

# Viscometric investigation of the aggregation and transfer reactions of polystyryllithium in ethylbenzene at elevated temperatures

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A high-vacuum falling-ball viscometric method has been used to measure the equilibrium constant for the aggregation of free polystyrylanions in ethylbenzene. The rate of the transfer reaction between polystyryllithium and ethylbenzene has also been measured. All measurements have been made in the absence of monomer under conditions relevant to large-scale polymerization processes, i.e. with solutions containing a high weight fraction of polyanions (approximately 15–70% w/w) and at temperatures in the region of 70°C. The equilibrium constant ( $K_d$ ) for the aggregation of polystyrylanions was found to be in the range  $2 \times 10^{-3} \text{ mol l}^{-1}$  to  $3 \times 10^{-2}$  for polystyryl anions of  $M_n$  30 to  $161 \text{ kg mol}^{-1}$  at 70°C. The chain-transfer constant ( $k_{tr}$ ) determined at 70°C over a range of polymer molecular weights and concentrations is  $(2.21 \pm 0.05) \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ . A number of assumptions have been made in order to arrive at the constants which are reported, including, (i) some concerning the viscosity behaviour of concentrated polymer solutions, (ii) that the polymers studied are essentially monodisperse, (iii) that polystyryl anions are two-fold associated in ethylbenzene, and (iv) that only the free polystyrylanions engage in the transfer reaction. © 1997 Elsevier Science Ltd.

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## INTRODUCTION

It is well known that alkylolithium compounds are aggregated in hydrocarbon solvents; the degree of association depends primarily on the nature of the monomer, solvent, and temperature. The degree of association has been established for certain polyanions but remains controversial for others<sup>1–6</sup>. In studying the transfer reactions of polymeric anions, it has been found possible to estimate the mean degree of association of polystyryllithium ion-pairs in ethylbenzene at 70°C by making a number of assumptions which are discussed in detail below. The value obtained is somewhat lower than 2.0 (i.e. dimeric polyanions predominate), the most commonly quoted value for polystyrylanions in hydrocarbon solvents at somewhat lower temperatures than those used here.

The equilibrium constant for the association/dissociation process of the ion-pairs in the same solutions at the same temperature has also been estimated. There have

been few previously reported equilibrium constants for the association–dissociation reactions of polyanions in hydrocarbon solvents<sup>7</sup>.

Most studies of living anionic polymerizations conducted in hydrocarbon solvents (such as cyclohexane and benzene) do not involve any chain transfer reactions between the propagating species and the solvent at the temperatures commonly used (0–50°C). Chain transfer reactions are known to take place between propagating anions and solvents which contain relatively acidic protons, such as toluene, and there have been a number of reports which illustrate the effect of transfer reactions on the kinetic behaviour and molecular weight distribution of the products from living polymerizations<sup>8–13</sup>. This work examines the transfer reactions which occur in living anionic polymerizations carried out in ethylbenzene at relatively high temperatures (~70°C) and high solid contents in the reaction mixtures (15–70% w/w polymer/solution). The transfer of a proton to the propagating species to terminate polymerization and form a lithiated adduct of the solvent is known to be a relatively slow reaction compared with polymerization under most circumstances and can usually be ignored during polymerization. However, the transfer reaction has a significant effect on the viscosity of solutions which contain significant quantities of polymeric anions after polymerization is complete, and an understanding of this process is necessary for the control of large-scale polymerizations which are sometimes carried out in

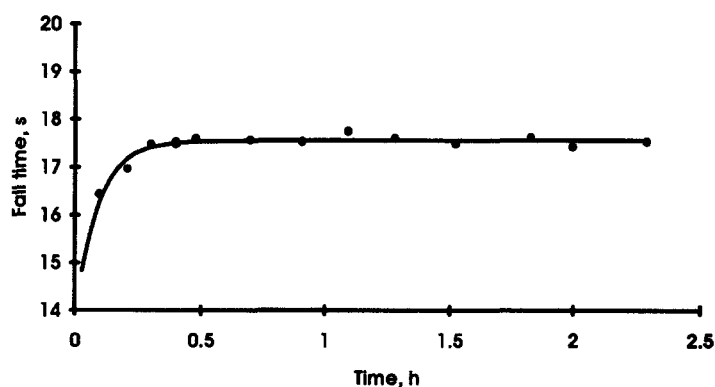
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**Figure 1** Viscosity of a concentrated polystyryllithium solution in cyclohexane as solvent. It is evident that the viscosity remains unchanged over long periods of time at 55°C. The initial increase in viscosity is the result of polymerization of the residual monomer present in the reaction mixture

solvents such as ethylbenzene at high temperatures and high solids content.

