

# The shear viscosity dependence on concentration, molecular weight, and shear rate of polystyrene solutions\*)

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**Abstract:** The solution viscosity of narrow molecular weight distribution polystyrene samples dissolved in toluene and trans-decalin was investigated. The effect of polymer concentration, molecular weight and shear rate on viscosity was determined. The molecular weights lay between  $5 \cdot 10^4$  and  $24 \cdot 10^6$  and the concentrations covered a range of values below and above the critical value  $c^*$ , at which the macromolecular coils begin to overlap. Flow curves were generated for the solutions studied by plotting  $\log \eta$  versus  $\log \dot{\gamma}$ . Different molecular weights were found to have the same viscosity in the non-Newtonian region of the flow curves and follow a straight line with a slope of  $-0.83$ . A plot of  $\log \eta_0$  versus  $\log M_w$  for 3 wt-% polystyrene in toluene showed a slope of approximately 3.4 in the high molecular weight regime. Increasing the shear rate resulted in a viscosity that was independent of molecular weight. The slope  $d(\log \eta)/d(\log M_w)$  was found to be zero for molecular weights at which the corresponding viscosities lay on the straight line in the power-law region.

On the basis of a relation between  $\eta_{sp}$  and the dimensionless product  $c \cdot [\eta]$ , simple three-term equations were developed for polystyrene in toluene and *t*-decalin to correlate the zero-shear viscosity with the concentration and molecular weight. These are valid over a wide concentration range, but they are restricted to molar masses greater than approximately 20 000. In the limit of high molecular weights the exponent of  $M_w$  in the dominant term in the equations for both solvents is close to the value 3.4. That is, the correlation between  $\eta_{sp}$  and  $c \cdot [\eta]$  results in a slope  $d(\log \eta_{sp})/d(\log c \cdot [\eta])$  of approximately 3.4/*a* at high values of  $c \cdot [\eta]$  where *a* is the Mark-Houwink constant. This slope of 3.4/*a* is also the power of *c* in the plot of  $\eta_0$  versus *c* at high concentrations.

**Key words:** Polymer solution, polystyrene, shear viscosity, master curve

## Notation

<i>a</i>	Mark-Houwink constant	$\dot{\gamma}$	shear rate ( $s^{-1}$ )
$B_1, B_2, B_n$	constants	$\dot{\gamma}_{crit}$	critical shear rate ( $s^{-1}$ )
<i>c</i>	concentration ( $g \cdot cm^{-3}$ )	$\eta$	viscosity ( $Pa \cdot s$ )
$c^*$	critical concentration ( $g \cdot cm^{-3}$ )	$\eta_0$	zero-shear viscosity ( $Pa \cdot s$ )
<i>K, K'</i>	constants	$\eta_s$	solvent viscosity ( $Pa \cdot s$ )
$K_H$	Huggins constant	$\eta_{sp}$	specific viscosity
<i>M</i>	molecular weight	$[\eta]$	intrinsic viscosity ( $cm^3 \cdot g^{-1}$ )
$M_c$	critical molecular weight	$\eta'$	dynamic viscosity ( $Pa \cdot s$ )
$M_n$	number-average molecular weight	$ \eta^* $	complex dynamic viscosity ( $Pa \cdot s$ )
$M_w$	weight-average molecular weight	$\omega$	angular frequency ( $rad/s$ )
<i>n</i>	slope $d(\log \eta_{sp})/d(\log c \cdot [\eta])$ at high $c \cdot [\eta]$	$\rho$	density of polymer solution ( $g \cdot cm^{-3}$ )
<i>PS</i>	polystyrene	$\sigma_{12}$	shear stress ( $Pa$ )
<i>T</i>	temperature (K)		

\*) Dedicated to Prof. Dr. J. Schurz on the occasion of his 60<sup>th</sup> birthday.

\*\*) Excerpt from the dissertation of Reinhard Kniewske: „Bedeutung der molekularen Parameter von Polymeren auf die viskoelastischen Eigenschaften in wäßrigen und nicht-wäßrigen Medien“, Technische Universität Braunschweig 1983.

