Magic Angle Spinning ^1H NMR Imaging of Polybutadiene/Polystyrene Blends

D. G. Cory,† J. C. de Boer, and W. S. Veeman*

Laboratory of Physical Chemistry II, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands. *Received May 19, 1988; Revised Manuscript Received August 17, 1988*

ABSTRACT: A simple method of obtaining ^1H NMR images of solids is introduced which relies on magic angle spinning for line narrowing. The spatial resolution of the method is less than 50 μm. The method is insensitive to many instrumental artifacts and only requires slight modifications of commerical equipment. Images are shown of a dynamically stressed polyisoprene phantom and of polybutadiene in two polybutadiene/polystyrene blends.

Introduction

^1H NMR imaging of solids has developed to a point where it may find application in polymer science. In general, an image of a material is obtained by acquiring its NMR spectrum in the presence of a large magnetic field gradient. Since the resonance frequency is directly proportional to the field strength, the gradient encodes the spatial location of each spin packet in the sample. Provided that the gradient-induced shift in the resonance frequency may be separated from other influences (i.e., chemical shifts and dipolar broadening), a 1-dimensional (1D) image of a sample is obtained. Two- and three-dimensional images are acquired by extensions of this approach (see ref 1-3 for reviews of imaging as applied to liquids).

NMR imaging is widely and successfully employed in medical science,[1,2] primarily to locate water in large objects. The methods used in medical imaging, however, are not directly applicable to imaging of solid materials due to the different NMR properties of the compounds being investigated. The compounds of interest in materials imaging generally have more than one inequivalent proton and their NMR spectrum is often greatly broadened by homonuclear dipolar interactions and chemical shift anisotropies (CSA). Two approaches may be taken to separate these interactions from that of the applied gradient field: sufficiently large gradient fields may be used such that the chemical shift and dipolar broadening are small compared to the effects of the gradient,[4] or line narrowing schemes may be employed to average or reduce these unwanted interactions.[5-10]

The use of large field gradients greatly reduces the sensitivity of an already insensitive technique since the signal-to-noise ratio of an NMR spectrum is inversely proportional to the square root of the bandwidth of the receiver, and large field gradients lead to correspondingly large spectral widths. Most proposed methods of solids imaging therefore rely on line narrowing. Line narrowing has generally consisted of multiple pulse coherent averaging (MP),[5,6] magic angle sample spinning (MAS),[7] or a combination of the two (CRAMPS).[8] For very rigid materials where the dipolar broadening has its full width (up to 100 kHz), MP methods are the only widely useful technique of line narrowing, but in many cases MAS alone significantly narrows the NMR resonance. Moreover, we have shown[9] that the application of MP severely limits the resolution of an image due to the narrow frequency range over which MP sequences perform uniformly. As MP sequences are applied further and further off resonance, such as by increasing the field gradient in an imaging experiment, the line width of the resonance and the scaling factor of the sequence may change. MP methods average undesired interactions by toggling them between various states,[11] the time average of which is zero, desired interactions may also be partially averaged by this process, and this is described by a scaling factor. To obtain an image from a MP spectrum in a straightforward manner, the scaling factor and residual line width should be independent of offset frequency. In practice this limits the strength of the gradient field such that the spectrum width is restricted to a few kilohertz. Combined with a residual line width of about 1 ppm, this results in only about 20-50 observable volume elements across a sample. One may still make these elements quite small by studying correspondingly small samples, but it is preferable to obtain images with a finer grain.

The result is that where MAS narrows the resonance, it is preferred to MP averaging. MAS spinning rates of up to 23 kHz[12] are achievable today, which are sufficient to average dipolar interactions in many systems. Even where MP methods must be employed, it is still worthwhile to include MAS. This averages the anisotropic contributions to the chemical shift as well as the dipolar interactions and allows selective imaging based on the isotropic chemical shift.

Once the dipolar and CSA broadening have been eliminated, there remain the isotropic chemical shifts. If ignored they may lead to artifacts in the image, depending on the number of resonances and the type of image reconstruction used. These are comparably simple to eliminate, and three means have been demonstrated for imaging of solids. By always acquiring the data points at a fixed time following a preparation pulse, and incrementing the strength of the field gradient between acquisitions, only evolution due to the gradient is observed in a constant time phase encoding scheme.[13] Alternately the isotropic chemical shift may be refocused by applying 180° pulses and inverting the field gradient at the refocusing pulse. In this refocused gradient scheme,[14] the evolution from only the gradient is mapped out by sampling the maximums of spin echoes in a oscillating field. A third method[15] obtains an image by deconvoluting the gradient broadened spectrum with the spectrum acquired in the absence of a field gradient.

