PII S0730-725X(98)00064–2

● *Original Contribution*

NMR RELAXATION STUDIES OF POROUS SOL-GEL GLASSES

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^{2}H relaxation times T_1, $T_{1\rho}$ and T_2 for D_2O in silica sol-gels are used to monitor porosity and surface interactions within the silica framework as a function of aging. Tetramethoxysilane gels are compared with composites containing low levels of poly(vinyl alcohol) (PVA) prepared under acidic conditions. Non-exponential decay of magnetisation in $T_{1\rho}$ and T_2 experiments is attributed to the fractal nature of the pore structure. © 1998 Elsevier Science Inc.

Keywords: Sol-gel; Porous silica; ^{2}H NMR; Relaxation times; Fractal geometry.

INTRODUCTION

The sol-gel process for making glasses has a number of inherent advantages. The ability to form the glasses from homogeneous solution at room temperature means that the composition can be easily controlled, organic templates and modifiers can be used and materials can be doped with temperature sensitive reagents.[1,2] The microstructure of silica sol-gels formed by hydrolysis of tetraalkoxysilanes, $Si(OR)_4$, depends significantly on the reaction conditions, including pH and solvent composition.[1] After the initial hydrolysis and gelation, aging and drying follow more slowly until a condensed glass is formed. In this paper, we use ^{2}H nuclear magnetic resonance (NMR) relaxation studies to monitor the evolution of the pore structure of silica gels as a function of aging. Gels are prepared by hydrolysis of $Si(OCH_3)_4$ (TMOS) under acidic conditions and modified with hydrophilic polymer additives.

The NMR relaxation properties of liquids confined within porous materials have been the subject of extensive experimental and theoretical investigations. The relationship between porosity and relaxation is complex, depending as it does on a combination of surface interaction and geometrical confinement effects as well as sample heterogeneity.[3–7] The NMR properties of liquids in rocks and other naturally occurring materials can also be complicated by the presence of paramagnetic impurities at pore boundaries which further enhances relaxation.[8]

NMR experiments on liquids in porous silica glasses have formed the basis of a number of studies aimed at elucidating the factors determining relaxation rates.[4,9] Spin-lattice relaxation times, T_1, depend strongly on surface interactions between the liquid and the silanol groups in the pore walls.[4,5] However, spin-spin relaxation, T_2, and spin-lattice relaxation in the rotating frame, $T_{1\rho}$, are dominated by the effects of confinement in small volumes.[6,7] For polar liquids with strong surface interactions in silica, assuming a two-phase fast exchange model, $T_2 < T_{1\rho} \ll T_1$ and the spin-lattice relaxation rate $1/T_1$ has a $1/r$ dependence on the pore radius, r.

Experiments

The TMOS gels were prepared by mixing $Si(OCH_3)_4$, 1.25 mL, water 1.15 mL and methanol 1.25 mL. 0.25 mL of $1.0.10^{-3}$ M NaOH solution was added to adjust the pH to 5.8–6. Cetyltrimethylammonium bromide, 0.25 mL, $8.2.10^{-2}$ M in methanol, was then added. The homogeneous solutions were divided into four sample tubes and left to stand at room temperature to produce monolithic glasses. TMOS-poly(vinyl alcohol) (PVA) gels were prepared by adding PVA solution (average M_W 13,000–23,000) to the homogeneous TMOS gel mixture prepared as described above. 0.30 mL of PVA (0.50 g in 5.0 mL

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Table 1. Relaxation times (ms) for TMOS gels (pH 5.8) and TMOS:PVA gels (pH 1.6) as a function of aging time. Dual exponential fits are shown for some $T_{1\rho}$ and T_2 experiments.

