An easy way to prepare pressurized glass inserts for MAS rotors

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Abstract

A novel technique to prepare pressurized glass insert samples for MAS rotors is described. In this technique, a small drop of epoxy is added to the tip of a piston and the gas is squeezed into the insert by pressing the piston. The amount of gas, i.e., pressure, in the sample can be controlled by the overall length of an insert test tube. As examples, ^{129}Xe NMR spectra taken from samples containing xenon gas, xenon gas and liquid crystal, and xenon gas, liquid crystal and porous solid, are shown. In principle, the method is feasible for making any kind of samples into glass inserts.
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1. Introduction

Recording of CP/MAS NMR spectra from air-sensitive samples, liquids or gels has, in the past, required flame-sealing of glass rotors or rotor inserts [1,2] or machining a Kel-F insert in which a machined cap is heat fused to the insert bottom [3]. There are many disadvantages to flame-sealing of glass inserts containing gas, liquid or even solid material. In most cases, the glass cell has to be immersed in liquid nitrogen and this may lead to the destruction of some of the materials (for example, biological tissues). Then the melting position of the insert is very close to the surface of the liquid nitrogen. Moreover, some loss in sample amount is frequently encountered because of the proximity of heat source to the sample, and this may cause the true composition of a sample to remain unknown. In addition, heat-sensitive liquids, such as liquid crystals, may be devastated in the heat sealing process. Also, the asymmetry of a glass rotor or insert causes difficulties during spinning. On the other hand, the Kel-F inserts are difficult to machine and sealing them using a hot rod while applying slight pressure on the insert cap may be imperfect. There are, however-

er, special rotors with O-ring seals that have been made available for CP/MAS experiments with air-sensitive or gelatinous samples (Wilmad Glass Co.).

Giammatteo et al. [4] reported an epoxy sealant that can be applied to a variety of rotor designs. They used a small drop of epoxy applied to the narrowing part of a Pyrex rotor insert to seal the sample. This kind of sealing can even be performed in the nitrogen atmosphere of a glove box, and thus it is ideal, for example, for air-sensitive solids. In addition it forms a symmetrical seal. In this paper, we proceed one step further and present an easy method for preparing pressurized MAS rotor insert samples. In the method a probe gas, in the present case xenon, which is heavier than air, is pressed into the insert by a piston with a small drop of epoxy in the tip. After the epoxy is set and dried to the narrowing, the insert is cut at the narrowing with a diamond file and refined symmetrically. The final pressure in the sample is proportional to the overall length of the insert test tube. It is also possible to prepare over pressurized samples that contain, for example, some fragile solvent or gel. We used ^{129}Xe enriched xenon gas as a probe to investigate pressure inside the samples. This is possible because the chemical shift of ^{129}Xe gas is known to be extremely sensitive to pressure [5,6]. ^{129}Xe NMR was also used in testing samples including liquid crystal, and

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liquid crystal and porous solid. This novel method makes feasible the enlargement of the armory of samples which can be studied using CP/MAS NMR.

2. Experimental section

In this study, we prepared altogether four samples of Pyrex MAS rotor inserts (Product No. DWGSK2356, Wilmad Glass Co. and Cat. No. NE-5010, New Era Enterprises Inc.). Two samples were prepared that contained only enriched ^{129}Xe gas. Enrichment of the gas was 99.95% and it was supplied by Chemgas (France). One sample contained ^{129}Xe gas and liquid crystal (LC) Phase 4 (N4), eutectic mixture of p-methoxy-p'-butylazoxybenzenes, obtained from Merck (Darmstadt, Germany) and one sample was made of xenon gas ^{129}Xe, LC Phase 4 and porous material Controlled Pore Glass 538 (CPG 538), obtained from CPG Inc. (Billerica, Massachusetts, USA). The mean pore diameter of the material is 538 Å, and according to the manufacturer about 80% of the pores have a diameter within ±9% of the mean pore diameter.

The preparation of the gas samples was started by fastening the insert tube to the vacuum line and removing gaseous impurities by pumping. After that, enriched ^{129}Xe gas was added. Next, the tube was carefully and slowly unfastened from the vacuum line. A small drop of epoxy resin (Super Epoxy, Henkel) was added to the tip and bluffs of the PVC (polyvinyl chloride) cylindrical piston of which

the outer diameter was the same as the inner diameter of the insert tube, and the gas was squeezed into the MAS rotor insert by pressing the piston down (see Fig. 1). The piston was kept pressed down until the epoxy resin hardened, which took about 10–15 min. Thereafter the sample was placed into an oven where its temperature durability was tested at ~90 °C. Finally, the sealed insert was cut from the narrowing with a diamond file and smoothed symmetrically. The final length of the insert was about 14 mm.

