphenol A structure [10,13,18]. Above the γ relaxation temperature, the phenyl groups become more mobile and the flipping rate is higher than the frequency of separation (~100 Hz) of the signals, so the peaks at 127.4 and 120.5 ppm at 20° and 100°C represent the averaged position of C-4, 4’ and C-3, 3’ carbons. Similar spectral features were observed for the silica-grafted PC oligomer (Fig. 6(B)), showing the increase of the ^{13}C line width, indicating a slower motion as the temperature decreases from 100°C to −100°C.

The dynamic mechanical behavior of high molecular weight PC has been extensively studied and reviewed [10,13,19], showing that the polymer undergoes three molecular relaxation processes, alpha (α), beta (β), and gamma (γ). The prominent α relaxation is attributed to large-scale segmental motion during the glass transition (T_g). The β relaxation corresponds to segmental motions, that is, a combined phenylene–carbonate motion. The γ relaxation is caused by the carbonyl motion in the specimen.

Fig. 7 shows $T_{1_\rho \mathrm{H}}$ values plotted as a function of temperature for the grafted PC oligomer (Fig. 7(A)) and neat PC oligomer (Fig. 7(B)). The $T_{1_\rho H}$ of the neat PC oligomer exhibits two minima (4.16 and 3.75 ms) over the observed temperature range while the grafted PC oligomer shows no obvious transition, but an increase in $T_{1_\rho \mathrm{H}}$ values as the temperature increases.

The minimum $T_{1_\rho \mathrm{H}}$ (3.75 ms) at the temperature of around 50°C is believed to be the α relaxation, which involve crankshaft-like segmental motion including molecular translational and rotational motions as reported [11]. It

