

NMR IMAGING OF ACETONE DIFFUSION PROCESS IN POLYCARBONATE

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ABSTRACTS

Acetone diffusion in polycarbonate was investigated by spin-echo ^1H NMR imaging method at room temperature. The result shows that the diffusion process satisfies Case II diffusion. The velocity of diffusion front is 13.8nm sec^{-1} (0.05mm/h).

INTRODUCTION

The diffusion of solvent in polymers plays an important role in characterizing polymer physics. Case II diffusion and Fickian diffusion are two typical cases. The characteristics of Fickian diffusion are: The concentration of the solvent increases exponentially from the core of polymer to completely swollen region; the diffusion distance is linear to the square-root of time. On the other hand, the concentration in Case II increases rapidly from zero to an equilibrium over a very short distance, while it keeps constant in the swollen region; the diffusion front moves linearly with the imbibed time. A lot of techniques such as optical microscopy^[1] or RBS^[2] (Rutherford backscattering spectrometry) are used in studying diffusion process. These methods, however, require the diffusion to be stopped, thus need many samples and bring about deviation. NMR imaging as a noninvasive analytical method just uses a single sample from which dynamical change can be supervised throughout the whole process and gets a comparatively direct, precise result. Several polymer/solvent systems have been studied by using NMR imaging in literature, such as polystyrene/toluene^[3], PMMA (poly-methyl-methacrylate)/Hydroxy-deuterated methanol(CH_3OD)^[4], nylon/water^[5] and so on. In this paper, we try to investigate the diffusion of acetone in polycarbonate(PC) by NMR imaging.

BASIC PRINCIPLES OF NMR IMAGING

In a sample with identical nuclei in an identical environment, all the spins experience the same magnetic field B , according to the resonance condition, have the same resonance frequency ω .

$$\omega = \gamma B \quad (1)$$

γ is the nuclei gyromagnetic ratio. If a time dependent linear gradient is imposed onto the static magnetic field B_0 , spatially resolved magnetic resonance is made possible.^[6]

$$B(r, t) = B_0 + G(r, t) \quad (2)$$

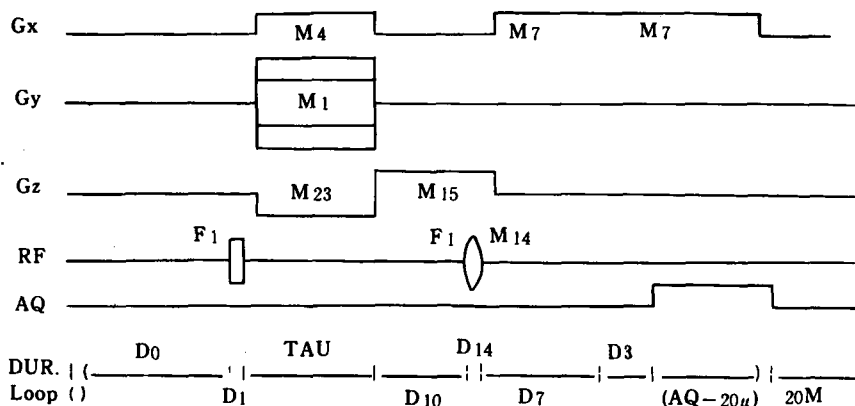
The gradient field $G(r, t)$ has a linear dependence on the position, for example,

$$G(X, t) = G_x X \quad (3)$$

From formula (1), (2), (3), there is:

$$\omega(X) = \gamma(B_0 + G_x X) \quad (4)$$

Therefore, given a gradient, planes of different field strength also become planes of different resonance frequency. This fundamental relationship between the spatial domain and the frequency in the presence of a gradient forms the basis of MRI. Spin-echo imaging:



Spin-echo single-slice imaging pulse sequence

SEVERAL KINDS OF IMAGES

Assuming TE , TR are spin-echo time and repetition time respectively, Q is the spin density of the proton. When $TR \gg T_1$, $TE \ll T_2$, the signal strength,

$$S(TE, TR) = Q \quad (5)$$

Each image represents the spin density of the protons in the corresponding volume.

If $TE \ll T_2$, then

$$S(T_1, TR) = Q(1 - e^{-TR/T_1}) \quad (6)$$

Equation (6) is the experimental conditions for T_1 -weighted spin-echo images.

When $TR \gg T_1$,

$$S(TE, T_2) = Qe^{-TE/T_2} \quad (7)$$

This is T_2 -weighted image.