## 1. Introduction

Studies of the properties of polymers in dilute solution by classical techniques of polymer characterization (light scattering, viscometry, ultracentrifugation,

etc.) yield information on the solution structure and conformation of single macromolecules, as well as on the thermodynamic interactions with the solvent. In the dilute concentration regime the measured quantities vary linearly with concentration,  $c$ , allowing one to extrapolate to vanishing  $c$ . A deviation from this linear dependence on concentration is observed above a critical concentration,  $c^*$ . The behaviour of the dissolved polymer is then more complicated, depending not only on the interaction with the solvent molecules and intramolecular interactions between polymer segments, but also on the intermolecular interactions between different macromolecules. In a previous study [1], the system polystyrene-toluene was investigated in the dilute concentration regime and the conformation and solution structure results were compared with corresponding findings for the system polyacrylamide-water [2], which exhibits similar solution behaviour.

The aim of this report is to present further information on the behaviour of polystyrene, especially in moderately concentrated solutions in which intermolecular interactions and entanglements are of increasing importance. The nature of entanglements at concentrations above the critical value  $c^*$  leads to the viscoelastic properties observable in shear flow experiments. The viscous part of the flow behaviour of a polymer solution is usually represented by the zero-shear viscosity,  $\eta_0$ , which depends on the concentration and molecular weight of the dissolved polymers. It has been found that if  $\eta_0$ , obtainable from shear experiments at relatively low shear rates,  $\dot{\gamma}$ , is plotted against the molecular weight in a double logarithmic plot, then the data follow two straight lines, which intersect at a critical molecular weight  $M_c$ . For concentrated solutions and melts one obtains [3]

$$\begin{aligned}\eta_0 &= K \cdot M^{1.0} & \text{for } M < M_c, \\ \eta_0 &= K' \cdot M^{3.4} & \text{for } M > M_c.\end{aligned}$$

The change in  $M$  dependence occurs smoothly but over a relatively narrow range in molecular weight.

The  $M^{3.4}$  behaviour of melts and concentrated polymer solutions is thought to be due to the existence of entanglements between the macromolecules [3].  $M_c$  is the molecular weight at which chain entanglements become important. Once the chains are long enough to become entangled, flow becomes much more difficult because forces applied to one polymer chain are transmitted to and distributed among many other chains. The slope of 3.4 is also predicted by the tube model (reptation concept) [4]. In some cases [5–7], the slope for  $M > M_c$  appears to be somewhat higher than 3.4, however, the 3.4 power is supported by data from

a remarkably wide range of linear polymers [3, 8, 9]. In the case of melts, the linear dependence of  $\eta_0$  on  $M_w$  below  $M_c$  is assumed to be due to the existence of small macromolecules that cannot build up entanglements. For moderately concentrated solutions, one similarly obtains two regimes with different slopes, however, the powers of  $M$  can be lower than 1.0 and 3.4. Furthermore, the transition region from the lower to the higher slope is broadened. The critical molecular weight,  $M_c$ , for polymer solutions is found to be dependent on concentration (decreasing as  $c$  increases), although in some cases the variation appears to be very small [6, 10].

An increase of the shear rate above a critical value,  $\dot{\gamma}_{\text{crit}}$ , leads to a deviation of the viscosity from its zero-shear value so that  $\eta$  becomes a decreasing function of  $\dot{\gamma}$ . Increasing concentration or increasing molecular weight leads to a decrease in the value of  $\dot{\gamma}_{\text{crit}}$ . The first part of this paper describes the dependence of the solution viscosity of polystyrene in toluene on  $c$  and  $M$ , followed by an evaluation of the shear rate effect on the shape of a  $\log \eta$  vs.  $\log M_w$  plot at constant concentration. The second part presents a correlation of the zero-shear viscosity with concentration and molecular weight for polystyrene in toluene and *t*-decalin on the basis of a simple equation developed for aqueous polyacrylamide solutions [6]. A number of useful studies have been published describing correlations between the zero-shear viscosity and either the concentration [11–13] or the concentration and molecular weight; some studies considered concentrated solutions [14–16] and others dilute solutions [17–19]. In this work, the concentration regime covered values from far below to far above the critical concentration,  $c^*$ , at which the macromolecular chains begin to overlap. It is assumed that below  $c^*$  the polymer chains can be considered to be isolated particles (particle solution), whereas above  $c^*$ , the coils can be interpenetrated or entangled [1, 2]. The molecular weights of polystyrene samples studied ranged from  $5 \cdot 10^4$  to  $23 \cdot 10^6$ .