Along with choosing the appropriate line narrowing scheme, the type of image reconstruction must also be considered. Back projection (BP) or two-dimensional Fourier imaging (2DFI) are most commonly used. BP methods are more sensitive,[1] however, and often simpler

* To whom correspondence should be addressed.
† Present address: Code 6120, Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5000.

0024-9297/89/2222-1618$01.50/0

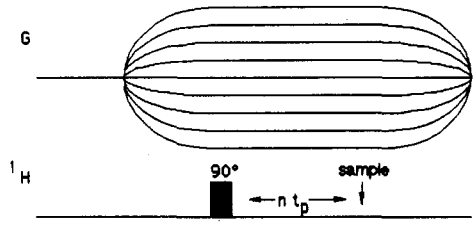

Figure 1. Diagram of the experiment used to obtain the images in Figures 2–4. In this experiment, the fids are mapped out one point at a time. First, the gradient is turned on and allowed to stabilize, followed by a 90° pulse and an encoding time equal to a multiple of the spinner period. At this time one data point is sampled. Subsequent data points are collected in an identical fashion, but the strength of the gradient field is stepped by ΔG between each one. A full set of 1D images suitable for BP reconstruction are acquired by varying the phase of the gradient field to the spinner over 180° in equal steps.

to employ, since they generally do not require gradient switching.

We present here a method of imaging suitable for materials which may be narrowed by MAS, using phase encoding during a constant encoding time and BP reconstruction. It will be shown to yield reliable images substantially free of artifacts with better than 50-μm resolution. In addition, it is a simple method to incorporate into an existing solid-state spectrometer.

Since MAS will only average dipolar interactions where the spinning frequency is greater than the dipolar line width, the method as presented is suitable for solids which are partially averaged or are ^{1}H dilute. Spinning at up to 23 kHz allows most amorphous polymers to be imaged. The rigid lattice dipolar line width may be as large as 100 kHz, however, and MAS will not narrow this. Multiple pulse modifications of this basic method[8] have been suggested to overcome this problem.

There are two important practical limitations to this technique: (1) the sample must be placed inside a MAS spinner and (2) the sample may deform during the experiment. It is assumed that the interest in NMR imaging of materials is to study small features of chemical interest, not large structural features which may be more easily observed acoustically or with an optical microscope. Since a resolution of a few micrometers is desired, the sample must be kept small to maintain a reasonable number of data points. We feel that the higher resolution and benefit of isotropic chemical shift selection that MAS imaging allows are sufficient motivation for taking a plug from the sample of interest.

The type of information that we foresee NMR imaging providing is the degree of mixing of components; the spatial extent of curing, degradation, and oxidation; the dispersions of fillers; and a variety of processing characteristics of the material itself, unrelated to its end use shape.

For soft samples, such as a polyisoprene rubber sample that we will discuss latter, MAS will stress and deform the material. This is inherent in this approach and may or may not be advantageous. Methods exist for imaging soft stationary materials which should be used when stressing the sample is undesirable. For resonances which are moderately dipolarly broadened, however, the resolution that is achievable with stationary imaging methods is presently worse than that shown here.[9]

Imaging Method

The pulse sequence used in this work is shown in Figure 1. MAS averages both the dipolar and CSA interactions.[16] Since the sample is spinning, it is convenient to spin the gradient synchronously with the sample. This has been described previously,[7,8] and when performed correctly each spin experiences a constant magnetic field. BP methods require that a set of 1D images be acquired at incremented orientations of the field gradient evenly spread over 180°. To vary the orientation of the gradient, the gradient is phage shifted relative to the spinner. Each point in the fid is acquired by first turning on the gradient field and letting it stabilize and then apply a 90° pulse followed by an encoding time equal to a integer number of spinner periods. The entire fid is acquired in this manner, with the strength of the field gradient varied from $-G$ to $+G$ in constant steps for each successive data point. The fid then appears as a pseudoecho, and Fourier transformation followed by a magnitude calculation yields a pure absorption line shape.[17,18]

The sequence in Figure 1 avoids distortions due to chemical shifts, spin–spin relaxation (T_2), and angular distortions in the gradient field. Distortions from the first two effects are avoided by acquiring at a constant time, such that no evolution due to them is observed. In a multiple-component sample, the intensity of each component is weighted by its T_2. We will take advantage of this property latter to acquire images of only polybutadiene in blends of polybutadiene and polystyrene.