The experimental methods which have been reported by others for the study of transfer reactions to solvent include the use of carbon-14 labelled agents<sup>10</sup> and u.v.-visible spectroscopy<sup>11</sup>. In this work, a simple falling-ball viscometric method is described for following the transfer reaction rates under high vacuum conditions at 70°C, a temperature at which the transfer reaction rate was convenient for the experimental method.

## EXPERIMENTAL

### Polymerization method

The techniques used for the purification of the reactants and the typical high vacuum equipment used have been described elsewhere<sup>14</sup>. All experiments were carried out with glassware which had been pre-washed with a solution of *n*-butyllithium to remove impurities immediately prior to use. The solvent was also purified by conditioning and distillation from *n*-butyllithium. The inhibitor was removed from the styrene (Janssen, Hyde, UK) used by passing through a column of activated basic aluminium oxide (Aldrich, Poole, UK). The monomer was stored over powdered calcium hydride at -15°C in a freezer and distilled under vacuum from the calcium hydride into the reaction vessel when needed. Having made up the monomer and solvent mixtures under high vacuum, the reaction vessel was subsequently pressurized with pure dry nitrogen. The initiator was added to the purified monomer solution through a rubber septum (appropriately protected for use with organic solvents) by syringe. Polymerization reactions were carried out to completion at 0°C, a temperature at which no significant transfer to solvent occurs during polymerization taken to complete conversion. All transfer measurements were made on reaction mixtures which had been taken to complete conversion of monomer at 0°C.

### Viscosity measurement

The viscosity measurements were accomplished by recording the falling-time of a ball in a calibrated tube connected to the reaction vessel. The calibration of the viscometer was carried out using glycerol<sup>15,16</sup> together with the standard published values for its density and viscosity in the temperature range 15–30°C.

The absolute viscosities of the polyanion solutions were calculated using the equation

$$\eta = K(\rho_b - \rho_s)t_f \quad (1)$$

where  $\eta$  is the absolute viscosity (cP),  $K$  is the ball constant,  $\rho_b$  is the ball density ( $\text{g ml}^{-1}$ ),  $\rho_s$  is the solution density ( $\text{g ml}^{-1}$ ),  $t_f$  is the falling time (s) for the tube length  $D_{\text{max}}$ , and  $D_{\text{max}}$  is the maximum length of tube used for the measurement.

Viscometric experiments (Figure 1) with polystyryllithium solutions in cyclohexane at room and elevated temperatures (55°C) showed that the viscosity remained unchanged for periods of many hours. Experiments of this type established that it was possible to sustain the living anions for long periods (days) without killing from the ingress of air or moisture, and that the viscometric measurements themselves induced no degradation of the species in solution as a result of repeated flow measurements.

The falling ball viscometer was attached to the high vacuum apparatus and the entire system was immersed in a water bath at 70°C during use. The viscosity measurements proved to be accurate and reproducible. In situations where the fall-time was short compared to the reaction time (e.g.  $t_f \approx 60$  s for viscosity measurements compared with several hours to reach the final limiting flow time), the viscosity of the solution was assumed to change linearly during the movement of the ball down the tube. Using this assumption, the mean viscosity during the fall-time interval was taken to be that at the half-way point. When the fall-time was more than 1% of the reaction time the viscosity variation was calculated as follows.

The distance traversed by the ball was followed with time. The velocity of the falling ball is given by

$$V = dD/dt \quad (2)$$

Using equations (1) and (2), the viscosity,  $\eta$ , is given by

$$\eta = \{KD_{\text{max}}\} \{(\rho_b - \rho_s)/V\} \quad (3)$$

In the above equations,  $V$  is the velocity and  $D$  is the distance traversed in tube.