EXPERIMENTAL

A cylinder 10 mm in diameter and 5 cm in length cut from a $\Phi 23$ mm PC (polycarbonate) stick (1m long) was put into a $\Phi 25$ mm tube which was filled with acetone. The cross section images of proton spin density were measured on a Bruker MSL-300 spectrometer equipped with imaging accessories, using spin-echo imaging. The selective rf pulses were typically 2ms long and used a Sine shape. Spin-echo time TE was 6.1 ms and repetition time TR was 0.42s. The nonselective pulses were $37 \mu s$ for the 90° pulse. The spectral width was 50KHz. The slice thickness was 1mm. The imaging time was 14min20s. Spatial resolution is $102 \times 102 \times 1000 (\mu m)$. (These parameters are for Fig.1)

RESULTS AND DISCUSSION

The images of a PC cylinder in acetone are shown in Figure 1,1h, 2h,11.6h

and 33.5h, respectively after PC is submerged in acetone. The image shows the bulk acetone as bright areas and the core of PC as dark. Image no. 3 shows a sharply bright front on the low left corner which is a crack probably due to the disunity of inner stress in PC. This phenomenon occurs in every sample tested. The chasm in diffusion procedure can be seen from image N.4, N.14 and N.21. Fig.2 is one of intensity profiles. We can view the intensity varying with the region. Fig.3 is the plot of diffusion distance vs. imbibed time at 20 °C. The front velocity is the slope of the linear least-square fit to the data. In this experiment, the front velocity is 13.8 nm sec⁻¹.

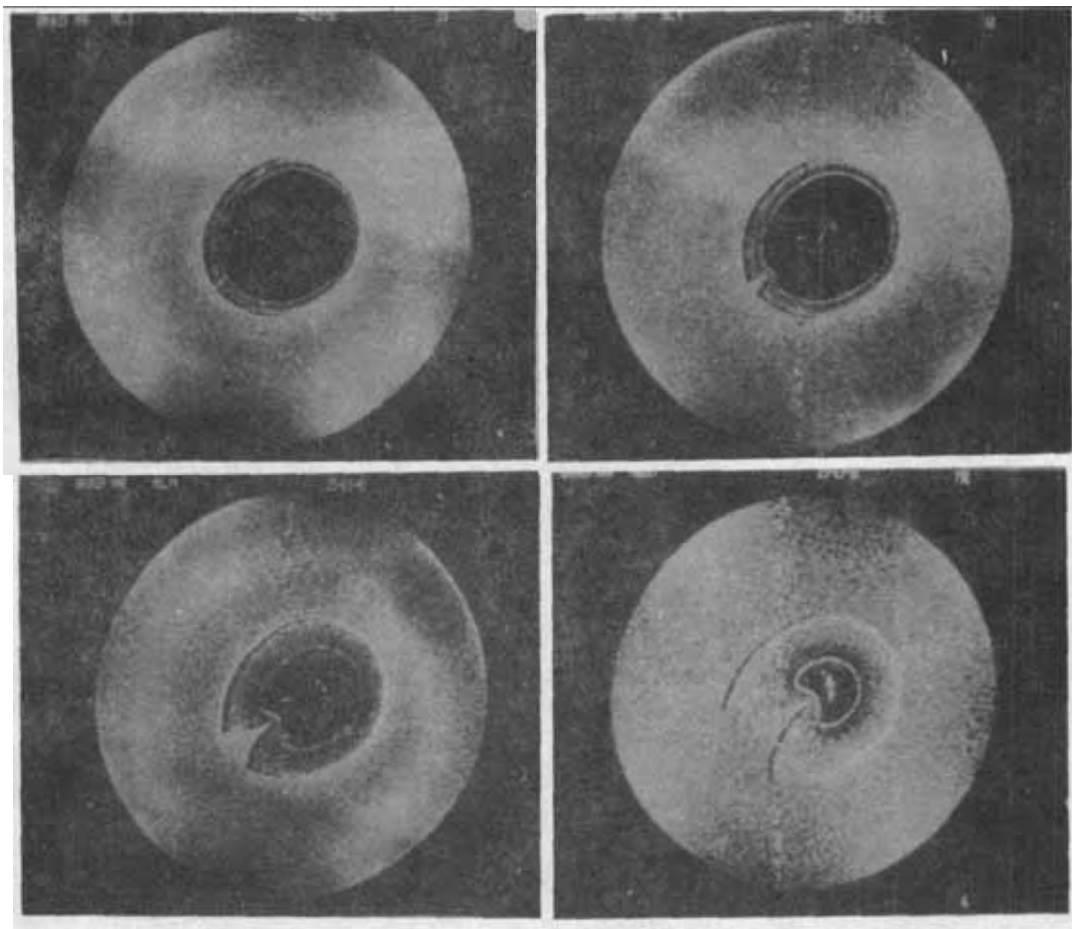


Fig.1 The images of a PC stick in acetone, 1h, 2h, 11.6h and 33.5h, respectively after PC is submerged in acetone

