

● Short Communication

MEASUREMENTS OF DIFFUSION IN POROUS POLYETHYLENE POWDER USING PFGSTE NMR

J.G. SELAND AND B. HAFSKJOLD

Department of Physical Chemistry, Norwegian University of Science and Technology, N-7034 Trondheim, Norway

Pulsed field gradient stimulated echo (PFGSTE) nuclear magnetic resonance (NMR) has been applied to study the diffusion of toluene in porous semicrystalline polyethylene powder. A pulse sequence with unequal bipolar gradients that reduces effects from internal gradients was used. The effects of different diffusion regimens and restricted diffusion in this system were indicated by use of a simple two-component analysis of the diffusion data.
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INTRODUCTION

The diffusion resistance to monomers during polymerization to solid polyolefin particles may have a significant effect on the reaction rate. This effect is, in general, unknown. In this study self-diffusion of toluene dissolved in porous semicrystalline polyethylene (PE) powder has been measured by nuclear magnetic resonance (NMR) using a pulsed field gradient stimulated echo (PFGSTE) sequence with unequal bipolar gradients.¹ This sequence removes artifacts due to internal magnetic field gradients, while the number of radio frequency (RF) pulses is kept to a minimum. It also reduces the effect of unwanted echoes caused by the series of RF pulses. The PE particles are semicrystalline and porous. It is expected that an added solvent occupies two main domains: the amorphous phase of PE, and the pores inside the particles.

MATERIALS AND METHODS

The experiments were performed on a Bruker DMX 200 instrument, operating on a resonance frequency for protons of 200.13 MHz. The experimental temperature was 300 ± 1 K. The PFGSTE sequence used, including the characteristic time intervals, is shown in Fig. 1. In

each diffusion experiment all time intervals were kept constant, while the intensity of the gradient pulses was varied.

In a bulk liquid the linear attenuation is given by:

$$\ln \frac{I}{I_0} = -(\gamma 2 \delta g_{\text{cal}})^2 D \left[\Delta + \frac{3}{2} \tau - \frac{\delta}{6} \right] \times \left[i - \frac{1}{2} \left(\frac{\Delta + \tau - \frac{\delta}{6}}{\frac{3}{2} \tau - \frac{\delta}{6}} \right) x \right]^2 \equiv -\zeta \left[\Delta + \frac{3}{2} \tau - \frac{\delta}{6} \right] D, \quad (1)$$

where g_{cal} is the gradient strength, which was calibrated to 4.5 ± 0.15 Gauss/cm/A.

The PE particles were a directly-from-the-reactor-sample delivered from Borealis A/S. The grain sizes were 250–500 μm . The porosity of the particles was determined to 8% by use of mercury porosimetry. The pore size distribution ranged from 0.05–10 μm , and the geometry was irregular.

The samples were prepared by adding excess toluene to a known amount of PE powder. The samples were

Address correspondence to Dr. J.G. Seland, Department of Physical Chemistry, Norwegian University of Science and

Technology, N-7034 Trondheim, Norway. E-mail: johnsel@chembio.ntnu.no

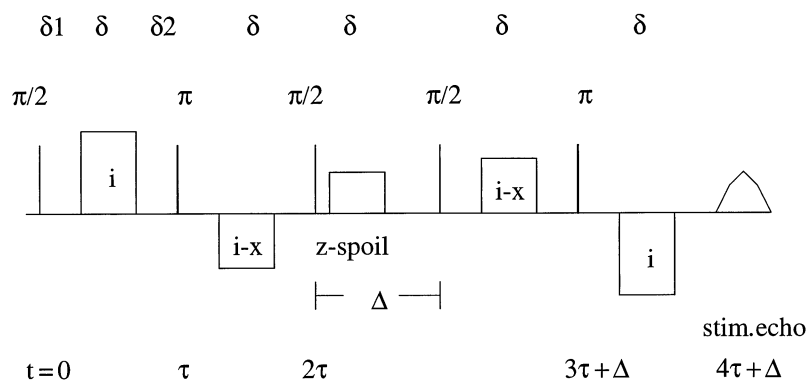


Fig. 1. Thirteen-interval PFGSTE pulse sequence. i and $i-x$ are the currents used in the two unequal bipolar gradients. The different time intervals are indicated. δ_1 was set equal to δ_2 .

then dried at 40°C until the interparticle liquid had evaporated; the remaining solvent was expected to be found mainly inside the particles.