The measured viscosity of the 'living' polymer eventually reaches a constant minimum value. After the addition of a few drops of methanol and the disappearance of the colour, i.e. when the live-ends no longer exist in the solution, the falling time recorded at the same temperature is identical to the minimum falling time of the coloured solution. This can be explained if it is assumed that all the polystyryllithium chain ends have reacted with the solvent, i.e. there is no more associated polymer in the solution. The lithiated molecules of ethylbenzene may be associated but the low molecular

weight of the aggregate and its low concentration are unlikely to modify significantly the viscosity of the polymer solution. This is actually confirmed since there is no decrease in the viscosity of the solution after addition of methanol. The colour of the solution changes throughout the experiment from yellow to red. These changes in colour and colour intensity have already been reported in non-aromatic solvents<sup>18,22</sup>, and have been assumed to be due to the reaction of the carbanion with a proton of the polymer chain. It is believed that the lithiated molecules of ethylbenzene produced in the reaction between the polystyryllithium and ethylbenzene have a structure similar to that of active chain-end in poly( $\alpha$ -methyl styryllithium). Poly( $\alpha$ -methyl styryllithium) solutions in hydrocarbons are well known for their blood-red colour and it is therefore not surprising that an intense colour is generated in the experiments described here. U.v.-visible spectroscopic measurements in the strongly absorbing ethylbenzene solvent have been carried out in support of the viscometric studies. These data will be reported elsewhere<sup>23</sup>.

#### Molecular weight measurement

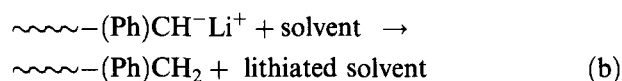
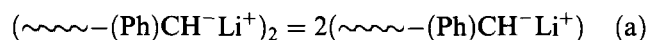
After 'killing' the polyanions with a small amount of methanol, samples from the reaction mixture were diluted with tetrahydrofuran to an appropriate concentration for analysis by gel permeation chromatography. A Waters Associates instrument was used fitted with a refractometer detector and two 30 cm columns filled with 100 Å, 10  $\mu$  polystyrene gel particles (PL Gel, Polymer Laboratories, Church Stretton, UK). Calibration was carried out with monodisperse polystyrene standards (Polymer Laboratories) and data reduction with in-house software<sup>17</sup> which was commercially available (Aston Scientific, Aston Clinton, UK).

#### REACTION MECHANISM

It is generally agreed that associated propagating chain-ends are in equilibrium with the unassociated chain-ends and in non-polar solvents only a very small proportion of the living chain ends are unassociated and that the rate of equilibration is very fast<sup>1,2,8</sup>. It is also generally agreed that the degree of association of polystyryllithium in hydrocarbon solvents is approximately 2.0, this value being obtained by kinetic and other methods<sup>3-6</sup>. If it is assumed that the degree of association in ethylbenzene is also 2.0, then the apparent length of the polymer chains will be almost twice that which might be otherwise expected for non-aggregated chains and the apparent viscosity of the 'living' polyanion solutions will be substantially greater than that of the same solution after the 'living' chains have been 'killed'. In kinetic studies of anionic polymerization reactions of the type used in this work, it is often assumed that it is only the unassociated living chain ends that are sufficiently reactive to engage in initiation and propagation reactions. It is likely that the unassociated chain ends are the reactive species in chain transfer reactions with solvent. When a 'living' polyanion engages in a transfer reaction with solvent (or any other species), it is 'killed' and will not thereafter be able to engage in association reactions with other 'living' species. The apparent chain length of the polymer chains in solution will therefore decrease as transfer takes place and the viscosity of the solution will reflect this decrease. Thus, by monitoring the viscosity of

a solution which is changing from an aggregated state to a disaggregated state as a result of 'killing' by transfer to solvent, it should, in principle, be possible to determine the mean degree of aggregation of the polymeric anions as well as the kinetic parameters for the transfer reaction to solvent. However, quantification of the transfer reaction rate from viscosity measurements is not straightforward, and can only be done by making a number of simplifying assumptions as described in subsequent sections of this work.