Generally speaking, the value of T_1 for the organic solvents such as acetone is in the order of several seconds, while the value of T_2 is a little smaller than that of T_1 . When $TR=10s$, $TE=4.82ms$, the image is approximately proton spin density image, see Fig. 4 (A). When $TR=0.35s$, $TE=4.82ms$, the image can be regarded as T_1 -weighted image, see Fig.4 (B). when $TR=10s$, $TE=24ms$, we can obtain T_2 -weighted image, see Fig.4 (C). From images, the brightness is not homogeneous on the borders as expected because of the differences in permeability.

In Fig.5, (D), (E), (F) are the intensity profiles respectively. There are two platforms which stand for bulk acetone (a) and imbibed acetone (b) with constant



Fig.2 One of intensity profiles

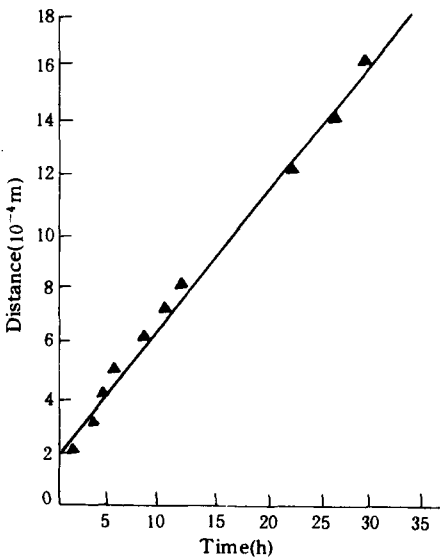


Fig.3 The plot of diffusion distance vs. imbibed time at room tepperature

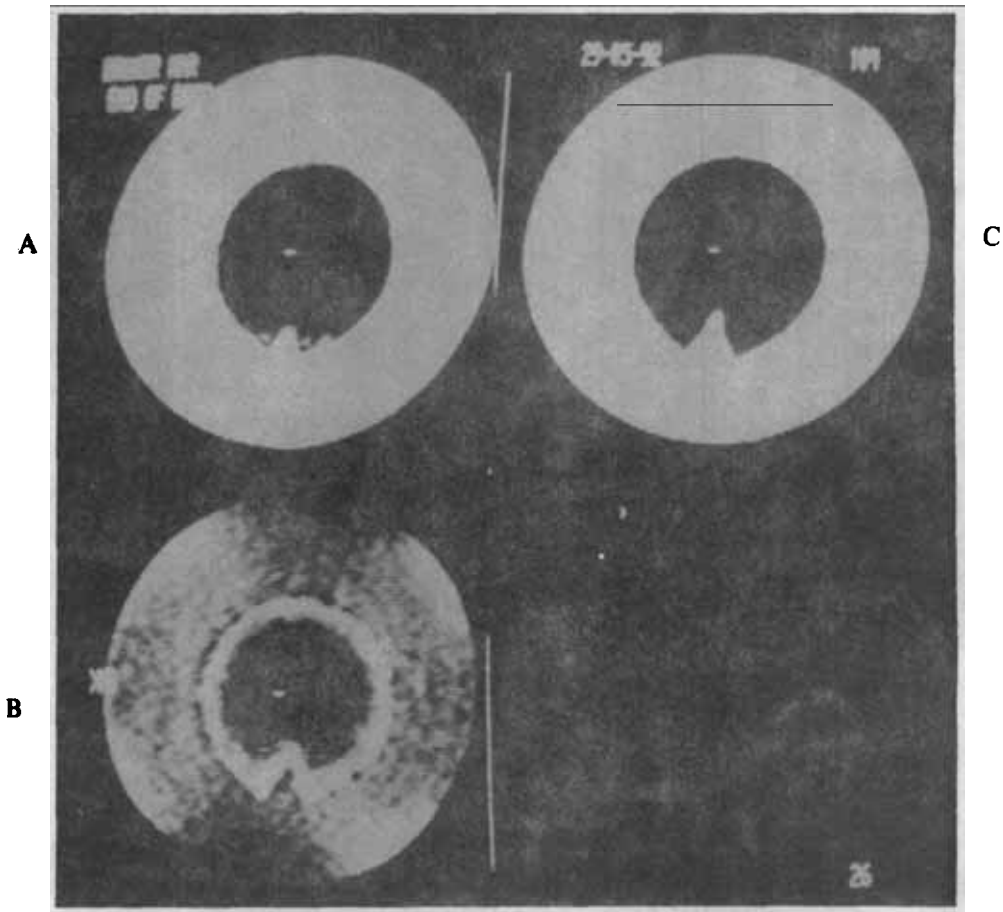


Fig.4 Various kinds of images

concentration in every region. The sharp front is (c) while (d) is the PC core where no signal is shown except for noise. Little difference can be seen between Fig.4 (A) and 4 (C), nevertheless, the brightest ring near the glassy core appears in the Fig.4 (B). Comparing Fig.5 (D) with Fig.5 (F), when TR is reduced from 10s to 0.35s, we can see that the intensity of the bulk solvent is attenuated remarkably while it changes little in swollen area. Therefore, the T_1 of bulk solvent is much greater than that of swollen region because the spins whose T_1 is shorter can relax back to equilibrium quickly. The brightness is gradually getting weak in Fig.4 (A) and Fig.4 (C) from out to the core. When spin-echo TE is changed from 4.82 ms to 24ms, the intensity of bulk region is practically unchanged, however, it decreases a lot in swollen region which indicates T_2 of imbibed acetone is shorter because only the spins of long T_2 , refocused in long TE, can be maintained, see Fig.5 (D) and Fig.5 (E). From the facts presented above, the motions of the solvents may be studied through NMR relaxation parameters.

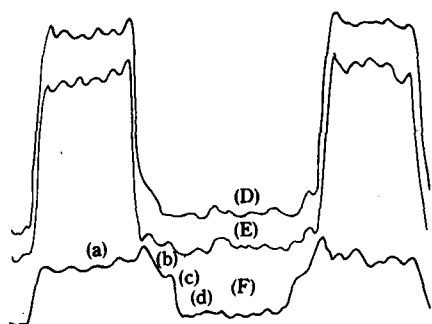


Fig.5 The intensity profiles D,E,F. corresponding to Fig.4 A,B,C. resp.