## 2. Experimental

The polystyrene samples with a narrow molecular weight distribution ( $M_w/M_n = 1.06 - 1.30$ ) used in this study were available commercially from Pressure Chemical Co. (Pittsburgh, USA) and Polymer Laboratories Ltd. (Church Stretton, UK). The detailed characterization data for these polymers from light scattering and viscometry measurements are described elsewhere [1]. The weight average molecular weights,  $M_w$ , and intrinsic viscosities,  $[\eta]$ , are listed in table 1 in section 3.3. A precise characterization of all samples

used was necessary to obtain accurate information on the molecular-weight dependence of the measured viscosities.

To measure the shear viscosities four types of rotational viscometers were used, namely a "Zimm-Crothers" viscometer ( $\dot{\gamma} \approx 10^{-3} \text{ s}^{-1}$ ), a Low Shear 100 viscometer<sup>1)</sup> ( $\dot{\gamma} = 10^{-4}$  to  $5 \text{ s}^{-1}$ ), a Haake rotational viscometer RV3<sup>2)</sup> with system HS1 ( $\dot{\gamma}$  up to  $5300 \text{ s}^{-1}$ ), and the Mechanical Spectrometer System 4<sup>3)</sup> with a cone and plate system ( $\dot{\gamma} = 10^{-2}$  to  $2500 \text{ s}^{-1}$ ). All measurements were performed at  $25^\circ \text{C}$  with reagent grade solvents. The solvent viscosities of toluene and *t*-decalin (99% trans) were measured at  $25^\circ \text{C}$  to be  $0.588 \text{ mPa} \cdot \text{s}$  and  $2.42 \text{ mPa} \cdot \text{s}$  respectively.

### 3. Results and discussion

#### 3.1. Flow curves of polystyrene in toluene

##### 3.1.1. Concentration dependence

Polymers in solution or as melts exhibit a shear rate dependent viscosity above a critical shear rate,  $\dot{\gamma}_{\text{crit}}$ . The region in which the viscosity is a decreasing function of shear rate is called the non-Newtonian or power-law region. As the concentration increases, for constant molecular weight, the value of  $\dot{\gamma}_{\text{crit}}$  is shifted to lower shear rates. Below  $\dot{\gamma}_{\text{crit}}$  the solution viscosity is independent of shear rate and is called the zero-shear viscosity,  $\eta_0$ . Flow curves (plots of  $\log \eta$  vs.  $\log \dot{\gamma}$ ) for a very high molecular weight polystyrene in toluene at various concentrations are represented in figure 1. The transition from the shear-rate independent to the shear-rate dependent viscosity occurs over a relatively narrow region due to the narrow molecular weight distribution of the *PS* sample.

##### 3.1.2. Molecular weight dependence

Qualitatively, the same behaviour is observed for the flow curves at a fixed polymer concentration but various molecular weights (figure 2). The shear rate dependence of the viscosity begins at lower  $\dot{\gamma}$  as the molecular weight increases. However, for the very high molecular weight 3 wt-% toluene solutions used in this study, the viscosities in the non-Newtonian region become equal for all the samples with various molar masses and follow a straight line of slope  $-0.83$ .

This slope is in good agreement with the theory of Graessley ( $-0.82$ ) [3] and other experimental data [20–22].

<sup>1)</sup> Contraves AG, Zürich (Switzerland).

<sup>2)</sup> Haake Meß-Technik GmbH u. Co., Karlsruhe (FRG).

<sup>3)</sup> Rheometrics Inc., Springfield, New Jersey (USA).

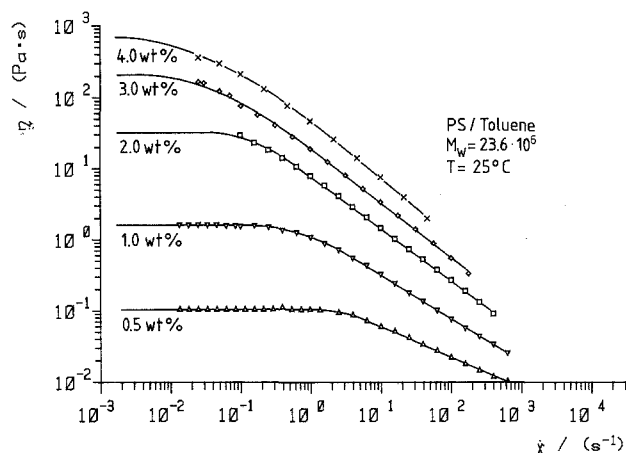


Fig. 1. Viscosity versus shear rate for polystyrene  $23.6 \cdot 10^6$  in toluene for various concentrations at  $25^\circ \text{C}$ .

