

# A Simple Method for $^{13}\text{C}$ CPMAS NMR Measurements under High Gas Pressures

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Magic angle spinning (MAS) NMR is a widely used and very powerful means for studies of static and dynamic structures of solid materials (1). To our knowledge, however, MAS NMR has not been performed under high pressure. In this Communication, we present a simple method for high-pressure MAS (HPMAS) by which pressure at least up to 7 MPa can be applied, and we show the  $^{13}\text{C}$  CPMAS NMR spectra observed for polystyrene (PS) under Xe or  $\text{CO}_2$  gas pressure.

HPMAS was performed as follows: a sealed Pyrex glass tube with an inner pressure of 3–7 MPa was introduced into a Chemagnetics 7.5 mm MAS spinner with an inner diameter of 5.9 mm. The outer diameter of the glass tube is  $5.85 + 0.05$  mm, which is well fitted to the inside wall of the spinner. The pressure limit  $P_{\text{max}}$  of the tube is estimated from the formula (2)

$$P_{\text{max}} = \frac{r^2 - 1}{r^2 + 1} \sigma, \quad [1]$$

where  $\sigma$  is the tensile strength, and  $r$  is the ratio of the outer diameter to the inner diameter. The value of  $\sigma$  is approximately 350–850  $\text{kg}/\text{cm}^2$  for most Pyrex glass. According to this formula, the inner diameter of 3.9 mm may be used to achieve  $P_{\text{max}} = 7$  MPa for the minimum value of  $\sigma = 350$   $\text{kg}/\text{cm}^2$ . Since there are various other unquantifiable characteristics of glass which may limit the performance at high pressure, we have adopted the inner diameter of 3.4 mm.

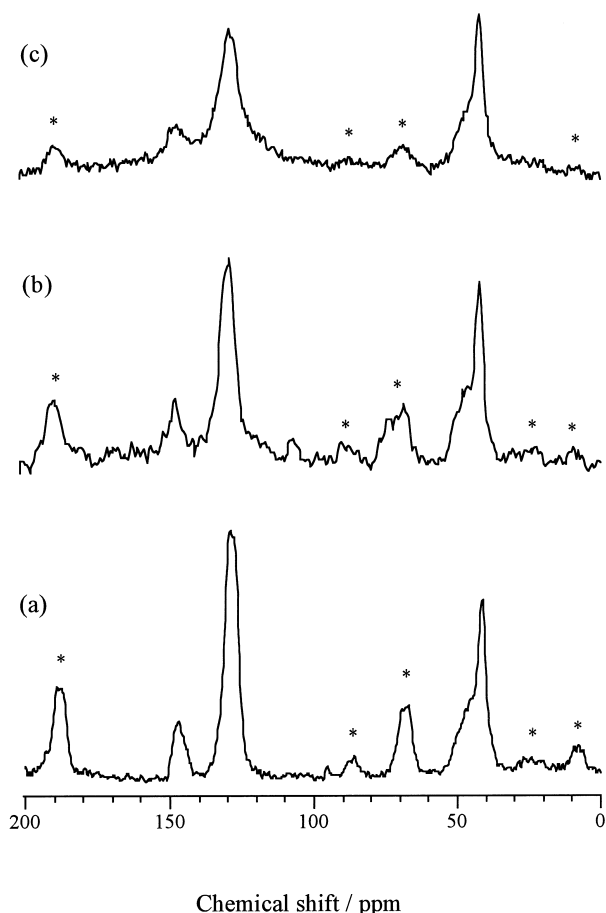
The top of the glass tube was constricted to an outer diameter of about 2 mm for sealing. The distance from the center of the constriction to the bottom is about 18 mm, and the capacity of the tube was measured to be 0.10 ml. After annealing the tube to remove strain, we introduced 30–40 mg of PS ( $M_w = 2500$ ) into the glass tube. The glass tube was attached to a vacuum line and degassed for several hours. Then the  $\text{CO}_2$  or Xe gas with the volume to

