Polarization Transfer across Interfaces. 1. ^{29}Si Cross-Polarization Dynamics at the Poly(vinyl alcohol)–Silica Sol–Gel Interface

Nicholas Zumbulyadis* and James M. O'Reilly

Corporate Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650–2110

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ABSTRACT: We discuss polarization transfer across interfaces as a family of solid-state NMR techniques for observing selectively the NMR spectra of surface and near-surface species. We apply one such technique to estimate the proximity of the backbone of poly(vinyl alcohol) (PVOH) to the surface of silica polymerized in situ through the acid-catalyzed sol–gel condensation of tetraethoxysilane (TEOS). Cross-polarization times measured in protonated, and selectively deuterated samples, can be analyzed semiquantitatively to yield approximate distance ratio information between the silica surface and the polymer backbone vs the hydroxyl groups. The distance ratio information will serve as an initial constraint for modeling the PVOH–silica interface using molecular dynamics calculations.

1. Introduction

The need for a better characterization of the structure and dynamics of polymers in interfacial regions cannot be overemphasized. In the area of high-performance polymers, compatibilization, reactive blend formation, and the fiber reinforcement of polymer matrices depend on interfacial phenomena. Polymeric thin films are important in the development of nonlinear optical materials and other applications in molecular electronics. Interfacial phenomena play a role in biocompatibility, adhesion, abrasion resistance, and the formation of diffusion barriers.

Nuclear magnetic resonance spectra are extremely sensitive to subtle changes in structure, conformation, dynamics, and molecular orientation. Thus chemical and hydrogen bonding at the interface, and differences in composition, chain conformation, packing, and mobility between the bulk and the surface, can be studied. Unlike some other surface characterization techniques, NMR does not require optical clarity of the sample. Offsetting these advantages, however, is the inherently low sensitivity of NMR detection and the need to selectively observe the interface against a strong background signal from the bulk.

The dynamic properties of the spin system can often be taken advantage of to selectively excite the solid-state NMR spectrum of surfaces or interfacial regions. An early example of this approach is the application of ^{1}H–^{29}Si cross-polarization techniques to the observation of silica surfaces by Sindorf and Maciel.[1-7] The selectivity in this case arises from the confinement of the protons to the silica surface and the short-range nature of the cross-polarization process.

In this paper we report on a different approach to interface selectivity, the transfer of spin polarization *across* an interface. Such a transfer can be accomplished through cross polarization, dynamic nuclear[8] polarization, or spin diffusion. All these phenomena are sensitive functions of internuclear distances, and some have been used previously to study the miscibility in polymer blends.[9-11] Our objective in this work has been to probe intermolecular distances at a polymer–silica interface by studying the dynamics of polarization transfer between protons on the polymer backbone and ^{29}Si nuclei on the glass surface.

The model systems we have chosen for the present study are composites of poly(vinyl alcohol) (PVOH) or poly(vinyl alcohol) with the hydroxy proton exchanged by a deuteron (PVOD) and silica prepared via the in situ hydrolysis and polymerization of tetraethyl or tetramethyl orthosilicate (TEOS or TMOS). We have compared the cross-polarization rates in purely inorganic sol-gel silica, PVOH–silica (1:1) composites, and PVOD–silica (1:1) composites. In the latter, the selective deuteration of *all* exchangeable protons (silanol groups in the silica network as well as alcohol groups on the polymer chains) ensures polarization transfer specifically from the vinyl protons of the polymer backbone to the ^{29}Si nuclei on the glass surface. We show that a comparison of these rates yields detailed geometrical information about the interaction of PVOH with the silica surface.

2. Cross-Polarization Dynamics

The cross-polarization process involves the flow of entropy (spin order) from a reservoir I of abundant spin (such as protons), cooled to a very low spin temperature in the rotating frame, to an infinitely hot reservoir S of isotopically dilute spins (such as ^{13}C or ^{29}Si). This is accomplished by bringing the two reservoirs into thermal contact by means of a radio-frequency pulse sequence. The extent of which the dilute spins are ultimately polarized depends on the contact time and on the balance between two competing processes, the cross-polarization rate T_{IS}, and the rotating-frame spin–lattice relaxation times ($T_{1\rho}$s) of the rare and abundant nuclear species. It also depends on the relative size of the two reservoirs. Assuming that the number of I spins, N_{I}, is much larger than N_{S}, the time dependence of the S-spin magnetization can be described by the following equation:[12]

$$M_{\mathrm{S}}(t) = M_0\lambda^{-1}(1 - e^{-\lambda t/T_{\mathrm{IS}}})e^{-t/T_{1\rho}^{\mathrm{I}}} \tag{1}$$