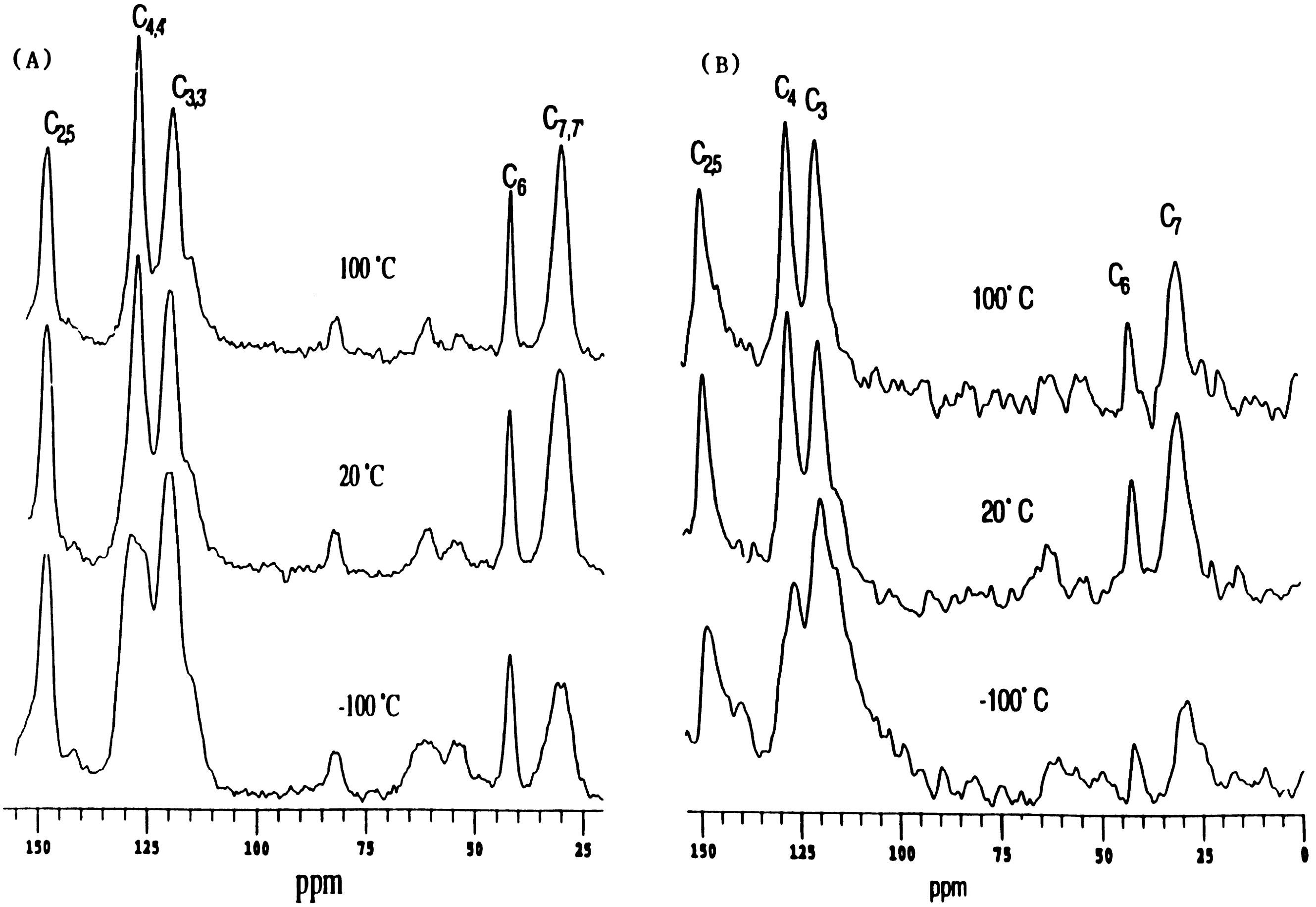


Fig. 6. 75 MHz solid state ^{13}C CP/MAS NMR spectra of the neat: (A) and grafted polycarbonate oligomer (B), measured at 100°C, 20°C and -100°C, with a magic angle spin-rate of 5 kHz, pulse delay of 2 s, contact time of 1 ms and 40 Hz line broadening.

corresponds to the glass transition (T_g). The $T_{1_\rho\mathrm{H}}$ minimum (4.2 ms) at about -20°C is possibly the β-relaxation process because of the isopropylidene and phenyl carbonate groups undergoing a torsional motion [13]. The region beyond the lowest temperature observed could be a γ relaxation resulting from the phenylene ring flip or wiggle and rotation of the carbonate group.

The effect of temperature on the $T_{1_\rho\mathrm{H}}$ values of the grafted PC oligomer in the kHz range is less complex, showing almost no minimum observed. $T_{1_\rho\mathrm{H}}$ appears to increase monotonically with temperature, suggesting that the transitional responses observed for the neat oligomer have disappeared. The disappearance of the α transition indicates that the PC molecules on the surface no longer exhibit translational motion and thus are strongly bonded to the silica surface. The increase in $T_{1_\rho\mathrm{H}}$ with increasing temperature, indicates that a shorter effective correlation time is related to longer $T_{1_\rho\mathrm{H}}$ times. The β relaxation remains observable, indicating that certain internal motions are still present in the grafted oligomer. The higher $T_{1_\rho\mathrm{H}}$ values for the grafted PC oligomer indicate that the grafted material is less densely packed at the surface in comparison to that of the semi-crystalline neat PC oligomer. A precise assignment of mechanical translations to molecular process is difficult, and the detailed interpretation of the measurements is beyond the scope of the present study. However, our temperature-dependent studies support the contention that PC oligomer has been grafted on the silica surface.

Further investigation using ^{29}Si CP/MAS NMR was carried out to confirm the results of the ^{13}C NMR studies. The ^{29}Si CP/MAS spectra of the grafted PC oligomer (Fig. 8(A)) and silica (Fig. 8(B)) are shown in Fig. 8. Three silica peaks (ratio 1 : 3 : 2) were observed at the silica surface sites [17,18], corresponding to the [–O2–Si– (OH)2], [–O3–Si–OH] and [–O2–Si–O2–], respectively. The spectrum for the grafted silica (Fig. 8(B)) shows the ratio of peak intensity to be (0.5 : 3 : 2.8), compared to (1 : 3 : 2) for the neat silica, indicating that PC oligomer reacted with the [–O2–Si– (OH)2] and [–O3–Si–OH] sites on the surface of the silica microspheres. The grafting reaction forming the Si–O bond resulted in increase of intensity of the [–O2–Si–O2–] peak in the grafted PC spectrum (Fig. 8(B)). The results of ^{29}Si NMR analysis of the neat silica and the PC/