The transfer reaction which is thought to take place is



It is not assumed here that the equilibrium favours the associated 'dimer' and that there are relatively few 'free' ion-pairs compared with associated species. The lithiated molecules of solvent formed during the transfer reaction could initiate the polymerization of monomer; however, this reaction is not important here since no monomer is present at the stage when transfer reaction is studied.

#### CONCENTRATED SOLUTION VISCOSITY

Polymer solution theories<sup>18-21</sup> for the zero shear viscosity of a concentrated polymer solution is given by

$$\eta = K' M w^a \quad (4)$$

where  $\eta$  is the absolute viscosity,  $K'$  is a constant for a given polymer of fixed concentration which also embodies a term for the segmental friction coefficient,  $Mw$  is the weight average molecular weight of the polymer, and  $a = 1.0$  for situations where  $\phi_p Mw < Mc$ , and  $a = 3.4$  for those where  $\phi_p Mw > Mc$ .  $Mc$  is the critical molecular weight for entanglement, and  $\phi_p$  is the polymer volume fraction in solution.

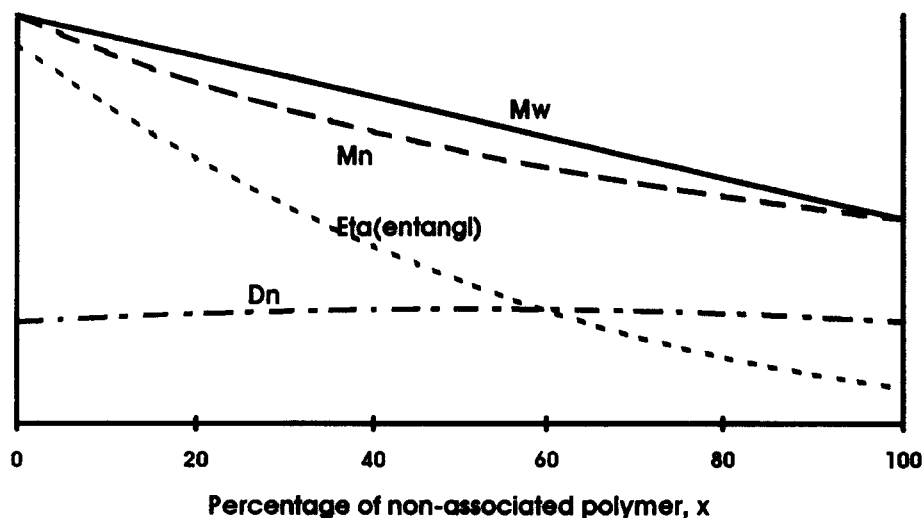
As the solvent molecules react with the free polymeric anions, the fraction of aggregated polymer decreases, and so does the overall average molecular weight of the species in solution. In these circumstances, the polymer solution contains essentially three types of polymer chains, namely the associated polystyryllithium chains,  $\text{LE}_{\text{aggr}}$ , the free polymeric anions,  $\text{LE}_f$ , and the non-aggregated dead polymer chains, PS, formed by the reaction of the polystyrylanions with ethylbenzene. From a viscosity standpoint, PS can be regarded as similar to the free polymeric anions. The conditions used to produce the polystyrylanions in this work give rise to essentially monodisperse chains (dispersity index typically = 1.04-1.07). On this basis, the number and weight average molecular weights and dispersity index can be expressed as a function of the percentage of non-associated polymer,  $x$ . Given that the overall mass balance of species is represented by

$$[\text{LE}]_0 = [\text{LE}]_f + [\text{LE}]_{\text{aggr}} + [\text{PS}] \quad (5)$$

while  $[\text{LE}]_0$ ,  $[\text{LE}]_f$ ,  $[\text{LE}]_{\text{aggr}}$  and  $[\text{PS}]$  are the concentrations of the individual species, then it follows that the percentage of non-associated polymer in relation to all species,  $x$ , is given by

$$x = 100 \cdot ([\text{LE}]_f + [\text{PS}]) / [\text{LE}]_0$$

If the apparent molecular weight of the non-aggregated polymeric chains is  $m$  ( $\text{g mol}^{-1}$ ) then that of the