In the above equation $T_{1\rho}^{\mathrm{I}}$ is the rotating-frame spin–lattice relaxation time of the abundant nuclei, protons in the present case. Assuming that $T_{1\rho}^{\mathrm{S}} \gg T_{\mathrm{IS}}$, the parameter λ is given by

$$\lambda = (1 - T_{\mathrm{IS}}/T_{1\rho}^{\mathrm{I}}) \tag{2}$$

The data from a measurement of cross-polarization intensity versus contact time fitted to eq 1 yield M_0, T_{IS}, and $T_{1\rho}^{\mathrm{I}}$.

The cross-polarization time, T_{IS}, contains valuable geometric information. For large spin-locking fields near resonance for both the I and S spins, T_{IS} is approximately proportional to $M_{2\mathrm{IS}}$, the second moment of the S spins due to dipolar interactions with the I spins, and to $J_{\mathrm{I}}(\Delta\omega_{\mathrm{eff}})$, the value of the spectral density of the spin–spin

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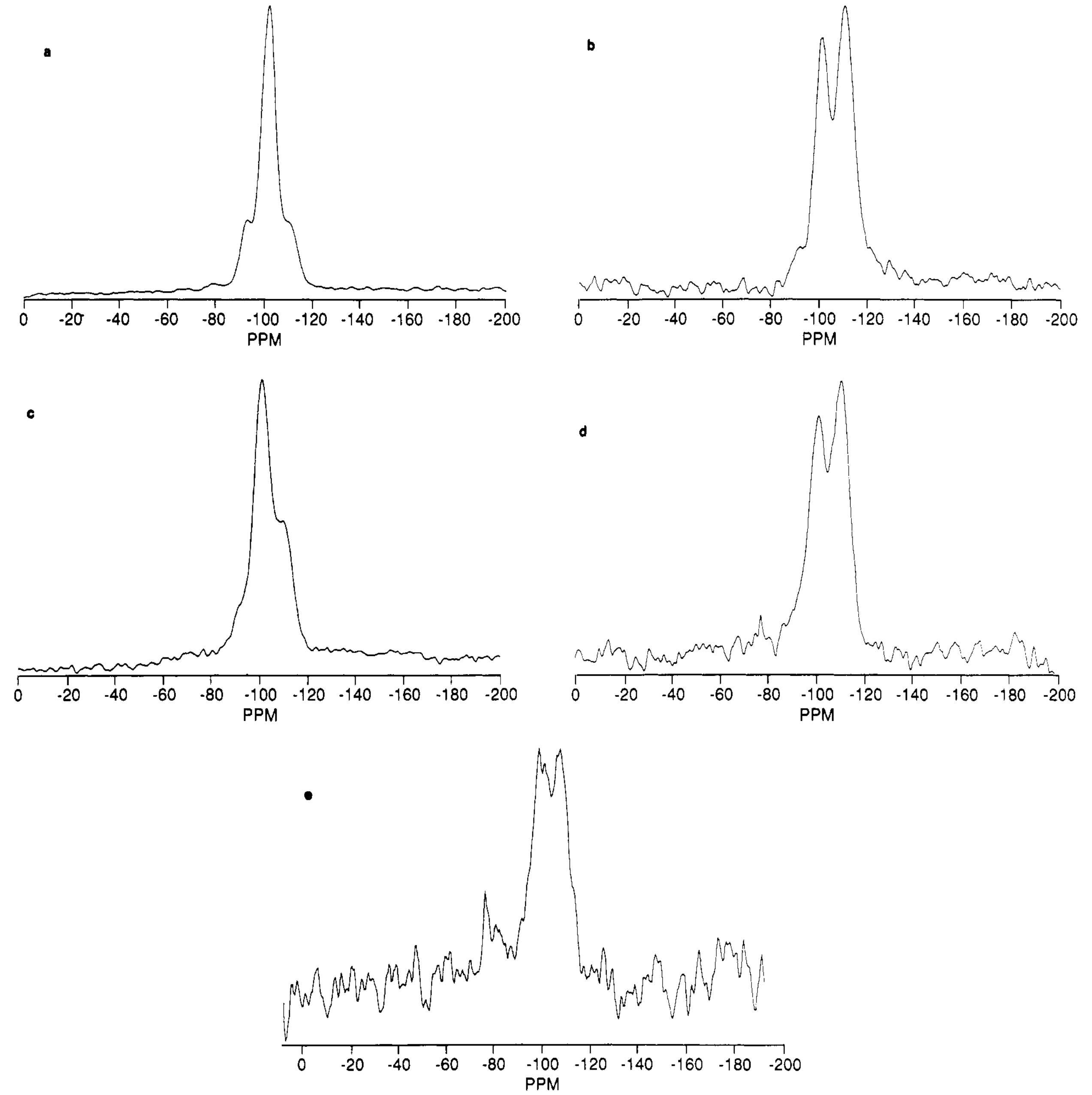