give a required pressure was transferred into the glass tube whose bottom was immersed in a liquid  $\text{N}_2$  bath. The glass tube was sealed, removed from the liquid  $\text{N}_2$  bath, and left over 12 h at room temperature. The error in estimation of gas pressure which originated from an error in measuring the capacity around the sealing point is small, because the capacity around the sealing point is very small. We coated the sealed point with adhesive to reinforce the sealing point and also to balance the glass tube. To further balance the MAS spinner containing the glass tube, we packed powdered glass or KBr into a MAS spinner with the sealed glass tube. Most of the MAS spinners containing the glass tube could be spun at a frequency of 4.5 kHz. Although we have adopted a somewhat large margin for the inner diameter, some glass tubes burst during measurements of NMR spectra. Since the volume of the tube is small, however, the bursting of the glass tube caused no serious damage to the NMR probe.

Figures 1a, 1b, and 1c show the  $^{13}\text{C}$  CPMAS NMR spectra of PS under atmospheric pressure, a Xe gas pressure of 3 MPa, and a  $\text{CO}_2$  gas pressure of 7 MPa, respectively. The signal around 40 ppm is the overlapped signal of the methine and methylene carbons. Those at 128 and 146 ppm are assigned to the protonated and nonprotonated aromatic signals, respectively. It is worth noting that the relative peak heights of the aromatic carbon signals decrease under a  $\text{CO}_2$  gas pressure of 7 MPa (Fig. 1c). Similar reduction is observed also under a Xe gas pressure of 3 MPa (Fig. 1b). The reduction of the peak height of the aromatic carbon is attributed to inefficient CP enhancement due to short spin–lattice relaxation times ( $T_{1\rho}$ ) in the rotating frame and also to the line broadening of the aromatic carbons. The decrease of  $T_{1\rho}$  values under high gas pressures will be reported in detail in a forthcoming paper.

Under a  $\text{CO}_2$  gas pressure of 7 MPa, the linewidth of the protonated aromatic carbon is evidently broadened, and the area intensity ratios of the individual spinning sidebands to the centerband are smaller than those under atmospheric

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**FIG. 1.**  $^{13}\text{C}$  CPMAS NMR spectra of polystyrene under (a) atmospheric pressure, (b) a Xe gas pressure of 3 MPa, and (c) a  $\text{CO}_2$  gas pressure of 7 MPa. The contact time is 1.0 ms in (a) and (b), and 0.5 ms in (c), and the MAS spinning frequency is 4.5 kHz. The peaks marked with an asterisk are spinning sidebands of the aromatic signals. The spectra were observed at 35°C with a Chemagnetics CMX 300 spectrometer operating at 300.5 MHz for  $^1\text{H}$ .

pressure. The observed line broadening is brought about by the interference between molecular motion and the artificial narrowing due to MAS or  $^1\text{H}$  decoupling (3, 4). The de-

crease of the sideband intensities indicates that the chemical-shift anisotropy for the aromatic carbon is reduced by molecular motion. These results indicate that the molecular motion of PS is enhanced by application of high  $\text{CO}_2$  or Xe gas pressure.

In general, a gas used as a pressure medium has two opposite effects on solid polymers. Gas molecules can dissolve in polymers and increase the interchain distances (5) (a plasticization effect), so that mobility of polymers increases. Simultaneously, they give pressure to polymers as a pressure medium, so that mobility is restricted. These competing effects control the molecular dynamics of polymers under high gas pressure (6). Therefore, the observation of the motional enhancement in PS means that the plasticization effect surpasses the other under the present gas pressures. Details of the structure and molecular motion of PS plasticized by a  $\text{CO}_2$  gas will be published elsewhere.

In this Communication, we proposed a simple HPMAS method. It opens a variety of applications, such as studies of polymer dynamics under high pressure.

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