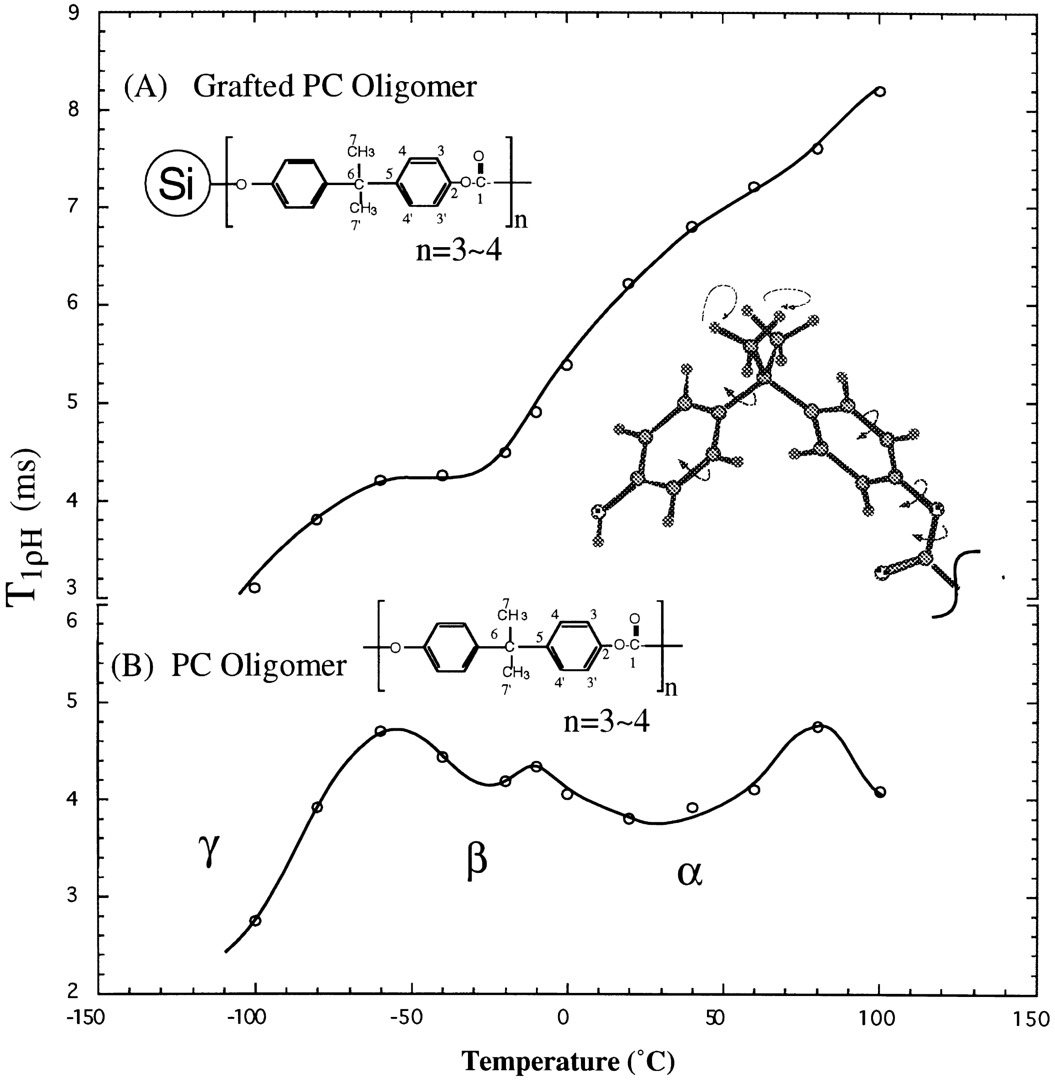


Fig. 7. Plot of $T_{1_\rho H}$ as a function of temperature (−100°C to 100°C) for the protonated aromatic carbon (C_4, 127 ppm) of: (A) grafted polycarbonate oligomer and (B) neat oligomer.

silica composites reconfirms the conclusion from the earlier studies.