Figure 1. ^{29}Si spectra of sol–gel silica and a PVOH–silica composite: CP/MAS spectrum of silica derived from condensation of TEOS (a). The corresponding Bloch decay spectrum with a relaxation delay of 200 s (b). CP/MAS spectrum of the PVOH–TEOS (1:1) composite; note the more intense Q^4 peak (c). The corresponding Bloch decay spectrum (d). CP/MAS spectrum of PVOD–silica (1:1) composite (e).

correlation function for the I spins at $\Delta\omega_{\mathrm{eff}} = \omega_{\mathrm{IS}} - \omega_{\mathrm{II}}$.[13] Hence, if the Hartmann–Hahn condition is fulfilled, we can write

$$T_{\mathrm{IS}}^{-1} = CM_{2\mathrm{IS}}J_{\mathrm{I}}(\omega=0) \qquad (3)$$

The spin–spin correlation function (not to be confused with correlation functions describing molecular motion such as rotational diffusion) is usually taken to be a Gaussian with a correlation time related to the line width of the I-spin spectrum (roughly the square root of the homonuclear second moment, $M_{2\mathrm{II}}$). As we will see below, an explicit knowledge of the shape of the correlation function is not relevant to our analysis.

The potential geometric information is contained in the $M_{2\mathrm{IS}}$, which to a first approximation varies as r^{-6}, the distance to the nearest protons. An analysis of cross-polarization dynamics along the lines outlined above has been used by Klein Douwel et al.[9] to study intermolecular distances in PMMA–PVF$_2$ blends, and by Hoh et al.[14] to study the mobility of aminosilane coupling agents.

3. Experimental Section

A. Preparation of Materials. The acid-catalyzed silica was prepared by mixing 43 mL of TEOS, 43 mL of ethanol, and 14 mL of 0.15 N HCl. The material was placed in a vacuum oven overnight at 90–100 °C.

The PVOH–silica sample was prepared by mixing a 5 wt % solution of PVOH, Elvanol 71-30 (Du Pont) in water with TEOS (1:1 molar ratio based upon polymer repeat unit). The resulting gel was evaporated in a hood over several days an then dried overnight in a vacum oven at 70 °C. PVOD was prepared from PVOH by exchanging twice with D$_2$O and drying overnight in a vacuum oven between exchanges. ^{1}H NMR analysis indicated an extent of deuteration over 95%. The PVOD solution (5% in D$_2$O) was mixed with TEOS (1:1 molar ratio) to prepare the PVOD–silica sample as above.