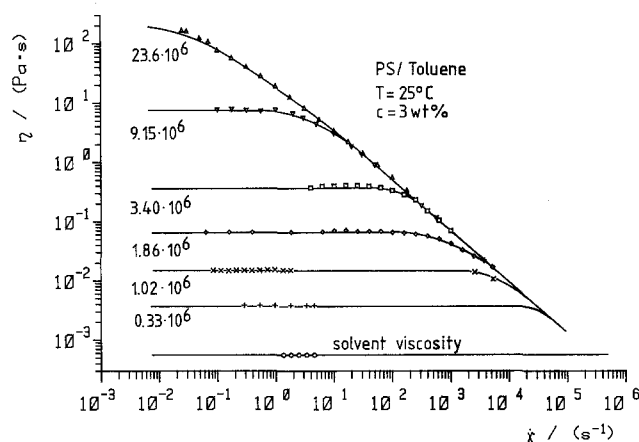


Fig. 2. Viscosity versus shear rate for polystyrene samples of various molar masses in toluene at  $25^\circ \text{C}$ .

For the system polystyrene in *n*-butylbenzene, a limiting slope of  $-0.83$  was found by Abdel-Alim et al. [20] by evaluating the non-Newtonian region using a dimensionless coordinate master curve plot. Attané et al. [21] observed a slope of about  $-0.85$  for polystyrene in dibutylphthalate at sufficiently high concentrations. Ballauf [22] determined a slope of  $-0.8$  for polystyrene in toluene, however, for polystyrene in *t*-decalin a smaller value of  $-0.5$  was found [22, 23]. The coincidence of the viscosities of different molecular weights at high shear rates has also been reported by Stratton [24] and Onogi et al. [25a] for polystyrene melts, and by Onogi and coworkers [25b] for polymethylmethacrylate and polyvinylacetate. For polystyrene melts, a limiting slope of  $-0.82$  was observed by Stratton [24], whereas Onogi et al. [25a] found a slope of  $-0.5$  by plotting the dynamic viscosity,  $\eta'$ , versus the angular frequency,  $\omega$ , in a double logarithmic plot. It has been concluded that the slope for thermodynamic good solvents is about  $-0.8$  and for poor solvents about  $-0.5$  [22].

The independence of viscosity on molecular weight at high shear rates is of fundamental importance, since it follows that it is not possible to distinguish between different samples if the viscosity is measured in the

power-law region. Moreover, a further conclusion can be drawn from figure 2, namely, that the evaluation of molecular weight degradation due to shear forces is impossible in the non-Newtonian region because samples with different molar mass all exhibit the same viscosity at a given shear rate. Degradation can only be observed if the shear rate is lowered to values at which zero-shear conditions exists. In this context it must be noted that light scattering measurements made in our laboratory showed that the very high molecular weight polystyrenes were not degraded by prolonged shearing at the highest shear rates used in this study. Abdel-Alim et al. [20] checked for possible polymer degradation by GPC analysis. No difference was detected between the polymer samples before and after shearing up to  $\dot{\gamma} \approx 10^5 \text{ s}^{-1}$  and so degradation could be excluded. The evaluation of chain scission by increasing the shear rate to the highest value and then immediately reducing the shear rate to the lowest value [23] can not give adequate information about polymer degradation because the zero-shear viscosity is not reached. The completion of the flow curves up to very high shear rates for the polymer samples studied (figure 1 and 2) was not possible in the present case, because of the limitations of the transducer sensitivity. On the basis of measurements on other polymer-solvent systems using other rheometers up to higher shear rates ( $\approx 10^5 \text{ s}^{-1}$ ) [23], which showed no indication of an onset of a second Newtonian region, we believe that the power-law regime in figure 2 can be linearly extrapolated to higher shear rates. The appearance of the start of a second Newtonian region, found in some cases at very high shear rates, may be due to flow instabilities causing a deviation from laminar flow conditions [23].

The lack of dependence of viscosity on molar mass in the power-law regime is also clear in the well-known plot of  $\log \eta$  versus  $\log M_w$  if the viscosity is plotted for various shear rates or shear stresses. Figure 3 presents the molecular-weight dependence of  $\eta$  for 3 wt-% polystyrene solutions in toluene at various shear rates. For high molecular weights the zero-shear viscosities depend on  $M_w$  to the power of approximately 3.4.

