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Diffusion Coefficients of Tracers in Glassy Polymer Systems Prepared by Gamma Radiolysis

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Introduction

Diffusion-controlled reactions are common in free radical polymerisation reactions, especially in glassy polymer matrices. Such reactions commonly have an important influence on the polymerisation process and final polymer properties. For example, the dominant growth-stopping event (bimolecular termination) is generally diffusion-controlled. In glassy polymer systems, where molecular mobility is very low, the chain growth mechanism (propagation) may become diffusion-controlled. At present, the mechanism for propagation in glassy polymers is poorly understood, but it is expected by the Smoluchowski expression applied to propagation to depend strongly on the diffusion coefficient of monomer. The objective of this study is to measure reliable diffusion coefficients of small tracer molecules in glassy polymers, and compare these with propagation rate coefficients (k_p) in similar systems, by the prediction above.

Experimental

Diffusion coefficients of tracer dye molecules in the glassy polymer samples (containing polymer, inert diluent, and a tracer dye) are measured by Forced Rayleigh Scattering (FRS).[1,2] Samples are required to have the following properties: must have the desired weight fraction polymer (w_p), must be homogeneous, and must be pure. Due to these constraints, gamma radiolysis of the samples is the best method for sample preparation. Samples are initially prepared in a sealed sample cell containing monomer, inert diluent, and tracer dye. After irradiation for several days, complete conversion of monomer to polymer can be obtained, even in the most glassy samples.

The FRS experiment consists of two distinct steps: the initial (writing) step induces a transient holographic grating in the sample; and the second (reading) step monitors the decay in the intensity of light diffracted through the hologram. The decay is best described by:[3]

$$I(t) = A + [B \exp(-t/\tau_1) + C \exp(-t/\tau_2) + E]^2$$

where τ_1 and τ_2 are decay constants which are dependent on the diffusion coefficients of the tracer dye and photoproduct as follows:

$$D_i = d^2 / 4\pi\, \tau_i$$

where D_i is the diffusion coefficient of species i, and d is the grating spacing.

A typical experimental decay is shown in figure 1.

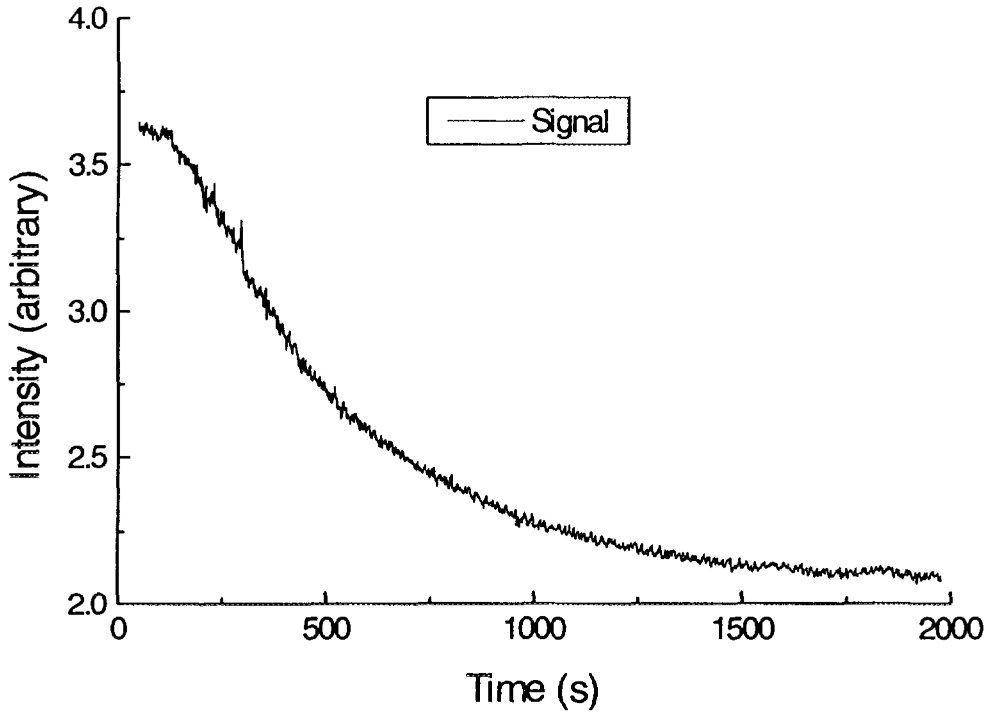

Figure 1: A typical FRS decay curve for diacetyl in pMMA, $D_{DA} = 8 \times 10^{-15}\ dm^2s^{-1}$.

Conclusions

Samples with the necessary properties for FRS experiments can be prepared by gamma radiolysis of a mixture of monomer, inert diluent, and tracer dye. The diffusion coefficients for two different tracer dyes have been measured as a function of weight fraction polymer in glassy poly(methyl methacrylate) samples. The measurement of such quantities are of fundamental importance to understanding the diffusion of small molecules in glassy polymers, and to understanding diffusion-controlled reactions in glassy systems.

References

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