Another interesting phenomenon is that the intensity profile of T_1 -weighted image is rough while it is quite smooth in T_2 -weighted image and spin density image. That is probably because the signal in T_1 -weighted image is attenuated so much that the ratio of signal to noise is poor.

Notes in this experiment: (1) the solvent must be chosen properly. Ethanol was once the candidate for the solvent, but the blurry images were obtained due to the overlapped images of various kinds of protons in the ethanol. For the solvent whose δH^1 of different groups are noticeably different (generally 2ppm above), the satisfactory images can be acquired by using chemical shift imaging. (2) The temperature must be kept constant. It is reported that the diffusion mechanism may be varied with the temperature. (3) TR can not be too short since the magnetization could not restore due to short repetition time. In this experiment, when $TR = 0.2s$, the image almost disappears. (4) TE can not be too long, when $TE \gg T_2$ the signal decay too much to be shown, as can be seen from equation (7). TE is limited by many parameters such as the acquisition time and the width of the selective rf pulse. (5) In a spin-echo experiment the spatial resolution is only defined if, during the echo time TE, the spins do not leave the voxel in which they have been excited, that is to say, $TE \ll \Delta x/v$. In this experiment, $102 \mu m / 13.8 nms = 7391 s = 2.05h \gg 14min20s$, which satisfies the condition given above. FLASH (Fast Low Angle Shot) pulse sequence can be tried for the rapid diffusion systems. (6) The effect of swelling of the polymer on the diffusion velocity is not considered in the experiment.

CONCLUSION

The diffusion of acetone in PC is linear to the imbibed time and the concentration in the swollen area is almost constant, which satisfies Case II diffusion well. NMR imaging is very suitable for studying diffusion of solvent, including diffusion

process from fluids into solids, interfluid diffusion, and dissolution of the polymer by the solvent. Thus NMR imaging provides an excellent tool for characterizing polymer physics.

Keywords:

NMR imaging; Diffusion; Polycarbonate/ Acetone

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