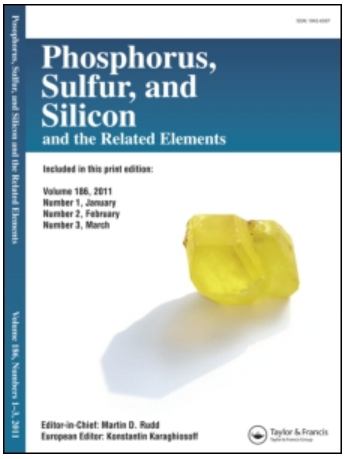

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ORGANIC-INORGANIC HYBRID MATERIALS 6: NMR STUDY OF THE POLYVINYLIMIDAZOLE-SILICA HYBRIDS

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ORGANIC-INORGANIC HYBRID MATERIALS 6: NMR STUDY OF THE POLYVINYLIMIDAZOLE-SILICA HYBRIDS

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The microstructure of the polyvinylimidazole-silica hybrids (PVI-SiO_2) containing various proportions of silica was examined by high resolution solid-state ^{29}Si and ^{13}C nuclear magnetic resonance spectroscopy. The ^{29}Si-^{1}H cross-polarization (CP) process revealed that the Q^3 and Q^4 species had different CP efficiency. Moreover, the time constant for the energy exchange between ^{1}H and ^{29}Si spin systems (T_{SiH}) for the siloxane units was less dependent on the silica content, and that was in the range of 2.0 to 4.0 ms. The spin-lattice relaxation time in rotating frame ($T^{H}_{1\rho}$) of hybrids suggested that the ^{1}H spin-diffusion between imidazole and siloxane units were on a nanometer scale estimated by spin-diffusion path length.

Keywords: Polyvinylimidazole; silica; hybrids; NMR; relaxation; spin-diffusion

INTRODUCTION

Investigation of polymers containing nitrogen as donor atoms is still strong due to the variety of application. Examples include: destabilizing negative collids in effluents and water clarification[1], electrophoretic deposition[2], curing agent[3], activativing electrode processes[4], recovery of trace metal ions[5,6], and anticorrosion coatings[7–9]. Polyvinylimidazole (PVI) is interesting to working with because it is relatively simple to synthesis[10] and can generate given permanent positive charge densities by a controlled quaternization[11]. Quaternized PVI-silica hybrids (PVI-SiO_2)

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has been prepared by two main procedures. The first was prepared by coating silica beads with a quaternized PVI,[12] and the second was crosslinked the PVI adsorbed on silica beads[13,14]. However, those hybrids do not create bonding sites between the PVI and the silica. In this work, a homogeneous PVI-SiO_2 hybrid, that creates a chemical bond between the silica and PVI with trimethoxysilyl functional group, was prepared by sol-gel method.

Several methods have been used to characterize the miscibility of organic-inorganic hybrids, including microscopy, scattering techniques, mechanical and thermal measurements, and spectroscopy. The relaxation processes can be influenced by several factors, such as the change of molecular mass, addition of a suitable polymer modifier, preparation of polymer hybrid, spinning in different conditions, and stretching. Different chemical and physical modifications for hybrids produce some changes of the molecular motions. NMR methods are sensitive to short range interactions. Little work, however, has been reported on the dynamics of the polymer complex of PVI and poly(methacrylic acid)[15]. Thus a study to estimate the extent of miscibility for hybrids is carried out by NMR using relaxation time measurements. The Si-H polarization transfer relaxation time constant (T_{SiH}) can be calculated from a double exponential fit of the NMR line intensity versus contact time. On the other hand, the technique of the rotating frame spin-lattice relaxation times ($T_{1\rho}$), owing to the low frequency and the restriction of spin-diffusion over the much shorter $T_{1\rho}$ times, is more sensitive to the structural changes and molecular motions than those of the laboratory frame spin-lattice relaxation times (T_1)[16].

EXPERIMENTAL

Materials

The monomer vinylimidazole (VI; TCI) was purified by distillation before use. [3-(Methacryloxy)propyl]trimethoxysilane (MSMA; TCI), and tetramethoxysilane (TMOS, TCI) were used without purification. Azoisobutyronitrile (AIBN; BDH) was recrystallized from ethanol just before use. Tetrahydrofuran (THF; Aldrich) was fractionally distilled in the presence of calcium hydride under nitrogen atmosphere. Deionized water (18 MΩ) was used for their hydrolysis.