B. Nuclear Magnetic Resonance Measurements. The ^{29}Si CP/MAS and Bloch decay measurements were carried out on

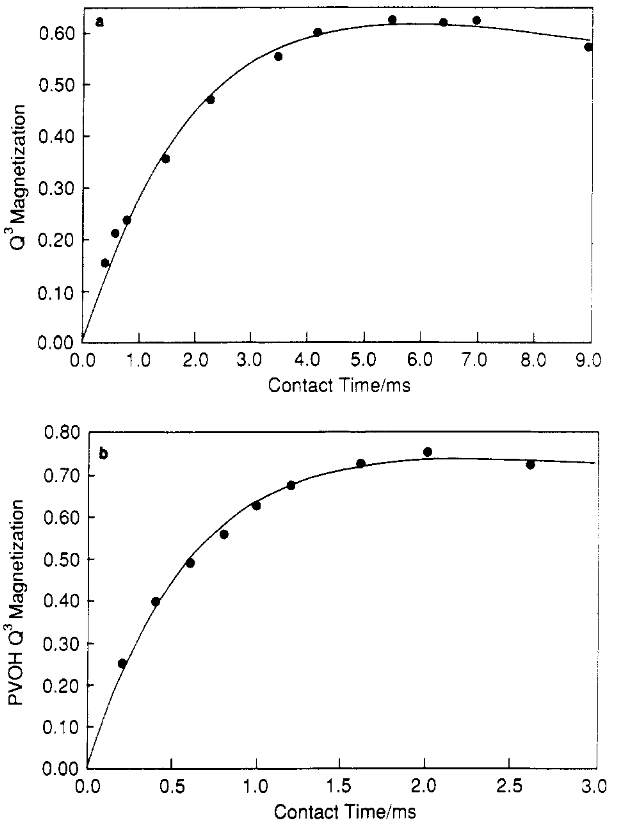

Figure 2. Nonlinear regression fit of eq 1 to cross-polarization data. Fit to integrated intensity of the Q^3 peak in silica (a) and the PVOH–silica (1:1) composite (b). Note the shorter time axis in the case of the composite.

Table I
^{1}H–^{29}Si Cross-Polarization Dynamics in PVOH–TEOS Composites Prepared by the Sol–Gel Method

sample	T_{CP}/ms	$T_{1\rho}$/ms	magnetization, % CP	magnetization, % Bloch decay
	Acid-Catalyzed Inorganic Sol–Gel			
Q^2	1.5	29	8	7
Q^3	2.1	26	43	31
Q^4	12.2		49	62
	PVOH–TEOS Composite			
Q^2	0.6	5.1	12	11
Q^3	0.6	5.0	44	34
Q^4	2.2	4.0	44	55
	PVOD–TEOS Composite			
Q^3	4.3	4.1		
Q^4	3.7	4.0	≈1:1	

a 200-MHz home-built instrument published elsewhere.[15] The 90° pulse widths were 4.8 μs, corresponding to cross polarization and decoupling fields of 52 kHz. The radio-frequency irradiation frequency was selected to be less than 2 kHz off-resonance. The Hartmann–Hahn condition was optimized by using the narrow signal of hexamethylcyclotrisiloxane, which served also as a chemical shift reference (−9.33 ppm from TMS). The spinning rate was 4 kHz. Each CP/MAS spectrum was the average of 500 (inorganic gel) or 5000 transients [PVOH–silica (1:1) composite]. The spectra are shown in Figure 1a, together with the corresponding Bloch decay spectra (Figure 1b). The peaks have been previously assigned to Q^2, Q^3, and Q^4 type silicons.[1] The experimental points were fitted to eq 1 by using a nonlinear regression procedure. The quality of typical data and theoretical fits is shown in Figure 2; the fit parameters are summarized in Table I. The Bloch decay spectra were averages of 1000 transients (inorganic gel) and 2000 transients [PVOH–silica (1:1) composite] with a relaxation delay of 200 s. Proton line shapes and $T_{1\rho}$ values were measured indirectly by monitoring the magnitude of the proton magnetization through cross polarization to ^{29}Si, after inserting the appropriate delays into the pulse sequence.[16,17]

4. Discussion of Results

A. Analysis of Cross-Polarization Dynamics in Purely Inorganic Sol–Gel Silica. Fits of experimental data to eq 1 yield three quantities of interest, namely, the cross-polarization time constant T_{CP}, the proton $T_{1\rho}$, and the equilibrium magnetization for the various Q^n moieties. We measured these quantities for a silica prepared by the sol–gel process under acid-catalyzed conditions. The cross-polarization results for this and the other materials studied in the present work are summarized in Table I.

The cross-polarization time constants, T_{CP}, and proton $T_{1\rho}$ obtained in this work are in reasonable agreement with those reported by Sindorf and Maciel[1] for silica gels used in chromatography. Widely varying numbers for T_{CP} have been reported, however, for various kinds of silicas by Pfleiderer et al.[18] and by Tuel et al.[19] Besides sample differences, there are several other possible systematic reasons for this variability such as the depencence of T_{CP} on the cross-polarization spectrum, resonance offset effects, and in the case of Tuel et al., the unjustified assumption that proton $T_{1\rho} \gg T_{CP}$.

There is also disparity among the proton $T_{1\rho}$ values reported in the literature, which in some cases appears to be associated with the degree of hydration of the gels. Again our results are more consistent with those of Sindorf and Maciel and agree with the indirectly measured $T_{1\rho}$ values we obtained using the methods in ref 16. It should be noted that for long proton $T_{1\rho}$ values the fit to the cross-polarization data is rather insensitive to $T_{1\rho}$. Thus $T_{1\rho}$s should be measured in separate experiments.