The pressure of the sample can be controlled by the overall length of the MAS rotor insert, h_2, because after the tube is unfastened from the over pressurized line, the gas pressure inside the tube becomes equal to the air pressure, p_a. Therefore, the gas pressure in the sample is roughly $(h_2/h_1)p_a$, where h_1 is the length of free space in the insert (see Fig. 1). The original overall length of the used MAS rotor inserts is 68 mm, and consequently, the maximum theoretical gas pressure in the sample that can be obtained using the above described procedure is about 7.6 atm. The maximum pressure, P_{max}, that the tube can take depends on the surface quality differences, wall thickness D and outer diameter d of the tube according to equation: $P_{max} = DK(t)/d$, where $K(t)$ is the tensile strength of the glass material. For the used Pyrex MAS rotor inserts $D = 0.51$ mm, $d = 5.59$ mm, and $K(t) = 2000$ p.s.i. (140.6 kg/cm^2) and the maximum pressure that the tube withstands is about 12.4 atm (Wilmad Glass Co.). The
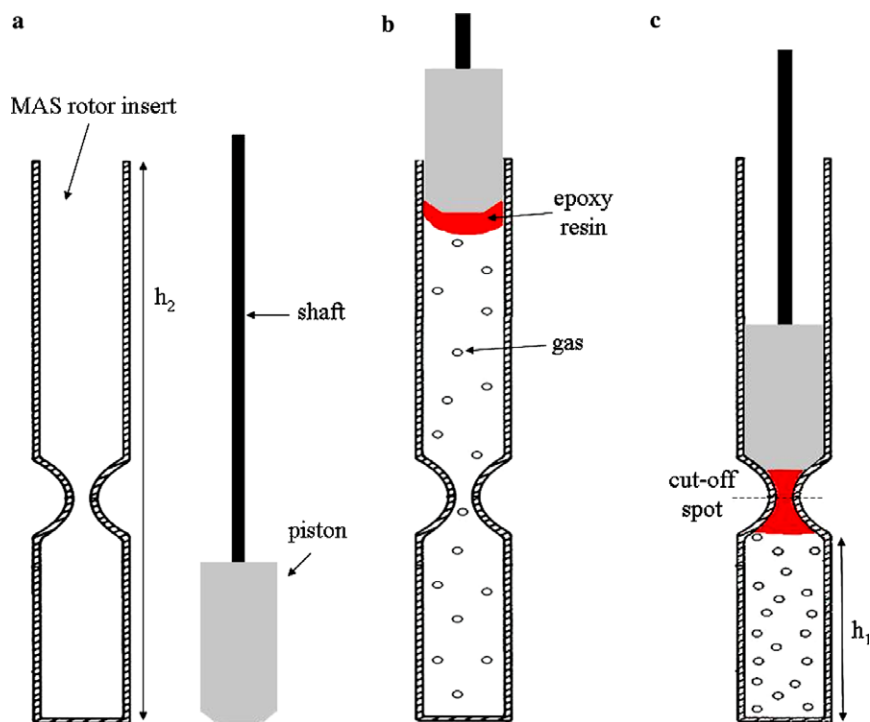

Fig. 1. Preparation method for pressurized MAS rotor insert samples. (a) MAS rotor insert glass tube and a cylindrical piston. The outer diameter of the piston is the same as the inner diameter of the glass tube. (b) The preparation starts by adding a small drop of epoxy resin to the tip and bluffs of the piston. The piston is then placed on the mouth of the insert containing the gas to be studied or used as a spy. (c) The piston is pressed to the bottom and kept there until the epoxy dries. After that the insert is cut off as shown in the picture. The pressure inside the insert is roughly proportional to h_2/h_1.

overall length of the insert tube, h_2, was 68 mm in the sample that contained only enriched [129]Xe gas. In the rest of the samples, tubes were cut shorter so that the overall length was about 40 mm. After the epoxy dried the length h_1 was about 9 mm in each sample. Liquid crystal was placed in the insert with a syringe or a pipette. The sample that contained porous material and LC was tamped through the narrowing using a thin wire and it was held in an oven in an isotropic phase for about an hour before adding xenon so that the LC could properly penetrate into the pores.