4. Conclusions

The grafting mechanism and dynamic properties of the PC oligomer before and after grafting using a silicon tetrachloride intermediary at the silica surface were studied by solid state CP/MAS and relaxation NMR. The chemical shifts and the $T_{1_\rho \mathrm{H}}$ values provide evidence that a covalent bond is formed at the interface, Si–O–C, between the tethered molecule and silica, which is then further confirmed by ^{29}Si CP/MAS NMR. These results are congruent with the observed high hydrolytic stability and high interfacial shear strengths of the grafted composites measured using other methods that were reported previously [7]. It is hypothesized that the grafting resulted in the formation of low density, randomly distributed and loosely packed monolayers of covalently bound molecules that shield the surface from diffusing water. The grafted monolayer cannot be removed by extraction with a good solvent and its presence is confirmed via DRIFT and GC/MS [7]. Solid state REDOR NMR is currently under way to study the density of the grafted PC oligomer at the silica surface.

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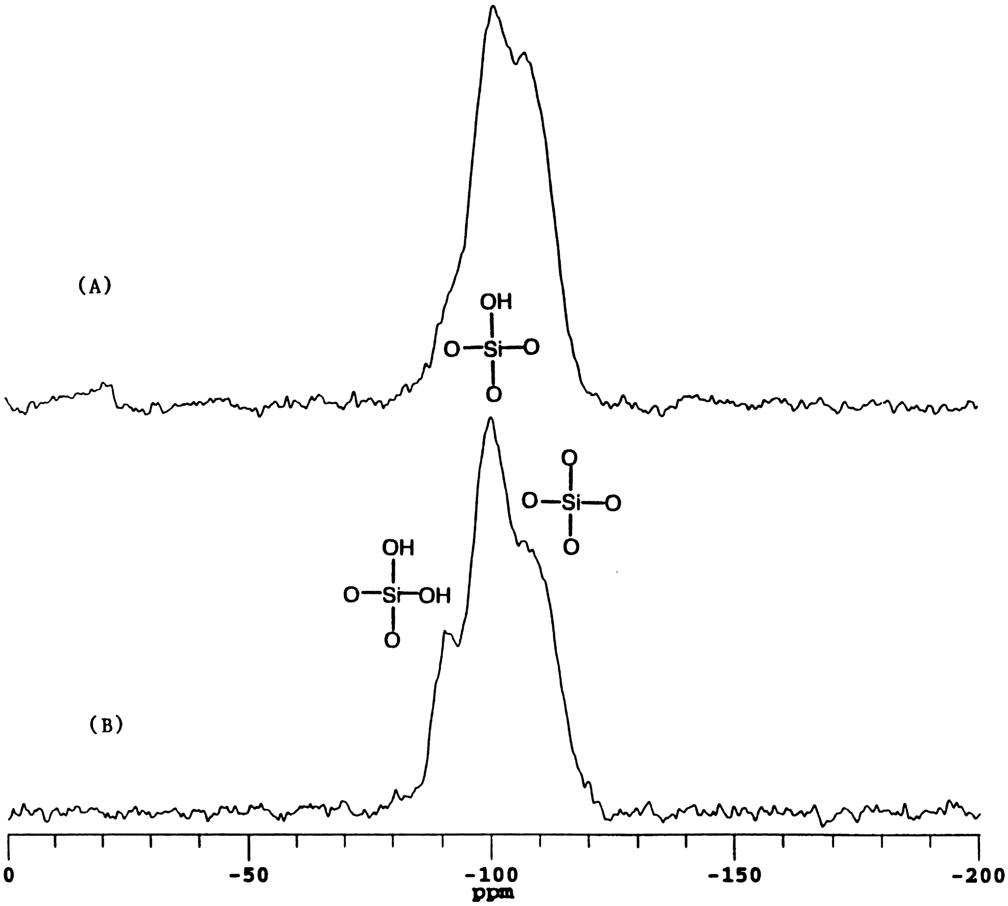

Fig. 8. ^{29}Si solid state NMR spectra (59.6 MHz) of: (A) oligomer grafted silica and (B) neat silica. The magic angle spin-rate was 4.7 kHz with contact time of 10 ms and a pulse delay of 5 s.

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