Since the spinner rotates an integer number of revolutions, n, during the encoding time, distortions due to variations in the gradient field with spinner position are not observed. The phase angle of the magnetization in the transverse plane, at time t, has the form

$$\vartheta(t) = \int_0^t (\vec{r}(t')\cdot\vec{G}(t') + \omega_0)\,dt'$$

which for this experiment may be written as

$$\vartheta(t) = |G|n\int_0^{t_p}\vec{r}(t')\cdot\hat{G}(t')\,dt' + \int_0^t \omega_0\,dt'$$

where $\vec{r}$ is the position of a spin packet, $\vec{G}$ is the gradient vector, $\hat{G}$ is a unit vector in the same direction as $\vec{G}$, and ω_0 is an offset frequency. Only the magnitude of $\vec{G}$, $|G|$, is varied between points in the fid, therefore the details of the path of the magnetization vector over a period, t_p, contained in the integral, are not observed. This is obviously only true of the angular dependence of $\vartheta(t)$ and axial distortions in the field gradient still influence the image.

The simplicity of this method and the lack of artifacts are achieved at the cost of a long experimental time. It is possible to acquire a complete fid suitable for BP reconstruction in a single shot[8,15] rather than mapping it out point by point as is done here. Such methods will eventually be of more value as standard techniques, but there are practical difficulties in implementing them which are avoided here. It is worthwhile to have a simple to apply method which one may be reasonably sure is free of distortions.

Two conditions are sufficient for selecting the experimental conditions. The gradient step is selected such that spins on opposite extremes of the sample evolve by 2π relative to one another in the smallest field gradient over a time nt_p

$$2\pi\Delta G l_s n t_p = 2\pi$$

The maximum field gradient is chosen such that the evolution over the smallest spatial element of interest is π

$$2\pi G_{max}\Delta l n t_p = \pi$$

In general, it is advantageous to spin as fast as possible

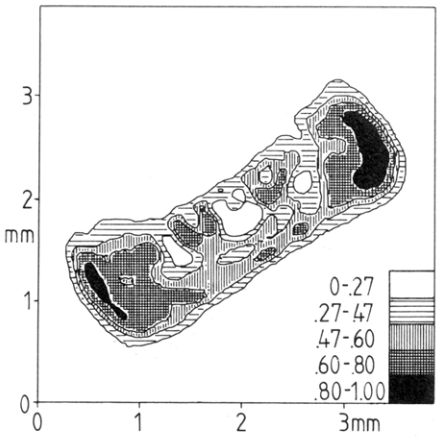

Figure 2. ^{1}H MAS image of a polyisoprene phantom spinning at 5 kHz. The static dimensions of the piece of rubber are 3.3 mm long × 1.0 mm wide × 0.75 mm thick. It has five 150–200 μm holes evenly spaced with centers 500 μm apart. The sample is a soft rubber which deforms due to MAS but returns to its original shape afterward.

to achieve the sharpest resonance. To improve the S/N, n should be as small as possible, but it is limited by the 90° pulse width, t_{90}.

For a straightforward image reconstruction to work, the excitation pulse must cover the full frequency width of the gradient field broadened spectrum, or

$$l_s G_{max} \leq t_{90}^{-1}$$

This limits the number of volume elements one may observe across a sample, NV, to

$$NV \leq nt_p/2t_{90}$$

For small samples and reasonable 90° pulse widths, this is rarely an important consideration.

Experimental Section

The NMR spectrometer operates at 180 MHz with a 94-mm bore Oxford magnet and is typical of homemade NMR's for multiple-pulse ^{1}H of solids. To synchronize the gradients to the spinner, the spinning speed is detected optically and phase locked to a pair of quadrature sinusoids. These may be phase shifted with respect to the spinner signal and their amplitudes varied in up to 512 evenly spaced increments. The quadrature sinusoids are each amplified by a 180-W amplifier and applied to a set of Golay gradient coils wrapped around the spinner housing. More details are given elsewhere.[7,8]

For the results presented here, the spinning speed was 5–5.3 kHz, stabilized by a spin-fix unit which regulates the spinner speed to within a few hertz. Sixty-four projections were acquired spaced evenly over 180°, and 64 data points were collected for each. In the analysis the fids were zero filled to 256 points prior to Fourier transformation. For each spectrum 16 transients were acquired with a waiting time of 1.3 s. The total time to acquire an image was approximately 24 h.

All of the images were calculated by the filtered back-projection algorithm.[19] The displayed images were plotted as contour plots after which the contours were filled in for easy visual interpretation. The scale is given in Figure 2.