Preparation of the Polyvinylimidazole-Silica Hybrids

The general synthetic scheme of the polyvinylimidazole-silica hybrid materials (PVI-SiO_2) is depicted in Scheme 1. For a typical example, a mixture of VI (95 mmol; 8.9414 g) and MSMA (5 mmol; 1.2418 g), AIBN (0.1 mmol) and THF (70 mL) was poured into a 250 mL round bottom flask under nitrogen, and the solution was stirred at 60°C (8 h) to initiate the copolymerization of the monomers. The polyvinylimidazole, M5, with 5 mol % trialkoxysilyl functional group was then prepared. Thereafter, a desired amount of THF, TMOS (3.9601 g) and HCl (1 %, 2.8097 g) was added, followed by vigorous stirred for condensation (~10 min) at room temperature. The resulting homogeneous mixture was precipitated by a large volume of *n*-hexane. The precipitated hybrid was collected by filtration, washed with THF, and dried. After drying at room temperature for 24 h under atmospheric pressure, the hybrid was dried in a vacuum oven for 24 h. Hybrid M5–65 was then obtained, where 65 donates that 65 wt % of M5 condenses with 35 wt % of TMOS based on weight of monomer. The formulations of the other hybrids are listed in Table I.

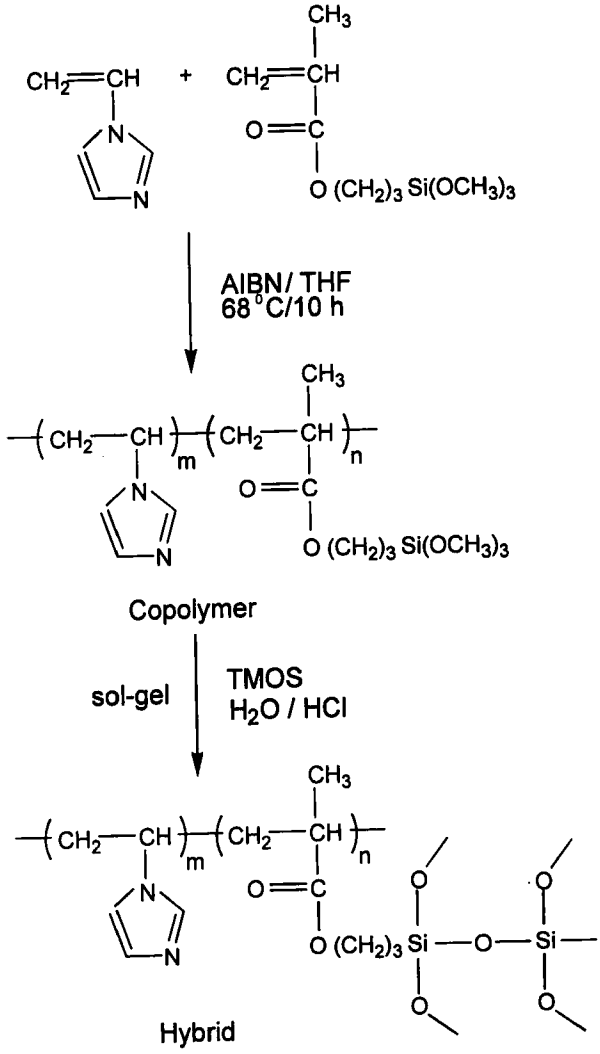
TABLE I Experimental conditions[a] for PVI-SiO_2hybrids

Hybrids Hybrids	*VI (mmol %)*	*MSMA (mmol%)*	*TMOS (wt %)*
M5–90	95	5	10
M5–85	95	5	15
M5–80	95	5	20
M5–75	95	5	25
M5–70	95	5	30
M5–65	95	5	35

[a]VI=vinylimidazole; MSMA=[3-(methacryloxy)propyl]trimethoxysilane; TMOS = tetramethoxysilane, $[H_2O]/[TMOS]=2$.