**Figure 2** Zero shear viscosity, dispersity index, number average and weight average molecular weights as a function of the percentage of two-fold aggregated monodisperse chains. ■,  $M_w$ ; ◆,  $M_n$ ; ○, zero shear viscosity assuming the entanglement regime; ◇, zero shear viscosity assuming non entanglement regime; ×, dispersity index. The y-axis is in arbitrary units

aggregated chains is  $nm$  ( $\text{g mol}^{-1}$ ) when the degree of association of the polyanions is  $n$ . When a polystyryllithium aggregate of molecular weight  $nm$  is destroyed by reaction with the solvent,  $n$  chains of molecular weight  $m$  are created. Thus, the first three moments,  $\lambda_0$ ,  $\lambda_1$  and  $\lambda_2$  of the molecular weight distribution are given by

$$\lambda_0 = \sum n_i = [\text{LE}]_0(100 + (n-1)x)/(n100)$$

$$\lambda_1 = \sum n_i M_i = [\text{LE}]_0 m$$

$$\lambda_2 = \sum n_i M_i^2 = [\text{LE}]_0 \bar{n} m^2$$

where  $\bar{n}$  is the mean degree of aggregation

$$\bar{n} = n(100-x)/100 + 1(x/100) \quad (7)$$

The apparent molecular weights and the dispersity index are hence

$$Mn = n100m/(100 + (n-1)x) \quad (8)$$

$$Mw = \bar{n}m \quad (9)$$

$$Dn = \bar{n}(100 + (n-1)x)/(n100) \quad (10)$$

Using the expression of  $Mw$  in equation (9) for  $n = 2$ , it is possible to compute the theoretical variation of the viscosity with the non-associated polymer fraction in the entanglement regime ( $\phi_p Mw > Mc$ ) with

$$\eta = K'(\bar{n}m)^{3.4} = K'[(200-x)m/100]^{3.4} \quad (11)$$

When  $\phi_p Mw < Mc$ , which is the case for the non-entanglement regime, then

$$\eta = K''(\bar{n}m) = K''[(200-x)m/100] \quad (12)$$

For  $n = 2$  the theoretical variations of  $Mn$ ,  $Mw$ ,  $Dn$  with  $x$ , and  $\eta$  for the two regimes, are illustrated in Figure 2 (ordinate is in arbitrary units for clarity of presentation).

#### THE EQUILIBRIUM CONSTANT FOR THE ASSOCIATION/DISSOCIATION PROCESS ( $K_d$ )

The variation of the viscosity with the unassociated polymer fraction  $x/100$  follows either equation (11) or equation (12), thus the ratio of initial/final viscosity should be

$$\eta_0/\eta_\infty = \bar{n}_0^a \quad (13)$$

where the value of  $a$  is either 3.4 or 1, respectively. If the polyanions are predominantly aggregated as dimers (i.e.  $n = \bar{n}_0 = 2$ ) and also if  $a = 3.4$  then the ratio of initial/final viscosity will be  $2^{3.4} = 10.56$ . If  $a = 1$  then the ratio will be  $\bar{n}_0$ . If one adopts the assumption of two-fold aggregation ( $n = 2$ ) then  $\bar{n}$  at any time must be in the range 1–2.

The value of the ratio of initial/final viscosity obtained experimentally in this work was in the range 2.7–3.4. Given this finding, it is necessary to assume that the entanglement regime predominates if two-fold aggregation of ion-pairs occurs. The molecular weights and polymer weight fractions used in the experiments reported in this paper are such that the entanglement regime hypothesis can be applied with a reasonable degree of confidence.

The initial percentage of non-associated polymer prior to any 'killing' by transfer reactions can be found from equations (7) and (13) where

$$n(100-x_0)/100 + 1(x_0/100) = \bar{n}_0 = (\eta_0/\eta_\infty)^{1/a} \quad (14)$$

Under the initial conditions relevant to this work where no terminated polymer chains are present, the equilibrium constant for the association/dissociation process ( $K_d$ ) can be expressed in terms of  $x_0$ . At any given time during the transfer process, the total live polyanion concentration is given by

$$[\text{LE}]_t = [\text{LE}]_f + [\text{LE}]_{\text{aggr}}$$

The fraction of free living polystyrylanions  $\alpha$  can also be defined as

$$\alpha = [\text{LE}]_f/([\text{LE}]_f + [\text{LE}]_{\text{aggr}}) = [\text{LE}]_f/[\text{LE}]_t \quad (15)$$