Images were repeated for different maximum gradient strengths and encoding times with no perceptible variations in the image other than the expected loss in S/N as the encoding time was lengthened. The images shown here were recorded with about a 1-ms encoding time and a 8 kHz/mm maximum field gradient.

The polyisoprene sample is a soft material which distorts under MAS but returns to its original shape when the spinning is stopped. Five evenly spaced holes were burned into the sample with a laser. The roughly rectangular sample was cut by hand.

The two polybutadiene/polystyrene blends are rigid materials which do not deform under MAS and do not contain any obvious voids. Both of these samples were 3.5 mm in diameter and about 0.75 mm thick.

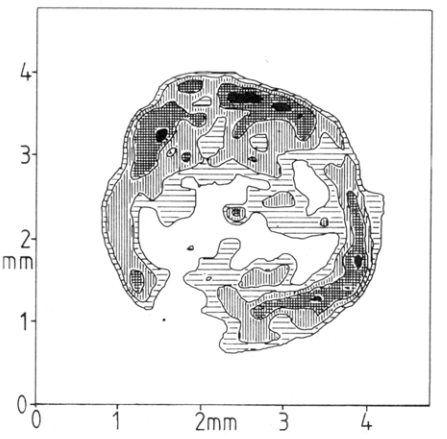

Figure 3. ^{1}H MAS image of polybutadiene in a mechanical blend with polystyrene.

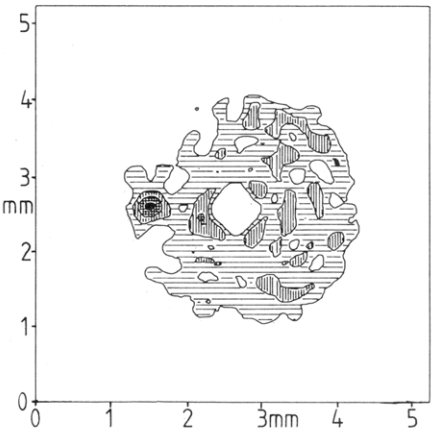

Figure 4. ^{1}H MAS image of polybutadiene in a film of a blend with polystyrene cast from toluene.

Results and Discussions

Figures 2–4 are three images which were acquired with the sequence diagramed in Figure 1. Images of the polyisoprene phantom were measured to investigate possible distortions. The ^{1}H NMR line width of static polyisoprene is about 1.5 kHz at 180 MHz, and MAS at 5 kHz reduces this to approximately 100 Hz. With 5-kHz spinning, the polyisoprene sample in Figure 2 is stretched and presses against the spinner walls. Though the sample is cut to be approximately the same thickness along its entire length, there is obviously more intensity where it has flowed against the spinner walls. The five 150–200 μm holes which were burned into the sample are still clearly visible, however. The three central holes have zero intensity inside them and are well-defined. The central hole has been stretched by the spinning. The two outermost holes have been partially closed by the deformation of the rubber and are less well-defined but still visible. In addition to the holes being shut by the spinning, the length of the hole (the sample is about 0.75 mm thick) may no longer be perpendicular to the gradient field.

At the ends of the piece of rubber the image is broader than in the middle. Some of this is from the deformation of the sample, but jitter in the phase lock loop of the gradient to the spinner leads to an artifact that looks similar. We have attempted to make this small by strongly locking the gradient and using very stable spinning, but we cannot rule out the possibility that jitter contributes to this shape. Overall we are led to conclude that the image

is an accurate representation of the phantom as it appears under MAS conditions.

Figures 3 and 4 are ^{1}H NMR images of the polybutadiene fraction of two polybutadiene/polystyrene blends. The spinning and static ^{1}H NMR line widths of polybutadiene are similar to those of polyisoprene at 180 MHz. MAS at 5 kHz does not aveverage the polystyrene line width, however, and its FID decays to zero in much less than 100 μs. For these images, the encoding time was about 1 ms and no signals from the polystyrene are detectable.

Both blends are approximately 50/50 mixtures. The sample corresponding to the image in Figure 3 is mechanically blended and that of Figure 4 is cast from toluene. If the polybutadiene was uniformly dispersed through the sample, a constant level would be observed in the images. The samples are 750 μm thick, which is much larger than the domains one would expect to observe. The intensities that are displayed in the images are summations of the intensity over this 750-μm thickness. The highest levels, black, are areas where the polybutadiene extends through almost the entire thickness of the sample, and the white areas correspond to areas devoid of polybutadiene. Since the sample is a solid disk, these regions contain predominantly polystyrene. The other levels correspond to a mixture of polystyrene and polybutadiene throughout the thickness of the sample.