Characterization of the Polyvinylimidazole-Silica Hybrids

The structure of PVI-SiO_2 hybrid was confirmed by infrared (IR) spectrum (Bomem DA 3.002). All hybrids present the characteristic VI peaks (3112, 1496, 1227, and 655 cm^{-1}) and MSMA peaks (1709 and 1282 cm^{-1})[17]. The absorption in the range 3700–3200 cm^{-1} and 950 cm^{-1}



SCHEME 1

in hybrids was characterized by silanol groups (Si-OH) that was formed during the hydrolysis of alkoxy groups in MSMA and TMOS. On the other hand, the broader Si-O-Si absorption band (1080–1030 cm^{-1}) increased with increasing the silica content. The ^{13}C and ^{29}Si nuclear mag-

netic resonance (NMR) spectra of the solid-state PVI-SiO_2 hybrids were determined (Bruker MSL-400) by using the cross-polarization/magic angle spinning (CP/MAS) technique. The nomenclatures of T^i and Q^i is taken from Glaser *et al*[18], where i refers to the number of -O-Si groups bounded to the silicon atom of interest. T^i and Q^i denotes species that have one and no organic side group, respectively. The relative proportions of the T^i-species and Q^i-species were calculated on the basis of the experimental spectra.

CP contact time studies can produce Si-H polarization transfer constant (T_{SiH}). The ^1H-^{29}Si spin contact time with the Hartmann-Hahn condition fulfilled in the rotating frame was typically about 5 ms, but optimized in the range between 0.1 and 20 ms. Proton spin-lattice relaxation time in the rotating frame ($T^H_{1\rho}$) were measured by using a ^1H spin-lock τ-pulse sequence followed by the cross-polarization. The ^1H 90° pulse width was 4.5 us, and the CP contact time was 2 ms. The length of delay time τ was in the range from 0.1 to 10 ms for $T^H_{1\rho}$.

RESULTS AND DISCUSSION

Si-H Polarization Transfer Constant T_{SiH}

The silanol group (Si-OH) that is formed during the hydrolysis of alkoxy groups in alkoxysilane and trialkoxysilyl groups in PVI induces crosslinked three-dimensional network materials. ^{29}Si CP/MAS NMR spectra of PVI-SiO_2 hybrids were nearly identical. The resonances of M5–80 hybrid (Fig. 1) show four peaks about at –57, –66, -100 and –108 ppm corresponding to T^2, T^3, Q^3 and Q^4 respectively. Moreover, two shoulders at –49 and –91 ppm, respectively designated T^1 and Q^2 structures. On the other hand, the relative proportion of T^i in hybrids decreases with increasing silica content, whereas that of Q^i increases (Fig. 1). It indicates that more three-dimensional silica network is developing as the TMOS proportion increases.

In the conventional CP process under Hartmann-Hahn conditions, ^1H and ^{29}Si spin systems are spin-locked in the rotating frames and thermally in contact with each other, thus exchanging their energies. The respective spin systems also exchange energies with the surrounding thermal reservoir, the so-called lattice. Figure 2 gives an example of the effect of con-

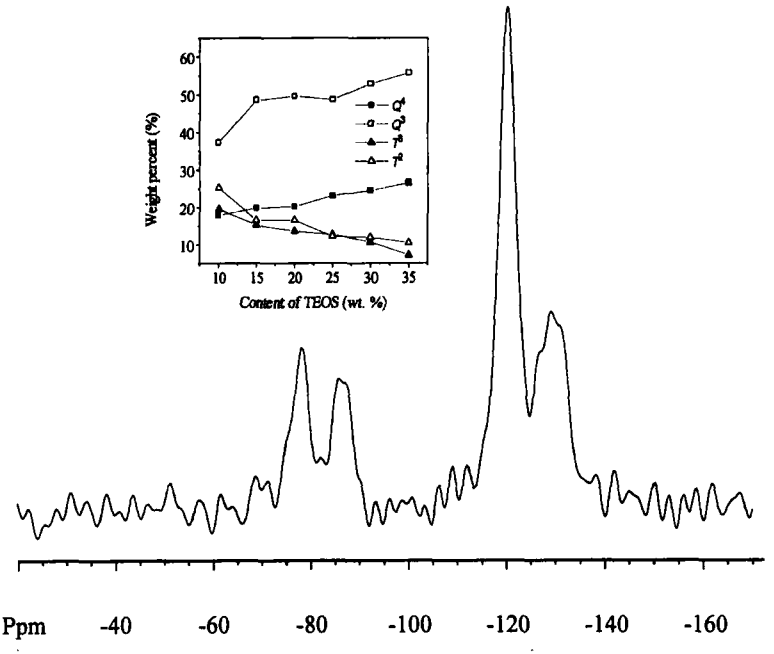


FIGURE 1 The ^{29}Si single pulse excitation MAS spectrum of M5–80 hybrid as well as relative proportions of T^2, T^3, Q^3 and Q^4 species