The equilibrium constant ( $K_d$ ) can be expressed in terms of  $\alpha$  as

$$K_d = \alpha^n [\text{LE}]_0 / (1 - \alpha) \quad (16)$$

From the definitions of  $x$  and  $\alpha$ , at time zero

$$\alpha_0 = x_0/100$$

$$K_d = (x_0/100)^n [\text{LE}]_0 / (1 - x_0/100) \quad (17)$$

## TRANSFER REACTION RATE

The viscosity of the solution can be linked to the rate of the transfer reaction through the percentage of the aggregated species,  $100 - x$ , since it is this quantity that appears in the rate equation. The kinetic analysis is based on reactions (a) and (b) with the assumptions that (i) only the free polystyrylanions engage in the transfer reaction, (ii) these equilibrate rapidly with their aggregated counterparts, and, (iii) the solvent,  $S$ , is present in sufficient molar excess for  $[S]$  to be constant with time.

The rate of the transfer reaction can be expressed as

$$d[LE]_t/dt = -k_{tr}[LE]_f[S] = -d[PS]/dt \quad (18)$$

where  $k_{tr}$  is the true rate constant for the transfer reaction. The transfer reaction is internally first order with respect to the free polyanions [equation (18)]. Our purpose here is to derive a rate equation in terms of the aggregated polyanions, since this is related to  $x$ . By combining equations (5), (15) and (16),  $[LE]_t$  and  $[LE]_f$  are eliminated from equation (18) by substitution to give a rate expression in terms of  $[LE]_{aggr}$  as shown in equation (19) for  $n = 2$

$$\frac{d[LE]_{aggr}}{dt} \left( \frac{1}{2\sqrt{[LE]_{aggr}}} + \frac{1}{\sqrt{K_d}} \right) = -k_{tr}[S]\sqrt{[LE]_{aggr}} \quad (19)$$

Integration of equation (19) gives

$$\frac{1}{2} \ln \frac{100 - x}{100 - x_0} + \frac{2\sqrt{[LE]_0}}{\sqrt{K_d}} \times \left( \sqrt{\frac{100 - x}{100}} - \sqrt{\frac{100 - x_0}{100}} \right) = -k_{tr}[S]t \quad (20)$$

This rate equation is linked to viscosity measurements by combining equations (1) and (11) to give

$$t_f = t_{f\infty} [1 + (100 - x)/100]^{3.4} \quad (21)$$

Hence

$$\frac{-1}{[S]} \left( \ln \sqrt{\frac{y}{y_0}} + 2\sqrt{\frac{[LE]_0}{K_d}} (\sqrt{y} - \sqrt{y_0}) \right) = k_{tr}t \quad (22)$$

where

$$y = \left( \frac{t_f}{t_{f,\infty}} \right)^{1/3.4} - 1 \quad \text{and} \quad y_0 = \left( \frac{t_{f,0}}{t_{f,\infty}} \right)^{1/3.4} - 1$$

If the assumptions which have been made are correct, equation (22) should be that of a straight line and plotting the left-hand side (LHS) against  $t$  allows  $k_{tr}$  to be obtained from the gradient.

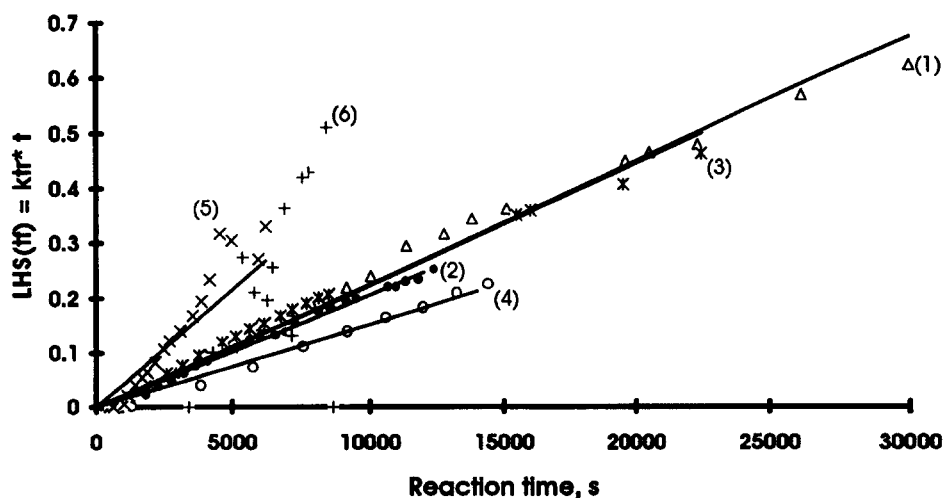
The experiment conditions used in the transfer experiments are summarized in *Table 1*.