Clearly, very small features are observed in the images, and the samples are obviously incompatible. Some idea of the degree of mixing and the domain size of the rubber particles may be seen, but we would prefer to have a thinner slice over which to investigate these properties. Some of the more gross features of the images are observable by optical microscopy.

It is reasonable to attempt to image these samples in a static experiment with conventional imaging equipment and larger gradients. Since MAS narrows the NMR resonance by about a factor of 15, to obtain the same image without line narrowing a magnetic field gradient 15 times larger is needed, and the imaging time is increased by the square of this.[9] A more practical alternative would be to image the stationary material with pulsed line narrowing.[6] In both cases the ability to obtain images of specific resonances based on their isotropic chemical shift is lost.

Conclusions

We have demonstrated a simple method of NMR imaging of materials which works well when MAS averages the ^{1}H homonuclear dipolar interactions without distorting the sample. Under these conditions, images with a resolution of better than 50 μm may be obtained. Schemes exist for faster versions of this experiment in which deconvolution[15] or refocused gradient methods[14] are employed to eliminate T_2 and chemical shift effects; however, practical difficulties limit their application at present. Both these methods are very susceptible to distortions from background signals which do not shift with the gradient and baseline artifacts, but clearly they will be of value in the future.

Part of the power of this method is the ease with which it may be combined with other experiments. Slice selection and selective excitation based on either chemical shifts or relaxation times may be tacked on to the front of this experiment, thus allowing narrower slices to be studied and chemically selective imaging. Multiple pulse schemes may be employed during the encoding time to image materials for which MAS alone is insufficient to average the dipolar broadening. As mentioned earlier, this has inherent limitations which makes it impractical for all but the most rigid materials, but for these there are at present very few other approaches to choose from.

Acknowledgment. We thank J. W. M. van Os for technical assistance. Financial support has been generously provided by the Koninklijke/Shell Laboratory (Amsterdam).

Registry No. Polybutadiene, 9003-17-2; polystyrene, 9003-53-6.

References and Notes

(1) Mansfield, P.; Morris, P. K. In *Advances in Magnetic Resonance*; Waugh, J. S., Ed.; Academic Press: New York, 1982; Vol. 12, Suppl. 2.
(2) Morris, P. G. *Nuclear* Magnetic *Resonance Imaging in Medicine and Biology*; Clarendon Press: Oxford, 1986.
(3) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, 1987; Chapter 10.
(4) Garroway, A. N.; Baum, J.; Munowitz, M. G.; Pines, A. *J. Magn. Reson.* **1984**, *60*, 337.
(5) Mansfield, P.; Grannell, P. K. *Phys. Rev. B: Condens. Matter* **1975**, *B12*, 3618.
(6) Chingas, G. C.; Miller, J. B.; Garroway, A. N. *J. Magn. Reson.* **1986**, *66*, 530.
(7) Cory, D. G.; van Os, J. W. M.; Veeman, W. S. *J. Magn. Reson.* **1988**, *76*, 543.
(8) Cory, D. G.; Reichwein, A. M.; van Os, J. W. M.; Veeman, W. S. *Chem. Phys. Lett.* **1988**, *143*, 467.
(9) Cory, D. G.; Veeman, W. S., submitted, for publication in *J. Magn. Reson.*
(10) Wind, R. A.; Yannoni, C. S. *J. Magn. Reson.* **1979**, *36*, 269.
(11) Haeberlen, U. In *Advances in Magnetic Resonance*; Waugh, J. S., Ed.; Academic Press: New York, 1976; Suppl. 1.
(12) Dec, S. F.; Wind, R. A.; Maciel, G. E. *J. Magn. Reson.* **1986**, *70*, 355.
(13) Emid, S.; Creyghton, J. H. N. *Physica B+C* **1985**, *125B+C*, 81.
(14) Miller, J. B.; Garroway, A. N. *J. Magn. Reson.* **1986**, *67*, 575.
(15) Cory, D. G.; Reichwein, A. M.; Veeman, W. S. *J. Magn. Reson.* **1988**, *80*, 259.
(16) Fyfe, C. A. *Solid State NMR for Chemists*; CFC Press: Guelph, 1983.
(17) Bax, A.; Mehlkopf, A. F.; Smidt, J. *J. Magn. Reson.* **1979**, *35*, 573.
(18) Bax, A.; Freeman, R.; Morris, G. A. *J. Magn. Reson.* **1981**, *43*, 333.
(19) Brooks, R. A.; DiChiro, G. *Radiology (Easton, Pa.)* **1975**, *117*, 561.