tact time t on the ^{29}Si resonance of M5–80 hybrid. Intensities in the Figure 2 reflect local cross-polarization dynamics which may vary from site to site. According to the simple theory in this CP process, magnetization, $M_c(t)$, is expressed as a function of the contact time as follow:[19]

$$M_c(t) = M_e[\exp(-t/T^{H}{}_{1\rho}) - \exp(-t/T_{SiH})]$$

Here, M_e, is the ^{29}Si equilibrium magnetization obtained when both spin systems fully interact with each other without any energy exchange with the lattice and therefore this value is proportional to the concentration of a given ^{29}Si nucleus in a material. T_{SiH} is the time constant for the energy exchange between ^{1}H and ^{29}Si spin systems, and $T^{H}{}_{1\rho}$ is the spin-lattice relaxation time in rotating frame. This equation indicates that the ^{29}Si magnetization appears at the rate of the order of $(T_{SiH})^{-1}$ and disappears at the rate of $(T^{H}{}_{1\rho})^{-1}$.

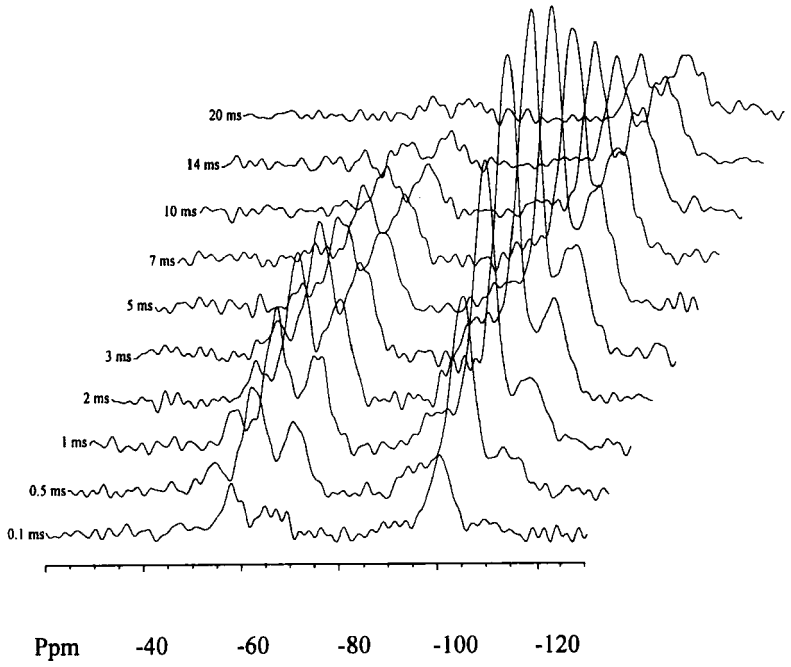


FIGURE 2 Stacked plot of the ^{29}Si CP-MAS spectra of M5–80 hybrid as a function of contact time

Figure 3 shows a semilogarithmic plot of the peak intensity as a function of the contact time for the silicon in M5–90 hybrid. A steeper slope is an indication of faster transfer of magnetization (shorter T_{SiH}) or faster relaxation by spin diffusion (shorter $T^{H}_{1\rho}$). The values of T_{SiH} and $T^{H}_{1\rho}$ estimated by the curve-fittings are summarized in Table II. T_{SiH} and $T^{H}_{1\rho}$values for Q^3 species are smaller than that for Q^4 species. It indicates that the Q^3 centers contains protons which can provide the Si-H dipolar coupling. The low CP efficiency of the Q^4 species may be due to a few nearby protons in the material matrix to facilitate the transfer of polarization. Moreover, the curve in Figure 3 is linear that suggests that large-scale phase separation of Q^i and T^i species does not occur in these materials. Thus, the ^{29}Si atoms of Q^i and T^i species must be within approximately 10 $\AA$ of a proton to facilitate polarization transfer[19]. Moreover, the intensities of the T^2 and Q^3 resonances in PVI-SiO_2 hybrids are less dependent on

the silica content and those reach a maximum approximately at 2.5 ms (Fig. 4). The result suggests that the flexibilities of the imidiazole and siloxane units are less dependent on the silica content from the values of T_{SiH} and $T^{H}_{1\rho}$.

