
● *Short Communication*

DIFFUSION OF LIQUIDS INTO SEMICRYSTALLINE POLYETHYLENE

S.G. HARDING AND L.F. GLADDEN

Department of Chemical Engineering, University of Cambridge, Cambridge, UK

Pulsed field gradient (PFG) nuclear magnetic resonance (NMR) and microimaging experiments have been performed to study the diffusion of liquid alkanes into a variety of semicrystalline polyethylene (PE) samples. The results highlight the importance of the crystalline phase in controlling the diffusion process in terms of both the geometric impedance imposed by the presence of impenetrable crystals and their effect on the mobility of the polymer chains comprising the amorphous material through which the penetrants migrate. © 1998 Elsevier Science Inc.

Keywords: Magnetic resonance imaging; Pulsed field gradient NMR; polymers.

INTRODUCTION

An understanding of the diffusion of small molecular penetrants through a polymer matrix is required for a variety of technological applications, including the design of materials for separation processes, controlled pharmaceutical and agrochemical release devices, and packaging materials. This paper summarises the results of a study of the transport characteristics of a number of alkane penetrants within nine different semicrystalline polyethylene (PE) samples. In a semicrystalline polymer, liquid penetration is believed to occur within the amorphous material;¹ a semicrystalline polymer can therefore be considered a porous material, with the amorphous material representing the pore space and the solid matrix represented by the crystallites.

MATERIALS AND METHODS

PE plaques (15 cm² and 2.8 mm thick) were prepared from commercially available PE pellets by moulding in a hot press held at 150°C for 10 min. Four high density polyethylene (HDPE) and five linear low density polyethylene (LLDPE) samples were studied in this work. The PE samples were characterised in terms of crystallinity and lamellar thickness using Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and relaxation time analysis, differential scanning calorimetry, and x-ray diffraction. The liquid alkanes to be used

as penetrants (hexane, cyclohexane, octane, decane, and dodecane) were obtained from Aldrich (Rouses Point, IL, USA) and were used as received. All penetration was performed at 40°C. Samples for the imaging experiments were prepared by immersing a square plaque (5 × 5 cm) in the liquid for a specified time (ranging between 30 min and 48 h). After penetration, excess liquid from the surface was removed, and a small section from the centre of the polymer was excised for the magnetic resonance imaging and pulsed field gradient (PFG) NMR studies. All imaging experiments were performed on a Bruker DMX 200 spectrometer (Bruker Spectrospin Ltd., Coventry, UK) equipped with a microimaging probe head tuned to 199.98 MHz. The probe insert consisted of a vertical saddle coil with a diameter of 5 mm. Quantitative liquid concentration profiles were obtained using a two-dimensional spin-echo imaging sequence,² and correcting for T₁ and T₂ relaxation contrast. An in-plane resolution of 39 μm was used in all imaging experiments. The T₂ of the polymer is sufficiently short that an ¹H signal is received only from the penetrating liquid. PFG experiments were conducted on a Bruker MSL 200 spectrometer equipped with a PFG probe head (Z32FHP-DIFF) and a Bruker B-Z 18B gradient unit capable of giving a maximum gradient strength of 215 G/cm. Samples were prepared which contained a measured amount of liquid and were left at 40°C in a sealed glass tube so that the liquid would distribute homogeneously through-

Address correspondence to Dr. L.F. Gladden, Department of Chemical Engineering, University of Cambridge, Pembroke

St., Cambridge CB2 3RA, UK. E-mail: gladden@cheng.cam.ac.uk

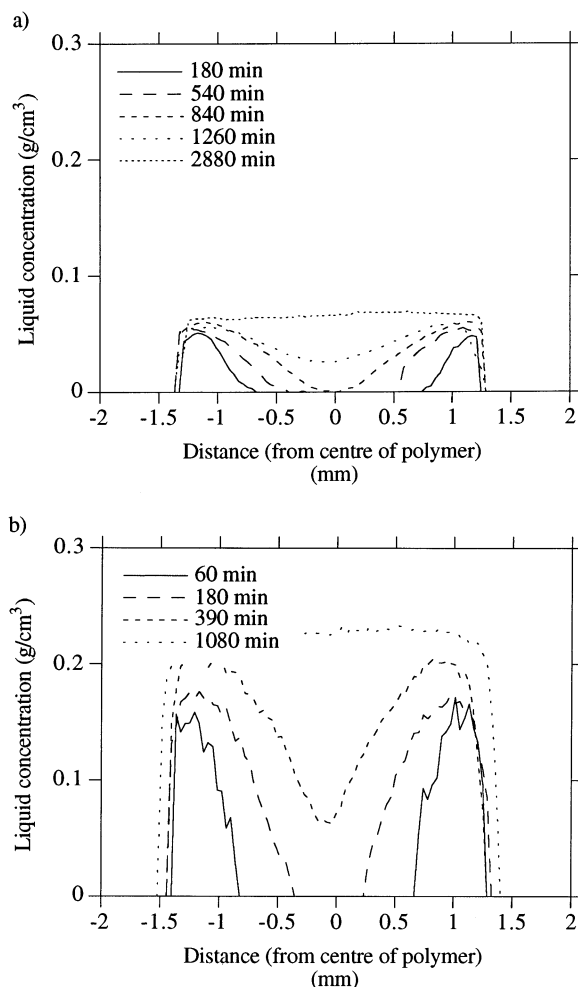


Fig. 1. Hexane concentration profiles for liquid penetration at 40°C for various times into (a) HDPE (degree of crystallinity 0.85) and (b) LLDPE (degree of crystallinity 0.27).

out the sample. The basic stimulated echo pulse sequence was modified based on the longitudinal eddy current delay PFG pulse sequence³ with a full 64-phase cycle. Gradient times δ of between 100 μ s and 2 ms were employed with diffusion times (Δ) ranging between 10 and 500 ms.