## RESULTS AND DISCUSSION

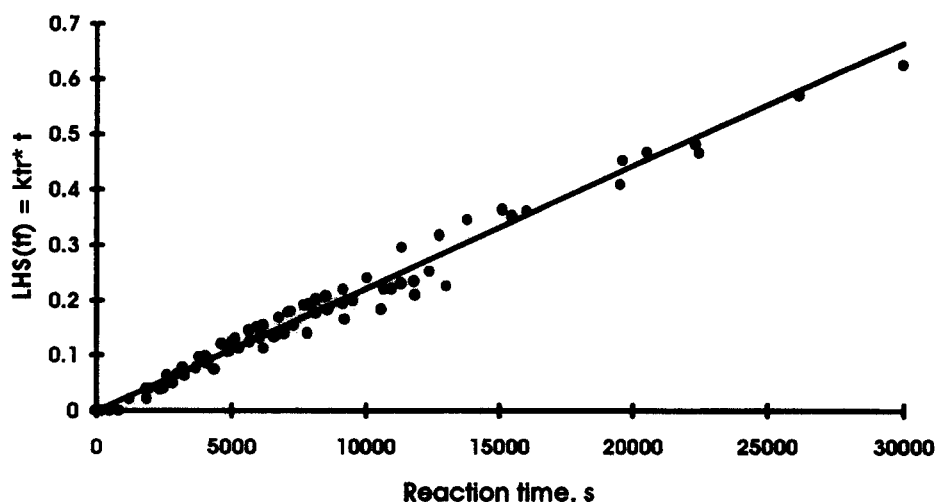
The plots of the LHS of equation (22) against time for polymers of different molecular weights and solution concentrations at temperatures in the region of 70°C are shown in *Figure 3*. It can be seen that in all cases straight line plots are obtained which makes it possible to obtain rate constants from the slopes of the plots. However, it is only in the case of experiments 1, 2 and 3 that the slopes are indistinguishable within experimental error, and these plots appear to vindicate the assumptions which have been made in arriving at equation (22). In the case of experiment 4, there appears to be a short induction period prior to the start of the reaction, but the final slope of the plot is similar to that in experiments 1–3, and hence a similar rate constant is obtained to those found in experiments 1–3. The induction period probably relates to the fact that  $t$  in equation (22) has been taken as the half-way point in the fall time in each of the falling

**Table 1** Falling ball viscometry measurements for the chain transfer rate constant,  $k_{tr}$ , for polystyryllithium in ethylbenzene [PS] and [S] are the polystyrene and solvent concentrations, respectively, and  $[PS] = [LE]_0$

No.	Temp. °C	[PS]		[S] mol l <sup>-1</sup>	Mn g mol <sup>-1</sup>	t <sub>0</sub> /t <sub>∞</sub>
		w/w%	mol l <sup>-1</sup> × 10 <sup>2</sup>			
1	71.0	59.1	1.842	3.434	28 600	2.94
2	70.5	46.2	0.923	4.497	44 300	2.99
3	70.0	35.7	0.252	6.910	161 300	3.39
4	70.0	58.6	2.190	4.373	30 000	2.68
5	71.7	15.7	—	6.934	—	1.49
6	70.0	68.6	—	2.646	—	1.67



**Figure 3** Falling ball viscometric experiments to measure the rate constant for the transfer reaction. The left-hand side of equation (22) (LHS) is plotted against reaction time. Captions (1)–(6) refer to experiments listed in *Table 1*