TABLE II T_{SiH} and $T^{H}_{1\rho}$ values of the respective resonance lines of PVI-SiO_2 hybrids, and L values of hydrids

hybrids	T_{SiH} *(ms)*				$T^{H}_{1\rho}$ *(ms)*				$T^{H}_{1\rho,av}$*(ms)/L (nm)*
	T^2	T^3	Q^3	Q^4	T^2	T^3	Q^3	Q^4	
M5–90	2.58	2.29	1.72	2.33	7.07	8.99	8.59	15.52	4.62/2.15
M5–85	2.10	1.94	2.35	2.44	7.72	12.40	9.82	21.27	4.17/2.04
M5–80	2.99	2.67	2.00	2.17	10.52	12.11	10.02	25.37	3.98/1.99
M5–75	2.44	2.90	1.90	2.07	13.84	14.26	9.73	35.16	4.31/2.08
M5–70	3.74	3.87	2.93	4.08	12.12	16.39	14.12	52.77	4.04/2.01
M5–65	3.74	3.87	2.93	4.08	12.12	16.39	14.12	52.77	4.58/2.14

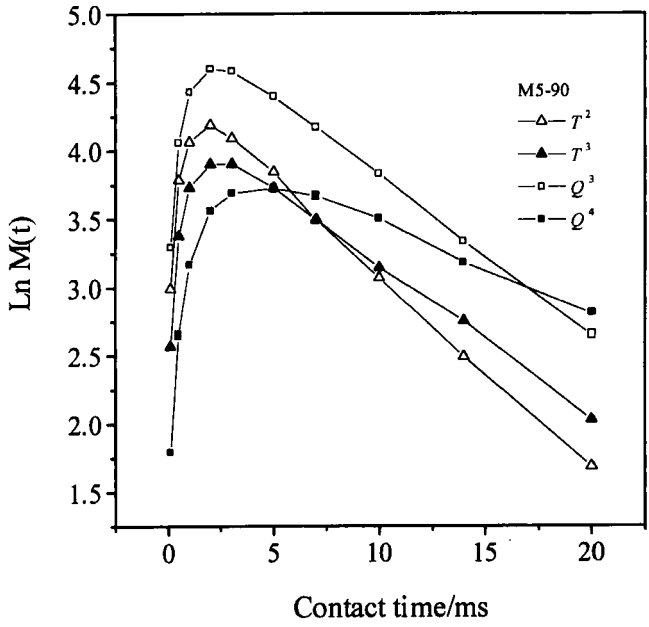


FIGURE 3 Semilogarithmic plot of the peak intensities of the T^i and Q^i species shown in Figure 2 as a function of the contact time