TMOS

Age (day)	T_1	$T_{1\rho}$ short	$T_{1\rho}$ long	T_2 short	T_2 long
2	304	5.6	9.0	4.8	8.8
7	189	1.3	2.0	1.35	2.6
14	90	0.55	0.93	0.59	2.6
28	72		0.65		0.56

TMOS:PVA

Age (day)	T_1	$T_{1\rho}$ short	$T_{1\rho}$ long	T_2 short	T_2 long
3.5	232	3.9	13.7	3.0	27
7	176	3.2	4.2	2.8	20
14	64		1.8		1.4
28	39		1.1		0.91

Fig. 1. Temperature dependence of T_1, for D_2O (□) and TMOS [2 day (◆)] and TMOS-PVA [3.5 day (○), 7 day (●)] gels

of 0.40 M HCl) was added to the TMOS solution, giving 5.3 mol % PVA. 0.5 mL of 5% w/w glutaraldehyde was then added as a cross-linking agent for the PVA.

Gels were deuterated by soaking in D_2O (1 mL x 2) for at least 24 h before the NMR measurements. ^{2}H NMR spectra were recorded at 76.67 MHz on a Bruker DMX500 spectrometer. T_1 and T_2 were acquired using the inversion recovery and Carr–Purcell–Meiboom–Gill pulse sequences, respectively. $T_{1\rho}$ was measured by applying a 90° pulse followed by a 90° phase-shifted spin-locking pulse of variable duration τ.

RESULTS AND DISCUSSION

Silica sol-gels formed from TMOS at pH 5.8 and TMOS modified by crosslinked PVA at pH 1.6, were allowed to age for periods of 2–28 days at room temperature. The gels were then rehydrated in D_2O, which causes deuteration of exchangeable -OH groups. This also removes excess acid and stops further condensation from occurring.[10] ^{2}H NMR relaxation measurements were then carried out on the D_2O phase within the gels (Table 1). For comparison, the relaxation times for bulk D_2O are $T_1 = T_{1\rho} = T_2 = 485 \pm 2$ ms.

A single spin-lattice relaxation value, T_1, is found for each sample, consistent with rapid exchange of ^{2}H between D_2O and -OD sites and fast diffusion of D_2O from the bulk liquid to the silica pore surfaces. The T_1 values for D_2O in the gels are systematically lower compared to bulk D_2O and show a consistent decrease as a function of gel aging. This reflects the reduced mobility of the solvent within the pores of the gels and the degree of surface
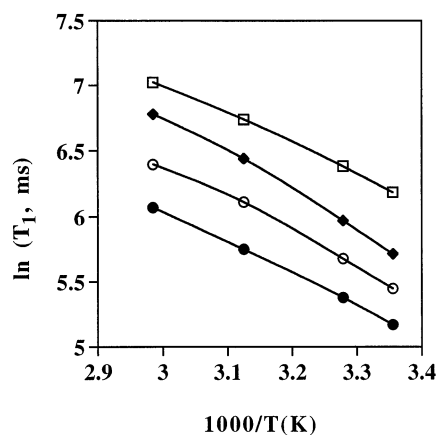
interaction with the pore walls, including exchange with strongly immobilised surface silanol groups. Comparing the two types of gel at long aging times, T_1 for TMOS gel is longer than that for TMOS-PVA. This difference cannot simply be due to differences in pore size, but must also involve the difference in the pore surfaces, the greater concentration of silanol groups in the acidic gel, combined with the presence of PVA enhancing the rate of spin-lattice relaxation.

A regular increase in T_1 as a function of temperature is observed for all gels, providing further evidence that the liquid phase is in the fast motion regime even in the most condensed materials. The temperature dependence of T_1 (Fig. 1) for D_2O and a series of gels follows parallel trends for all samples.

Results of $T_{1\rho}$ and T_2 relaxation experiments show two major differences compared to T_1. Firstly, these relaxation times are almost two orders of magnitude smaller than the spin-lattice relaxation times T_1. This is characteristic of liquids in confined pores of diameters approaching molecular dimensions as explained earlier. So even at the early stages of gelation where T_1 values are still relatively long, the short values for $T_{1\rho}$ and T_2 reveal the effects of liquid confinement in layers next to the pore walls. Secondly, in many samples, magnetization decays cannot be fitted by single exponentials, particularly for younger gels and at higher temperatures. Dual exponential fits were therefore carried out on these samples to see whether the results were physically reasonable. Table 2 shows a detailed data set for a 3.5 day TMOS-PVA gel, though similar non-exponential behaviour is found for other samples. Two relaxation times are derived which are denoted "short" and "long." Both the relaxation times themselves and their relative contributions to the magnetization decay plots are consistent for $T_{1\rho}$ and T_2 experiments giving confidence that the non-expo-

Table 2. Dual exponential decays for $T_{1\rho}$ and T_2, in a 3.5 day TMOS-PVA gel. Relaxation times in ms.