**Figure 4** Determination of the rate constant for the transfer reaction. The left-hand side of equation (22) (LHS) is plotted against reaction time. The slope equals  $k_{tr}$ . Temperature 70–71°C; polymer w/w = 36–59%;  $M_n = 21$ –161 kg mol<sup>-1</sup>; slope =  $(2.21 \pm 0.05) \times 10^{-5}$  l mol<sup>-1</sup> s<sup>-1</sup>

**Table 2** Equilibrium constant of association and chain transfer rate constant for polystyryllithium in ethylbenzene. Experiments are evaluated individually

No.	$\bar{n}_0$	$\alpha_0$	$K_d$ /[PS]	$K_d \times 10^2$ mol l <sup>-1</sup>	$k_{tr} \times 10^5$ l mol <sup>-1</sup> s <sup>-1</sup>	$k'_{tr} \times 10^6$ (l mol <sup>-1</sup> ) <sup>0.5</sup> s <sup>-1</sup>
1	1.37	0.627	1.05	1.94	2.25	3.14
2	1.38	0.619	1.01	0.931	2.06	1.99
3	1.43	0.568	0.75	0.189	2.23	0.97
4	1.34	0.663	1.31	2.86	1.53	2.58
5	1.12	0.876	6.16	—	4.32	—
6	1.16	0.838	4.32	—	—	—

ball experiments. A similar error can be seen in each of the plots when the data at low reaction times is examined closely. The slopes of the plots for experiments 5 and 6 show poor agreement with all others. The results from experiment 6 are readily explained as the time taken to carry out the viscosity experiment is long relative to the rate of the transfer reaction when the solids content of the reaction mixture is high (69% w/w), making calculations based on the ratio of  $t_{fo}/t_{\infty}$  invalid. It is not immediately obvious why the results of experiment 5 are not in agreement with those of experiments 1–4. The only significant difference in the conditions used in this experiment is that the solids content of the solution was significantly lower than in other experiments. It is possible that the lower concentration of polymer reduces the entanglement condition in the solution to a level which makes the entanglement regime assumption invalid. The impact of solids content on the measured viscosity of a polymer solution containing polymer of a fixed molecular weight is being explored further.

The experimental results for experiments 1–4 have been combined in Figure 4 from which the mean  $k_{tr}$  is  $(2.21 \pm 0.05) \times 10^{-5}$  l mol<sup>-1</sup> s<sup>-1</sup>.

The value for  $K_d$  for the polyanion equilibrium reactions at 70°C has been calculated from equation (17) and the values at different live-end concentrations are shown in Table 2. The assumption which has been made is that polystyrylanions dimerize in hydrocarbon solvents. The magnitude of  $K_d$  will depend on the veracity of this assumption, but the method which has been employed is applicable irrespective of the degree of aggregation; the latter has simply to be substituted into equation (17).

## CONCLUSIONS

The falling ball viscometric method is simple to use and gives reproducible results under the conditions used in this work. Because the total viscosity measurement time is of the order of several minutes, the mid-point of the total fall time was taken as the flow time for each viscosity measurement during the overall transfer process. This method is only acceptable when the total reaction time is very long relative to the measurement time.

The weight of evidence from published work is that polystyryllithium is two-fold aggregated in hydrocarbon solvents. There are no similar data available for ethylbenzene at the relatively high temperatures used in this work and for this reason it has been assumed that the predominant form of aggregate is also a dimer. Given this assumption, it has been possible to arrive at a general expression which allows  $K_d$  to be calculated for any known degree of association. The value of the equilibrium constant for the rapid association–dissociation equilibrium of polystyryllithium and its dimer in ethylbenzene at 70°C was found to be in the range  $0.19$ – $2.9 \times 10^{-2}$  depending on the experimental conditions.

Once the order of magnitude of  $K_d$  had been obtained, it was possible to calculate the rate constant for the transfer reaction between polystyryllithium and ethylbenzene ( $k_{tr}$ ) from the rate of change of viscosity. The value found for  $k_{tr}$  at 70°C was  $(2.21 \pm 0.05) \times 10^{-5}$  l mol<sup>-1</sup> s<sup>-1</sup>. It was possible to obtain a more precise value for  $k_{tr}$  since the total data set from four experiments (nos. 1–4), which were in good agreement, could be used.

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