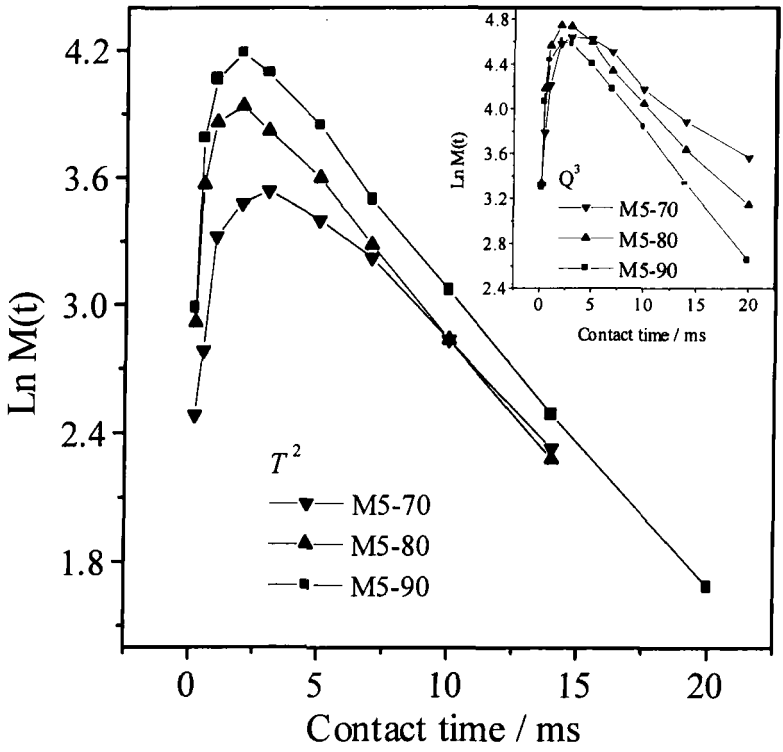


FIGURE 4 Semilogarithmic plot of the peak intensities of the T^2 and Q^3 species as a function of the contact time

^{1}H Spin-Lattice Relaxation Time in the Rotating Frame

^{13}C CP/MAS NMR spectra of PVI-SiO_2 hybrids were nearly identical. The resonances in Figure 5 at around 138, 131 and 117 ppm can be assigned to the imidiazole ring, while those at 177, 70, 24, 18 and 10 ppm are due to MSMA units. Additionaly, the resonances arround 53 and 44 ppm result from overlapping lines from both components. The relaxation time $T^{H}_{1\rho}$ of the protons is a quantity which is averaged within domain of 1–2 nm diameter. $T^{H}_{1\rho}$ can therefore be treated as a phase quantity, at least in those cases where there is sufficient dipolar coupling among the protons to provide spin-diffusion over the range of 1–2 nm. It should

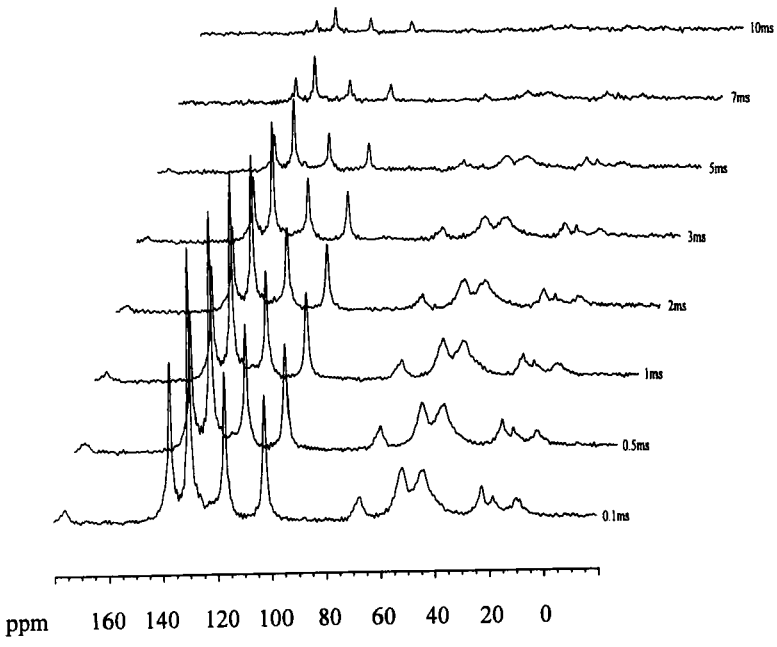


FIGURE 5 Stacked plot of the ^{13}C CP-MAS spectra of M5–80 hybrid as a function of delay time

be noted that the $T^{H}_{1\rho}$ values in Table II are obtained by the analysis of the CP process. Based on the spin-locking mode employed in $T^{H}_{1\rho}$ measurement, the magnetization of resonance is expected to decay according to the following exponential function:[19]

$$M_\tau = M_0 \exp[-\tau/T^{H}_{1\rho}].$$

Here, τ is delay time used in the experiment and $M_\tau$corresponds to resonance intensity. Figure 5 shows the effect of delay time τ on the ^{13}C resonance of M5–80 hybrid. The $T^{H}_{1\rho}$ values of the respective carbon of hybrids measured by using the standard pulse sequence is shown in Figure 6. The cause of the difference with Table II is not clear at present but the values indirectly determined may contain some unknown contributions in the CP process. It seems, therefore, plausible to discuss relative changes in $T^{H}_{1\rho}$ instead of absolute values, as in previous section. As is clearly seen in Figure 6, the $T^{H}_{1\rho}$ of the imidazole ring in PVI-SiO_2