As the shear rate increases to  $10^5 \text{ s}^{-1}$ , the non-Newtonian region is reached for the samples with  $M_w$  equal to  $23.6 \cdot 10^6$  and  $9.15 \cdot 10^6$ . For further increases in shear rate, lower molecular weight polymers also exhibit the same viscosity at a given shear rate (see fig. 2) and the slope in the  $\log \eta$  vs.  $\log M_w$  plot becomes zero for  $\dot{\gamma} = \text{const.}$ , as shown in figure 3. This shear-rate-dependent viscosity behaviour could not be verified up to day by experimental measurements on polymer solutions, probably because of a lack of very high molecular weight fractions with narrow molecular

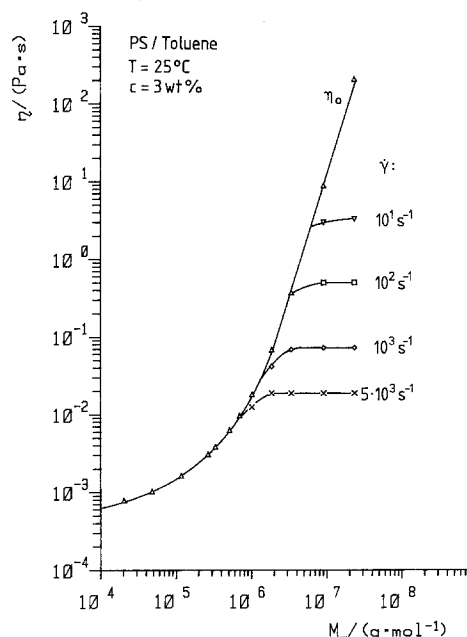


Fig. 3. Viscosity dependence on molecular weight  $M_w$  for polystyrene in toluene at various shear rates.  $c = 3 \text{ wt-\%}$ ;  $T = 25^\circ \text{C}$ .

weight distributions. For polymer melts, however, such molecular-weight-independent viscosities at very high shear rates have already been reported by Casale et al. [7] for polymethylmethacrylate, by Stratton [24] and Onogi et al. [25a] for polystyrene, and by Onogi et al. for polymethylmethacrylate and polyvinylacetate. Although Onogi and coworkers [25] plotted  $\log |\eta^*|$  versus  $\log M_w$  for various angular frequencies, their findings are in agreement with our results in figure 3, since the complex dynamic viscosities  $|\eta^*|$  coincide with the shear viscosities  $\eta$  (satisfying the Cox-Merz rule).

Several shapes of the  $\log \eta$  vs.  $\log M_w$  plots, in which  $\dot{\gamma}$  is the parameter, have been described in the literature (see fig. 4). It is often reported that beyond the critical molecular weight  $M_c$  increasing the shear rate leads to lower slopes in the  $\eta - M_w$  plot with a limiting slope of one [24, 25a, 26]. Such behaviour is shown schematically in figure 4a. The type of  $\eta - M_w$  behaviour shown in figure 4b would be expected if  $M_c$  were to increase as  $\dot{\gamma}$  or  $\sigma_{12}$  increased. The slope would remain equal to 3.4 for molecular weights above  $M_c$ , but  $M_c$  would vary with the shear rate [26, 28]. Another possible form is presented in figure 4c. The straight line for  $\dot{\gamma} \rightarrow 0$  may become curved as  $\dot{\gamma}$  increases and reach asymptotic values of viscosity at very high molecular weights [26, 28]. This type of shear rate influence on the viscosity, however, should have a linear limit with the slope one [27, 28], as shown by the dashed line in figure 4c. The shear rate dependence of the viscosity (slope zero for high  $\dot{\gamma}$  and  $M_w$ ) shown in figure 3 and also found for polystyrene [24, 25a], polymethylmethacrylate [7, 25b] and polyvinylacetate [25b] melts leads to the form presented in figure 4d. We suggest that the molecular weight independence of viscosity at high shear rates will always be

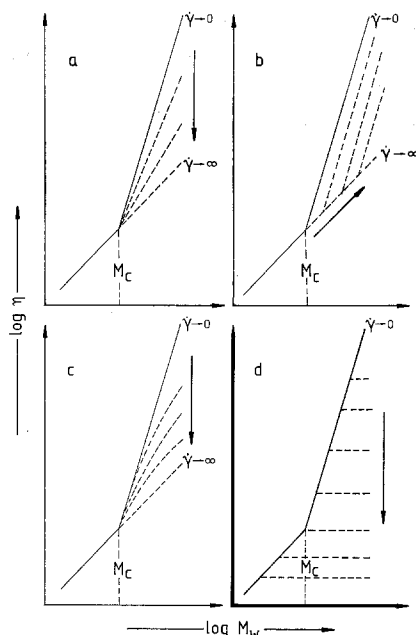


Fig. 4a–d. Variations of the dependence of viscosity on molar mass with increasing shear rate. Solid lines denote  $\eta_0$ . Dashed lines denote higher shear rates, which increase in the direction of the arrows.

found for polymer solutions and melts provided that the molecular weights of the samples are sufficiently high and the molecular weight distributions sufficiently narrow, or the accessible shear rate range is great enough.

