

# Solvent self-diffusion in semidilute polystyrene solutions. Pulsed-gradient spin-echo measurements on a standard Fourier transform n.m.r. spectrometer

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Measurements of solvent self-diffusion coefficients in the systems polystyrene/dichloromethane and polystyrene/cyclopentane recorded on a standard Fourier transform n.m.r. spectrometer are reported. The ratio  $D_s/D_{s,0}$  was found to decrease linearly with increasing volume fraction of polystyrene, over the interval studied ( $\phi_{PS} < 0.27$ ), for both systems. For PS/cyclopentane an increase in temperature from 12.5°C (close to UCST) to 40°C was not found to alter the concentration dependence of the ratio  $D_s/D_{s,0}$  significantly.

## INTRODUCTION

An important quantity for the understanding of motions at the molecular level in binary polymer systems is the self-diffusion coefficient of the low molecular weight compound (often solvent). A convenient method to determine self-diffusion coefficients is offered by the pulsed-field gradient spin-echo n.m.r. technique.

A number of reports<sup>1-12</sup> on diffusion in polymer systems utilizing spin-echo (proton) n.m.r. have been published. In these studies the contribution from the polymer protons to the echo has either been assumed to be negligible<sup>2-5,7,8,10,12</sup> or has been accounted for<sup>1,6,9,11</sup> in the evaluation of the solvent self-diffusion coefficient. However, with Fourier transformation of the echo signal, the selective measurement of the self-diffusion coefficient of each component is *in principle* possible.

The pulsed-gradient Fourier transform n.m.r. technique was introduced by James and McDonald<sup>13</sup> for the selective measurement of self-diffusion coefficients in a two-component system. This technique has been further extended and elaborated<sup>14</sup> and has been applied to multicomponent systems.

We report here studies employing the pulsed-field gradient spin-echo method on a standard Fourier transform n.m.r. spectrometer for the determination of the self-diffusion coefficient of dichloromethane (DCM) in the polystyrene(PS)-DCM system at 25°C (good solvent conditions) and of cyclopentane (CP) in the PS-CP system at 12°C (close to the upper critical solution temperature), 21°C (theta solvent condition) and 40°C from 0 to 0.27 volume fraction of polymer. In this series of measurements the solvent quality has been altered from very poor to good in order to study the effect of a change in thermodynamic conditions on solvent self-diffusion in polymer solutions in the semidilute regime, i.e. the régime where the polymer chains overlap considerably, but the solvent fraction is still large (see for instance ref 15).

## EXPERIMENTAL

### *Sample preparations*

Anionically-polymerized PS with nominal molecular weight  $M = 390\,000$  (manufacturer's data for lot no. 3b) supplied by the Pressure Chemical Co., USA was used as received. Characteristic data for this sample are  $\bar{M}_n = 396\,000$ <sup>16</sup> and  $\bar{M}_{s,D} = 420\,000$ <sup>17</sup>.

The solvents dichloromethane (DCM) and cyclopentane (CP) (u.v. spectroscopic grade, Merck) were utilized as supplied.

All solutions were prepared by weighing. After addition of solvent, the polymer was allowed to swell and, thereafter, the solution was homogenized by stirring for several days. The volume fraction of polymer  $\phi_{PS}$  was calculated from the weight fraction assuming that the partial specific volumes of solvent and polymer are equal to solvent density and partial specific volume at infinite dilution, respectively.

Standard 5 mm medium-walled tubes were filled with the non-degassed solutions and sealed.

### *N.m.r. measurements*

The Fourier transform nuclear spin-echo measurements of solvent self-diffusion coefficients were taken at 99.6 MHz using methods described previously<sup>14</sup> with the exception that  $T_2$  of the solvent molecules was measured directly. These latter measurements were made with the CPMG pulse sequence supplied with the JEOL software package for the FG/BG system. This pulse sequence is an FT implementation of the Carr-Purcell-Meiboom-Gill method<sup>18</sup> for the determination of transverse nuclear relaxation times ( $T_2$ ).