The one-dimensional [129]Xe NMR test experiments were performed on a Bruker Avance DPX400 spectrometer (resonance frequency 110.678 MHz for [129]Xe) using a 10 mm high-resolution BBO-probehead. An insert (outer diameter 5.59 mm) was placed inside a medium or thin walled 10 mm NMR sample tube and this construction was transferred into the magnet. Consequently, the symmetry axis of the insert was not parallel with the applied magnetic field, B_0, which caused line broadening in the spectra. Gas samples were recorded at room temperature applying a 17° pulse flip angle, 3 s repetition time and accumulating 1k scans. The sample containing LC and xenon gas was measured at a temperature of 315 K. The number of accumulated scans was 128k, a pulse flip angle of 17° and repetition time 1 s. The actual sample temperature was determined with the aid of the ^{1}H NMR spectrum of a standard temperature calibration sample (80% ethylene glycol in DMSO-D$_6$) [7]. The [129]Xe chemical shift was measured relative to the signal of bulk xenon gas (6.16 atm) in a 10 mm NMR sample tube.

[129]Xe MAS NMR measurements from the xenon gas dissolved in the LC Phase 4 confined to pores were performed on a Bruker Avance DSX300 spectrometer ([129]Xe frequency 83.028 MHz) at room temperature using a Bruker high-temperature probe. The rotation frequency of a 7 mm rotor with the inserted sealed glass tube was 700 Hz. The FIDs were recorded with 30° preparation pulses of 2.08 μs duration and 5 s recycle delay, and 4k scans were accumulated. For a non-spinning [129]Xe NMR spectrum, 24k scans were accumulated.

3. Results and discussion

Fig. 2 displays the [129]Xe NMR spectra of the two samples containing exclusively xenon gas. The spectra were measured at room temperature on the day when they were prepared and after the samples were aged 21 days. The reference has been corrected to correspond to the chemical shift of zero pressure gas by using the virial expansion for the dependence of chemical shift of xenon gas on density [8]

$$\delta(\rho, T) = \delta_0 + \delta_1(T)\rho + \delta_2(T)\rho^2 + \delta_3(T)\rho^3, \tag{1}$$

where δ_0 is the chemical shift in vacuo and ρ is the density in amagats. Temperature dependent virial coefficients δ_i ($i = 1, 2, 3$) arise from two-, three- and four-body interactions. The chemical shifts of the resonance signals of xenon correspond to the initial pressures of 6.46 ± 0.04 atm and 2.72 ± 0.04 atm in the inserts of which the overall lengths were originally 68 mm and 40 mm, respectively. A simple model calculation with the aid of the lengths h_1 and h_2 and air pressure leads to the pressures of 7.56 atm and 4.44 atm for the 68 mm and 40 mm length test tubes, respectively. These are somewhat larger than the actual pressures. The reason for these differences is most likely a slight leakage from the piston. After three weeks from the sample preparation and first experiments, the chemical shift of xenon had decreased to some extent which is a consequence of the small leakage in the epoxy plug. However, the overall leakage is pretty slow and insignificant during the experimental time.

Fig. 3 shows the [129]Xe NMR spectrum from the sample that contained LC Phase 4 and xenon gas. This is an indication that it is possible to make glass insert samples that contain heat-sensitive solvents and probe gas using the method described above. The conventional flame-sealing method would have most likely destroyed the liquid crystal.

Fig. 4 displays the fourth example. It shows the static and 700 Hz [129]Xe MAS NMR spectra at room temperature from a glass insert put inside a 7-mm MAS rotor containing xenon gas, LC Phase 4 and porous CPG 538. The resonance signal of xenon near 10 ppm originates from the xenon gas bubble
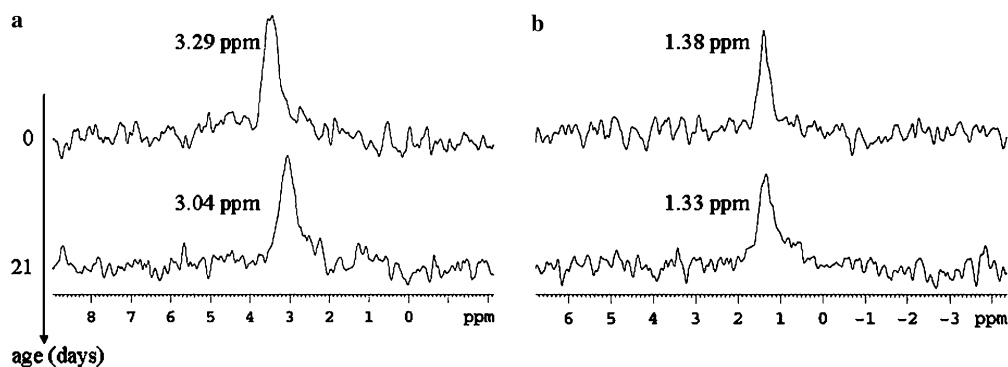