RESULTS AND DISCUSSION

Typical profiles for hexane diffusion into a HDPE and a LLDPE sample are shown in Fig. 1. The liquid concentration profiles are in excellent agreement with gravimetric mass uptake experiments. There is very little swelling in the samples; the total density of the system must therefore be increasing on absorption of the penetrant. The maximum liquid concentration at the surface was found to increase with time, a result of the viscoelastic response of the polymer to the penetrating liquid.

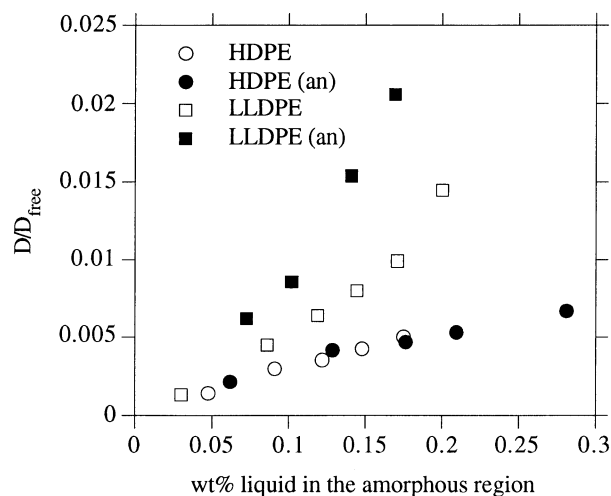


Fig. 2. Self-diffusivity (normalised to the self-diffusion coefficient of bulk liquid) of hexane as a function of loading for as received and annealed (an) samples of LLDPE and HDPE.

Figure 2 shows the results of bulk PGSE experiments for HDPE and LLDPE samples containing hexane. Hexane diffusivity within each polymer is shown for the case of diffusion in the as-prepared sample and a sample of the same material annealed at 120°C for 72 h. As the crystalline regions of the PE are thought to be impenetrable by the liquid penetrants, diffusivities are plotted as a function of weight fraction in the amorphous region rather than within the whole sample. The LLDPE sample is seen to have a higher diffusivity at any given penetrant concentration than the HDPE sample. This is consistent with the lower crystallinity of the LLDPE sample resulting in fewer obstructions to the path of the diffusing species; the higher content of branched chains might also result in a greater free volume within the polymer and hence higher penetrant mobility in the amorphous region. Annealing, which is observed to increase crystallinity in any given sample, is found to yield a significant increase in penetrant diffusivity in the amorphous region of the polymer in the case of the LLDPE sample and a negligible increase in the case of the HDPE sample. If penetrant diffusivity is plotted directly against weight percent liquid in the whole polymer sample (i.e., both amorphous and crystalline regions), then an increase in penetrant diffusivity is observed for both HDPE and LLDPE samples upon annealing. Because it is accepted that the penetrant will only exist within the amorphous regions, a plot of the form of Fig. 2 gives additional insight into the effect of annealing on the concentration dependence of the penetrant mobility within the amorphous polymeric material. A detailed investigation of the diffusivity of single component hexane, cyclohexane, octane, decane, and dodecane in an already prepared LLDPE sample

showed that the variation of penetrant diffusivity, normalised to the diffusivity of the bulk liquid, as a function of liquid concentration within the polymer lies on the same curve for all five penetrants. This observation suggests that the liquid diffusivity within the polymer is predominantly determined by the diffusion characteristics of the penetrant itself.

CONCLUSIONS

The results described above indicate the importance of polymer crystallinity in determining the diffusivity of simple organic penetrants in semicrystalline PE. The effects of annealing of the polymer on the liquid diffusivity have been investigated.

Acknowledgments—S.H. thanks the Ministry of Agriculture, Fisheries, and Food (MAFF) for financial support.

REFERENCES

1. Hedenqvist, M.; Gedde, U.W. Diffusion of small-molecule penetrants in semicrystalline polymers. *Prog. Polym. Sci.* 21:299–333; 1996.
2. Hyde, T.M.; Gladden, L.F.; Mackley, M.R.; Gao, P. Quantitative nuclear magnetic resonance imaging of liquids in swelling polymers. *J. Polym. Sci. A33*:1795–1806; 1995.
3. Gibbs, S.J.; Johnson, C.S. A PFG NMR experiment for accurate diffusion and flow studies in the presence of eddy currents. *J. Magn. Reson.* 93:395–402; 1991.