Although the solvent  $T_2$  value was found to decrease with increasing polymer concentration, the contribution of the  $T_2$  term to the echo attenuation was insignificant compared with the diffusion term throughout the

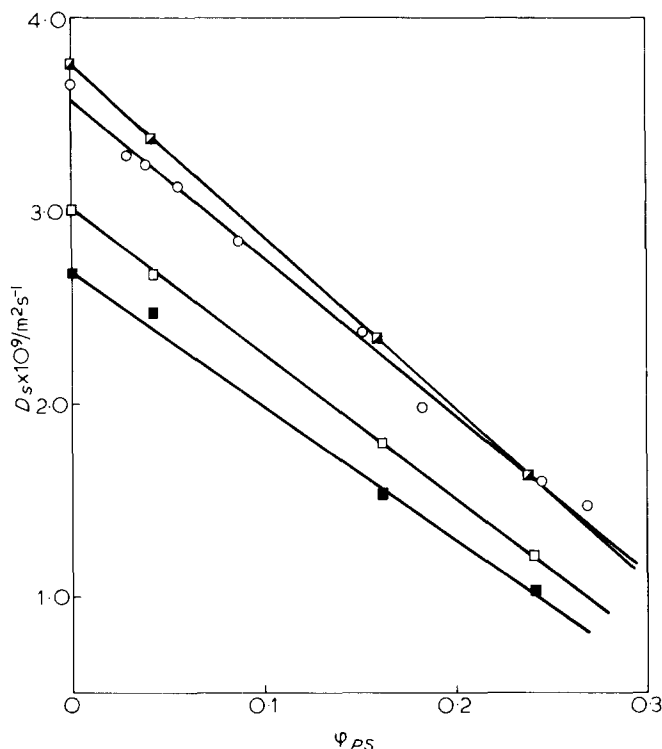


Figure 1 Solvent self-diffusion coefficients,  $D_s$ , versus volume fraction polystyrene,  $\phi_{PS}$ :  $\circ$ , polystyrene/dichloromethane, 25.0°C;  $\blacksquare$ , polystyrene/cyclopentane, 12.5°C (close to UCST);  $\square$ , 21.0°C (theta conditions);  $\blacksquare$ , 40.2°C

measurement series. In the polymer solutions solvent  $T_2$  was shorter than  $T_1$ .

Measurements were made on the system PS/DCM at  $25.0 \pm 0.5$ °C and on the system PS/CP at  $12.5 \pm 0.5$ ,  $21.0 \pm 0.5$ ° and  $40.2 \pm 0.5$ °C. The homospoil-pulsed magnetic field gradient factor,  $\gamma^2 G^2$ , was determined as reported previously<sup>14</sup>, using the self-diffusion coefficients of cyclopentane, interpolated from data in ref 19, and of cyclohexane at 25.0°C<sup>20</sup>, and was found to be reproducible within  $\pm 2.5\%$ .

The experimental inaccuracy, which is manifest in the scatter of the experimental points, is approximately  $\pm 3\%$  and is limited by the reproducibility of the field gradient. The precision, however, in a single measurement is  $\pm 3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ .

## RESULTS AND DISCUSSION

The solvent self-diffusion coefficients,  $D_s$ , versus volume fraction polystyrene,  $\phi_{PS}$ , are illustrated in Figure 1 for the systems PS/DCM and PS/CP. The decrease in  $D_s$  with increasing polymer fraction can be represented by a straight line, over the entire concentration regime investigated, for both systems and at all temperatures.

The slope of the lines in Figure 1 for the system PS/CP, which increase with temperature, is in qualitative accordance with observations for other polymer-solvent systems<sup>5,6,8,9,12</sup>. However, no marked upward curvature at lower polymer volume fractions is discernible within experimental error, for either of the systems studied. This is in contrast to previous reports on solvent self-diffusion in polymer systems utilizing the spin-echo n.m.r. technique<sup>1,12</sup>. However, it is important to note that the echo attenuation is dependent upon both  $T_2$  and  $D_s$ . The reported curvature can be explained by the lack of the

contribution from the  $T_2$  term at higher polymer concentrations and possibly from echo contributions from the polymer protons. For the present systems the contribution from the  $T_2$  term was found to be negligible at all concentrations, but it should be mentioned that with increasing  $\phi_{PS}$  the solvent  $T_2$  values decrease rapidly at low polymer concentrations ( $\phi_{PS} < 0.1$ ) to approach an almost constant value.