hybrids (~3.2 ms) is lower than that in pure PVI polymer (~7.4 ms). It suggests that the motion of the imidazole ring is slightly restricted by the bonding between the PVI copolymer and silica. Moreover, the $T^{H}_{1\rho}$ values of the resonance 55 and 46 ppm are around 4.5 ms that between the values for the imidiazole ring (~3.2 ms) and MSMA units (~5.5 ms). This result reveals that most of imidazole and silica units are compatible in hybrids in a scale of several nanometer.

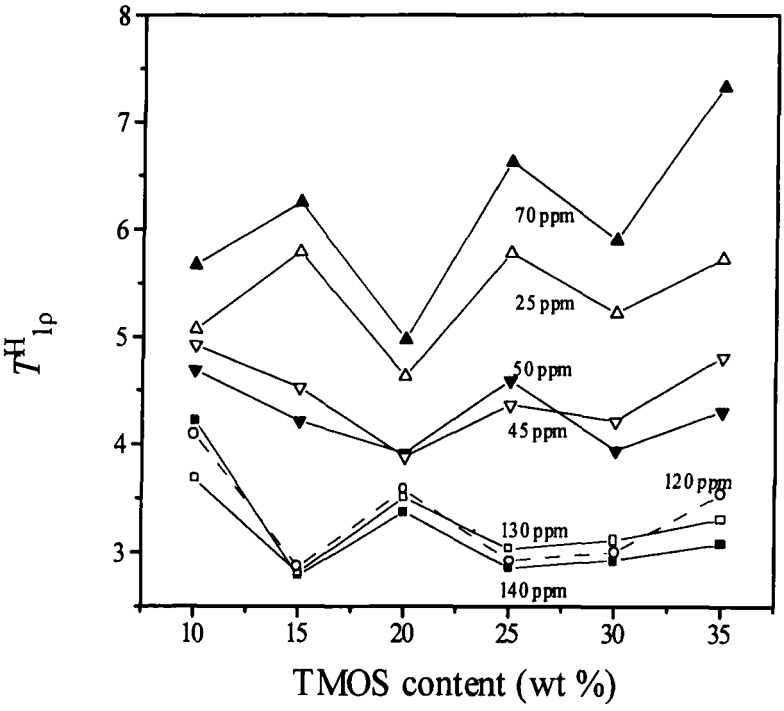


FIGURE 6 The dependence of $T^{H}_{1\rho}$ calculated by the spin-locking method on the TMOS content in PVI-SiO_2 hybrids

A fast spin-diffusion occurs among all protons in hybrids, which averages out the whole relaxation process. Thus, the domain size of hybrids is smaller than the spin-diffusion path length within $T^{H}_{1\rho}$ time. The spin-diffusion path length, L, can be estimated using the following equation:[20]

$$\langle L^2 \rangle = (T^{H}_{1\rho}/T_2)\langle l_0{}^2 \rangle$$

Here l_0 is the distance between protons, typically 0.1 nm, and T_2 is the spin-spin relaxation time which, below T_g, is ca. 10 μs[20], and then $<L^2>$ can be evaluated. It can be seen that the L values of the hybrids are clearly around 2 nm (Table II).

CONCLUSIONS

The microstructure of the polyvinylimidazole-silica hybrid materials, prepared via free radical addition and sol-gel techniques by mixing TMOS with PVI, were characterized by high resolution solid-state NMR spectroscopy. The CP efficiencies of the Q^3 and Q^4 species were determined by local chemical environment of the protons which provided the Si-H dipolar coupling. A less tractable CP dynamic of Q^4 species, as silica content increased can be accounted for by a the lower hydrogen concentration in their vicinity. The flexibility of the imidiazole was restricted by silica but the values of T_{SiH} and $T^H_{1\rho}$ was independent on the silica content. From spin-diffusion path length examination, the distance between imidazole and siloxane units in hybrids were in a nanometer scale.

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