The third quantity extractable from fits to eq 1 is the relative composition of Q^n moieties. Table I shows, however, that there are significant differences between the results derived from CP and Bloch decay studies. We believe fits of cross-polarization dynamics to eq 1 measure the amount of Q^4 directly bonded to either Q^3 or Q^2. Given the r^{-6} dependence of the cross-polarization process, the assumption of such an "all-or-nothing" effect is reasonable. This assumption would place stringent constraints on molecular models of silica gel, and we are investigating this possibility in our laboratory.

B. Cross-Polarized Dynamics in PVOH–Silica and PVOD–Silica Composities. The CP and Bloch decay MAS spectra of the PVOH–silica composite are shown in parts c and d of Figure 1, respectively. As indicated in Table I, in the presence of PVOH the cross-polarization times for *all* Q^n are drastically reduced. In the absence of deuteration the protons closest to ^{29}Si are still the silanol OHs. The enhancement of the cross-polarization rate can be ascribed to at least two factors.

First, we have observed through indirect detection[17] that the proton second moment M_{2II} is increased in the composite (cf. Figure 3). The indirectly detected proton line width of the composite is ≈24 kHz compared to ≈2.5 kHz for the inorganic gel. The latter value is consistent with dipolar dephasing/CRAMPS work reported by Bronnimann et al.[20] for the non-hydrogen-bonded silanol groups. It is possible that the Hartmann–Hahn condition is not exactly matched (i.e., $\Delta\omega_{\text{eff}} \neq 0$) in the inorganic gel and the value of $J(\Delta\omega_{\text{eff}})$ increases as M_{2II} increases. We consider this factor of secondary importance.

The primary factor is an increase in the ^{1}H–^{29}Si dipolar coupling (and consequently the heteronuclear contribution to the second moment, M_{2IS}, which appears in eq 3). Evidence for such an increase is provided by the dipolar dephasing experiments[21] shown in Figure 4. While after

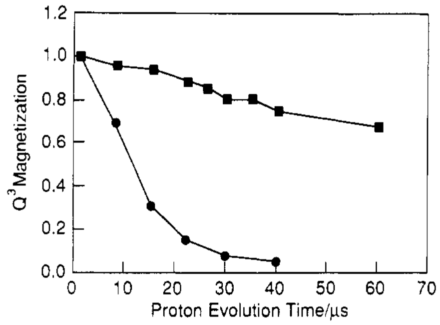

Figure 3. Comparison of indirectly detected proton FIDs using the pulse sequence of ref 17. Notice the much faster decay of proton magnetization in the PVOH–silica (1:1) composite.

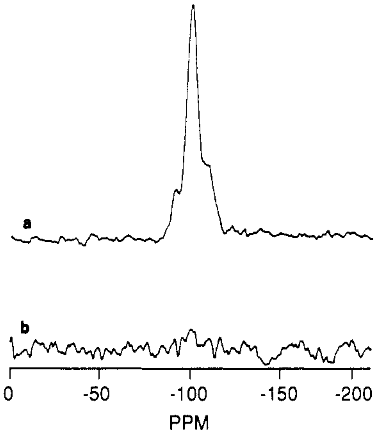

Figure 4. Dipolar dephasing after 25 μs of interrupted decoupling in silica (a) and the PVOH–silica (1:1) composite (b).

25 μs of the dipolar dephasing most of the ^{29}Si signal remains intact in the inorganic gel (Figure 4a), it has virtually vanished in the composite (Figure 4b). We ascribe this increase to an immobilization of the silanol protons by the absorption of PVOH on the silica surface. This interpretation implies that in the inorganic gel the silanol protons are mobile, perhaps exchanging between various chemical environments, and their dipolar coupling to ^{29}Si is attenuated.

Upon deuteration of all exchangeable protons, on both silanol as well as alcohol groups, the only protons remaining in the system are those of the $-CH_2-$ and $-CH-$ groups on the polymer backbone. As Figure 1e shows, it is possible to cross polarize ^{29}Si from these protons, albeit with less efficiency, as T_{CP} is now approximately equal to proton $T_{1\rho}$ (cf. Table I). A longer T_{CP} is of course consistent with the longer distance between the backbone protons and ^{29}Si. Furthermore, T_{CP} is equal for Q^3 and Q^4, as one might expect if the polymer backbone has an equal probability of being in the proximity of any silicon on the surface regardless of its functionality. This is not surprising since all oxygens in Si–O–Si bonds are expected to be good hydrogen bond acceptors. We postulate that hydrogen bonding is the driving mechanism for the interaction of PVOH with the silica gel surface.