For the system PS/CP straight lines were found to represent the experimental points in an Arrhenius plot at all weight fractions of polymer. The activation energy for solvent self-diffusion,  $E_D$ , was found to increase linearly by 30% over the concentration regime studied, consistent with observations on other systems<sup>5,6,8,9</sup>. For pure solvent  $E_D$  was evaluated to be  $9.2 \pm 0.7 \text{ kJ mol}^{-1}$  which can be compared with  $11 \pm 1.5 \text{ kJ mol}^{-1}$  calculated from data in ref 19 for the corresponding temperature interval.

In Figure 2 the ratio  $D_s/D_{s,0}$  is plotted as a function of  $\phi_{PS}$ ;  $D_{s,0}$  is the value of the solvent self-diffusion coefficient (in Figure 1) extrapolated to infinite dilution. The most striking features in Figure 2 are that  $D_s/D_{s,0}$  decreases linearly with increasing  $\phi_{PS}$  and that the data for the two systems fall on nearly the same line. However, there is an indication that the cyclopentane data might be represented by a steeper line than the dichloromethane data; the line in Figure 2 is drawn through the DCM data:  $D_s^{DCM} = D_{s,0}^{DCM} (1.00 - 2.26 \phi_{PS})$ .

Furthermore, there seems to be no significant difference between the concentration dependence of the relative solvent self-diffusion in semidilute cyclopentane solutions of polystyrene at conditions close to the upper critical solution temperature (UCST), at theta conditions or at approaching good solvent conditions (see Figure 2). However, a slight decrease in slope with increasing temperature cannot be excluded. These features might be explained by the following tentative arguments. Although the polymer molecules in a semidilute solution form a transient network<sup>15</sup>, the volume fraction is still low. The translational motion of a solvent molecule will, therefore, on average mainly be impeded by other solvent molecules and not by direct interactions with the polymer chains.

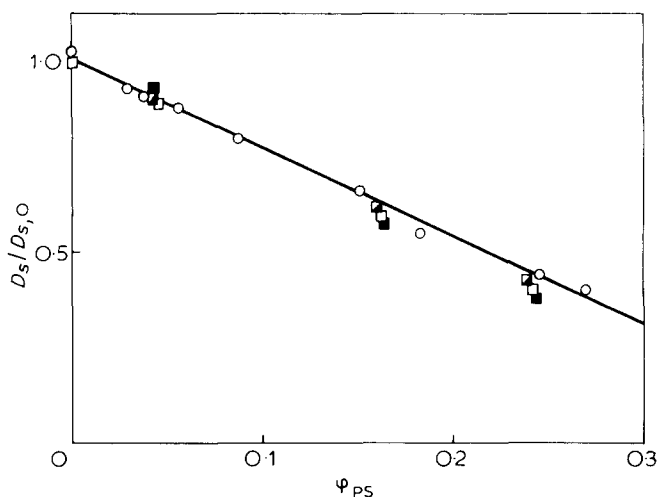


Figure 2 The ratio  $D_s/D_{s,0}$  versus volume fraction polystyrene,  $\phi_{PS}$  ( $D_{s,0}$  is the value of the solvent self-diffusion coefficient in Figure 1 extrapolated to infinite dilution):  $\circ$ , polystyrene/dichloromethane 25.0°C; polystyrene/cyclopentane  $\blacksquare$  12.5°C (close to UCST);  $\square$  21.0°C (theta conditions);  $\blacksquare$  40.2°C. The line is drawn through the dichloromethane data (see the text)

The polymer molecules merely create a 'long-range order' in the solution which gains importance with increasing number of polymer molecules present. An increase in temperature will lead to enhanced molecular motions and to a reduction of this 'order', and hence an increase in relative solvent self-diffusion is not unlikely. For a rigorous discussion, however, enhanced solvent-solute interactions with increasing temperature must also be considered.

The increase in the ratio  $D_s/D_{s,0}$  with increasing temperature at a fixed polymer fraction is within experimental error for the system PS/CP (see Figure 2) but is clearly observable for the system polystyrene/trans-decalin<sup>21</sup>. It is plausible that this difference may be associated with structural differences between these solvent molecules and ultimately in differences in their molecular volume.

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