RESULTS AND DISCUSSION

The diffusion coefficient of bulk toluene was $2.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 300 K.

Three samples with different amounts of toluene were examined, and by setting τ equal to 3 ms, the signal from solid amorphous PE was eliminated at the time of the echo.

The diffusion measurements at different values of the Z-storage time, Δ (see Fig. 1), showed nonlinear attenuation, concaved upward. As no signal from solid PE at the time of the echo was observed, and signal from other unwanted echoes is excluded, this nonlinear effect is assumed to be eliminated. Solvent is believed to occupy different domains of the particles, and pores are found in a broad range of sizes, so the effects of several diffusion domains and restricted diffusion were expected. Considering different diffusion domains, a simple model is:

$$\frac{I}{I_0} = \sum_i p_i \exp \left[-\zeta \left(\Delta + \frac{3}{2}\tau - \frac{\delta}{6} \right) D_i \right], \quad (2)$$

where p_i and D_i are, respectively the fraction and the diffusion coefficient of domain i . ζ was defined in Eq. (1). It is then assumed that there is no exchange of solvent between the domains during diffusion, i.e., no significant coupling between diffusion and relaxation.

Diffusion in amorphous PE and pores was considered, and the plots of two-component fits of Eq. (2) to the experimental results at different diffusion times are shown in Fig. 2. The results from three samples with

different amounts of toluene are shown in Table 1. The various pore sizes can result in a distribution of diffusion coefficients, and this may explain the variation in D_1 with the amount of toluene. The same variation in D_2 may be explained by the use of free volume theory for polymers.² Both diffusion coefficients show dependence on Δ , which indicates restricted diffusion. To make a model that takes all these effects into account, more knowledge of the system is needed.

CONCLUSION

The application of PFGSTE to diffusion of solvent in porous, amorphous PE particles was demonstrated, and a

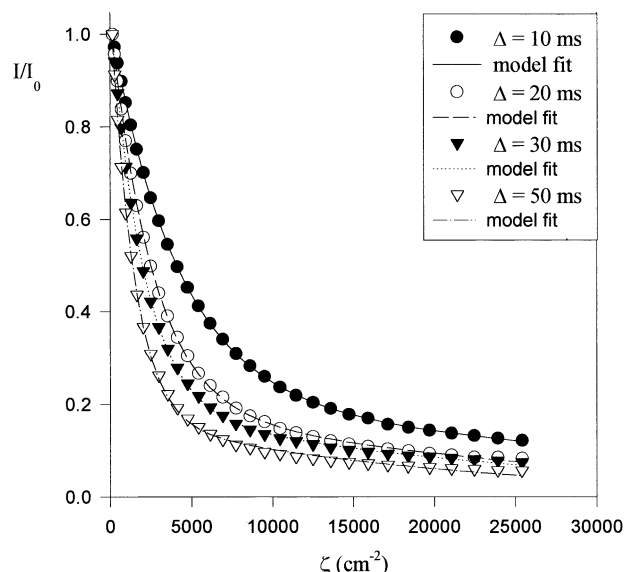


Fig. 2. Two-component fits to the experimental data at different diffusion times. ζ is defined according to Eq. (2).

Table 1. Calculated diffusion coefficients at different Δ values and amounts of toluene (per 0.10 g of PE), based on a two-component model, considering diffusion in pores ($D_1/10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and in amorphous PE ($D_2/10^{-6} \text{ cm}^2 \text{ s}^{-1}$)

Δ (ms)	22 μL		17 μL		14 μL	
	D_1	D_2	D_1	D_2	D_1	D_2
10	1.71	1.89	1.50	1.18	1.33	0.87
20	1.63	1.64	1.37	1.00	1.27	0.70
30	1.46	1.20	1.21	0.76	1.10	0.55
50	1.32	0.95	1.05	0.55	0.88	0.34

The uncertainty was estimated to be $\pm 15\%$.

two-component analysis was performed. The variation of the calculated diffusion coefficients with various amount of solvent and diffusion time indicates the effects of a broad pore size distribution and restricted diffusion. This suggests that a more complex, continuous, multicomponent analysis of the data should be made, but the quality of the data to date do not justify this.

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