Fig. 2. The [129]Xe NMR spectra of the two samples containing xenon gas measured at room temperature on the day of sample preparation (upper spectra) and three weeks after (lower spectra). The chemical shifts have been corrected to correspond to the chemical shift of zero pressure of an external xenon gas reference sample. The overall length of the test tube, h_2, was 64 mm in (a) and 40 mm in (b). The positions of the signals were obtained by fitting a Gaussian/Lorentzian line shape function to the spectra.
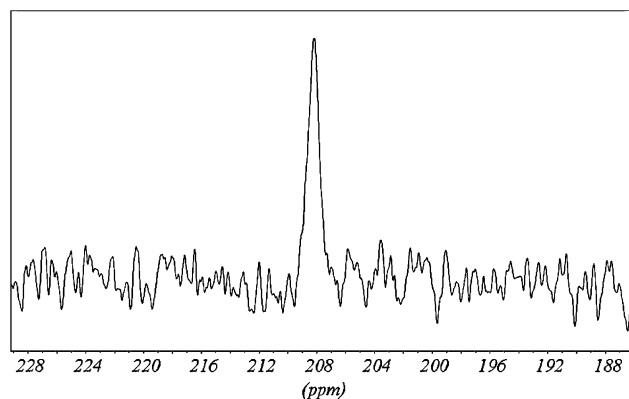
Fig. 3. The ^{129}Xe NMR spectrum of the sample containing xenon gas and LC Phase 4 measured at 315 K where the liquid crystal is in the nematic phase.
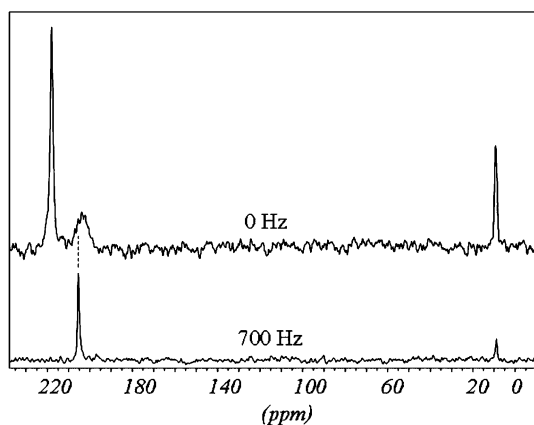

Fig. 4. Static (upper) and 700 Hz ^{129}Xe NMR MAS (lower) spectra from the xenon gas dissolved in the LC Phase 4 confined to CPG 538 porous material measured at room temperature. The number of accumulated scans was 24k in the upper spectrum and 4k in the lower one. For the assignment of the resonances, see text.

in the sample. The broad resonance in the upper spectrum arises from xenon in the LC confined in the pores of CPG 538 whereas the peak at the highest chemical shift stems from xenon in the LC in between the solid particles of CPG 538. In the lower spectrum, the two last mentioned resonances average to the same chemical shift as a consequence of the MAS. The ^{129}Xe chemical shift of xenon in a bulk LC can be written as $\delta^{exp} = \delta^{iso} + \delta^{aniso}$, where the latter term arises from the anisotropy of the shielding tensor. The anisotropic shielding tensor is a consequence of the deformation of the originally spherical electron cloud distribution of xenon by anisotropic forces acting in liquid-crystalline phases. The broader signal in Fig. 4 at about 205 ppm is a CSA powder pattern with the same δ^{iso} as in the preceding case. The powder pattern stems from the isotropic orientation distribution of the channel axes in CPG 538 and the anchoring effect which forces the LC molecules to orient along the channel axes. Thus MAS averages the anisotropic contribution out and the two resonances in the upper spectrum of Fig. 4 overlap. The spectra

are a part of another research project [9] and will be discussed in a future paper. The shown 700 Hz ^{129}Xe MAS NMR spectrum is, however, evidence supporting the idea that it is possible to prepare MAS rotor insert samples that contain probe gas, liquid, and solid material and that the insert is well-balanced, making MAS experiments conceivable. The possibility to easily prepare new kinds of samples now enables the study of a whole new gamut of substances by MAS NMR spectroscopy.

4. Conclusion

A new method of preparing pressurized MAS rotor glass insert samples is described. The method is very simple: the gas under investigation or used as a probe is squeezed into the insert by a piston with a small drop of epoxy on top of it. After the epoxy has dried, the insert is cut from the narrowing. The amount of gas in the insert can be controlled by the overall length of test tube. Samples which contain fragile or heat-sensitive liquids or solid materials and probe gas and used to be very difficult or even impossible to make are now easily prepared.

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