The proton $T_{1\rho}$ of the composite in both its protonated and deuterated forms is considerably shorter than the one measured for the inorganic gel and reflects the $T_{1\rho}$ of the PVOH. The relative proportions of the Q^n moieties as obtained from the fits are not changed appreciably by the presence of the polymer. The same applies to the values obtained from the Bloch decay data (cf. Table I).

C. Interpretation of the Cross-Polarization Time Constant; Geometrical Constraints for Modeling. The proton line width and $T_{1\rho}$ of the composite imply that the silanol and PVOH protons form a tightly coupled spin system reflecting the line shape and relaxation behavior of the PVOH backbone. Observation of cross polarization from the polymer backbone to the silica gel surface in the PVOD–silica composites reinforces this conclusion. Stronger ^{1}H–^{29}Si dipolar interactions in the composite are also consistent with our multiple-contact cross-polarization results reported earlier.[22]

An interpretation of the relative T_{CP} rates in PVOH–silica and PVOD–silica composites along the lines of Klein Douwel et al.[9] can provide geometrical information about the polymer on the surface. We believe that a key feature of our experiments compared to previous such studies is the fact that $J_I(\Delta\omega_{eff})$ does not change upon deuteration. The proton second moment, M_{2II}, is determined primarily by the strongly dipolar coupled methylene and methine protons of the backbone. It is the dynamics of these protons that determine the dipolar fluctuation spectrum. Thus the ratio of cross-polarization times can be directly related to the ratio of second moments $(M_{2IS})_{PVOH}$–$(M_{2IS})_{PVOD}$. Following the approach of Klein Douwel et al.,[9] the sixth root of these ratios can be related to an average silicon–proton distance. For PVOH–silica the main source of cross polarization is the silanol and possibly alcohol protons, their *average* distance to ^{29}Si represented by $r_{Si\cdots HO}$. Similarly, in the deuterated composite the protons of interest are the backbone protons with an average distance $R_{Si\cdots HC}$. For Q^3 this ratio becomes

$$[(r_{Si\cdots HC})/(r_{Si\cdots HO})] = [(T_{CP})_{PVOD}/(T_{CP})_{PVOH}]^{1/6} = (4.3/0.6)^{1/6} \approx 1.4 \quad (4)$$

A similar calculation for Q^4 yields approximately 1.1. Distance ratios obtained in this manner can only be as good as the theory used to interpret cross-polarization times. While the expression for cross-polarization dynamics given by Demco and Waugh may contain certain approximations, the overwhelmingly dominant factor is an inverse sixth power dependence on internuclear distances. This dependence minimizes other sources of error or ambiguity. Nevertheless, our distance ratios should still be regarded as semiquantitative since the ratio of the second moments, which are infinite series, has been replaced by the ratio of the leading terms of those series. Also unlike solution 2D NMR techniques we are not measuring polarization transfer between two specific nuclei. A more accurate determination of internuclear distances in solids can be attained by the detection of heteronuclear dipolar couplings using REDOR techniques[23] and isotopically labeled materials. A quantitative interpretation of the second moment ratios must await molecular dynamics simulations, which, in addition to these distance constraints, should also incorporate the relative proportion of Q^n moieties and other structural data.[20,24] Such calculations are currently underway in our laboratory, and preliminary results confirm our findings.

5. Conclusions

In this paper we have introduced an approach based on judicious deuteration that allows the interpretation of cross-polarization dynamics in terms of internuclear distances with fewer assumptions than previous studies of this kind. Using our approach, we have obtained information about the proximity of the backbone of an adsorbed polymer chain to an inorganic surface. We plan to expand these studies to other polymers, particularly poly(methyl methacrylate), whose interaction with sol–gel silica appears to be dependent on the pH of the sol–gel reaction.

The information on silica surfaces obtained using techniques such as the one presented here may have wider implications, e.g., in the study of silicas and silica–aluminas that are used as catalyst supports. It may also be applicable to studying chemistry on surfaces other than silica, such as carbon fibers.

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Registry No. PVOH (homopolymer), 9002-89-5; TEOS (homopolymer), 118418-91-0; SiO_2, 7631-86-9.