T (K)	$T_{1\rho}$ short	$T_{1\rho}$ long	% short ($T_{1\rho}$)	T_2 short	T_2 long	% short (T_2)
298	3.9	14	95	3.0	27	98
305	3.5	54	93	2.8	70	93
320	2.5	176	75	2.0	198	76
335	1.9	192	67	1.7	172	68

nential behaviour is not simply an artefact. The contribution of the long component to the relaxation decreases in older gels and is no longer present in the most highly condensed samples (Table 1). The temperature dependences of the short and long components are quite different (Fig. 2). The long relaxation time shows an increase in $T_{1\rho}$ and T_2 with temperature, behaviour characteristic of a bulk liquid phase. Conversely, the short components consistently decrease with temperature, for both $T_{1\rho}$ and T_2.

These non-exponential magnetization decays cannot be attributed to macroscopic sample heterogeneity or to slow diffusion since the spin-lattice relaxation results show well-behaved fast diffusion behaviour. The impact of surface irregularity on magnetization decay in irregular pores has been modelled using fractal descriptions of the surface geometry.[3,7] For fractal pores of diameter L, having a smaller cutoff dimension ℓ in "offshoots" to the main pores, non-exponential decay occurs in the finite surface relaxation regime.[7] Defining Λ as $D/(a \mu_s)$, where D is the diffusion coefficient of the bulk liquid, a is the monolayer thickness at the surface and μ_s represents a uniform surface relaxation rate, this regime occurs when $\ell < \Lambda < \ell(L/\ell)^{(D^{f-1})}$. In this situation, liquid in narrow offshoots undergoes rapid surface relaxation, while liquid from the bulk of the pore must first diffuse
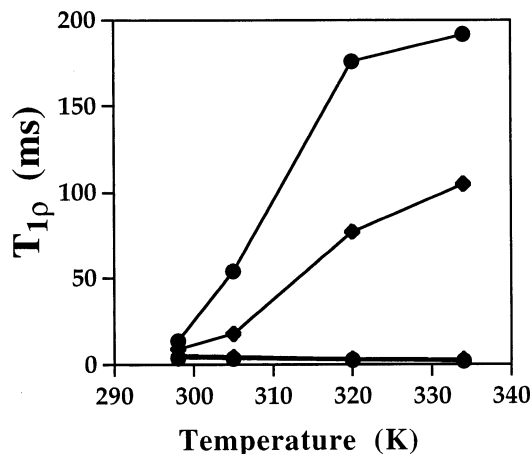

Fig. 2. Temperature dependence of the short and long contributions to $T_{1\rho}$, for TMOS [2 day (◆)] and TMOS-PVA [3.5 day (●)] gels.

to the surface. Thus although diffusion may be fast, the surface irregularity leads to non-exponential decay of magnetization. Silica gel pores are highly irregular and fractal dimensions have been reported for several types of porous silica.[11] Thus we propose that the ^2H relaxation results presented here are consistent with finite surface relaxation behaviour. Confinement effects introduce a rapid relaxation component to the decay of $T_{1\rho}$ and T_2 magnetizations. In the early stages of gelation, a separate bulk relaxation can be identified. As the gels age and condense, an increasing fraction of the pore liquid is surface confined and eventually a contribution from the pore bulk is no longer resolved.

CONCLUSIONS

The gelation and aging which occur during silica sol-gel processing can be followed by ^2H NMR relaxation measurements on sorbed D_2O. Relaxation times are typical for liquids in confined geometries having $T_2 < T_{1\rho} \ll T_1$. Non-exponential magnetisation decays observed in $T_{1\rho}$ and T_2 experiments are attributed to the fractal nature of the silica pore geometries.

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