The behaviour shown in figure 4a, which has been observed in several cases [29], is possibly due to the use of polymer samples with broad distributions and relatively low molecular weights. The broadening of the molar mass distribution results in a broadening of the transition region in flow curves from the zero-shear viscosity to the non-Newtonian regime [30]. Based on this behaviour the flow curves of samples with different molecular weights, but the same concentration, will be equal only at higher shear rates; but such high shear rates can normally not be obtained due to experimental limitations.

Figure 4d implies that a molecular-weight-independent viscosity at very high shear rates occurs both above and below the critical molecular weight  $M_c$ . The figure was constructed on the assumption that a single macromolecule in a dilute solution exhibits non-Newtonian flow characteristics at very high shear rates [31]. This needs to be verified by experimental measurements. For melts, however, Onogi et al. [25a] have observed that polystyrene samples having molecular weights much lower than  $M_c$  show non-Newtonian behaviour i.e. shear thinning at high shear rates. Thus, the behaviour shown in figure 4d is to be expected.

### 3.2. $\eta_0 - M - c$ correlation

In the preceding sections, the dependence of the viscosity on concentration and molecular weight has been presented for polystyrene in toluene at various

shear rates. In this section the zero-shear viscosity,  $\eta_0$ , a definitive parameter for the description of the viscous part of a polymer solution, is correlated with the concentration and molecular weight, because of the fundamental and practical importance of such a superposition or master curve. However, the usual plot of  $\log \eta_0$  versus  $\log (c \cdot M_w)$  does not lead to a satisfactory correlation for every polymer-solvent system [3, 32], because  $\eta_0$  depends on different powers on  $c$  and  $M_w$ . A more successful method is to correlate the viscometric behaviour with the dimensionless product of  $c \cdot [\eta]$  or  $c \cdot M^a$  [6, 19, 26b, 33–35], where  $[\eta]$  is the intrinsic viscosity. Indeed, the zero-shear values,  $\eta_0$ , or the specific viscosities,  $\eta_{sp}$ , can be described by a single master curve for a given polymer-solvent system if plotted against  $c \cdot [\eta]$ , as shown recently for the system polyacrylamide-water [6]. The simple equation, developed for the dependence of the viscosity on  $M_w$  and  $c$  on the basis of a master curve  $\log \eta_0$  vs.  $\log (c \cdot [\eta])$  [6] is used in this study to derive an  $\eta_0 - M - c$  relationship for polystyrene in the good solvent toluene and the pseudo-ideal (theta) solvent *t*-decalin. The procedure is described below.

The zero-shear viscosity,  $\eta_0$ , depends on the concentration and molecular weight of the dissolved polymer i.e.,

$$\eta_0 = f(M, c), \text{ solvent, pressure, } M_w/M_n. \quad (1)$$

A general virial equation can be written for the specific viscosity when the zero-shear value is expressed in its specific form

$$\eta_{sp} = \sum_{K=1}^n [B_K (c \cdot [\eta])^K] \quad (2)$$

where

$$\eta_{sp} = \frac{\eta_0 - \eta_s}{\eta_s}. \quad (3)$$

When all parameters having exponents higher than 2, are collected in one term, one obtains

$$\eta_{sp} = B_1 \cdot c \cdot [\eta] + B_2 (c \cdot [\eta])^2 + B_n (c \cdot [\eta])^n. \quad (4)$$

The Huggins-equation [36] is a truncated version of eq. (4) and is defined as follows:

$$\eta_{sp} = c \cdot [\eta] + K_H (c \cdot [\eta])^2 + B_n (c \cdot [\eta])^n. \quad (5)$$

A plot of  $\log \eta_{sp}$  versus  $\log (c \cdot [\eta])$  results in a linear relationship for high values of  $c \cdot [\eta]$ . The unknown quantities,  $B_n$  and  $n$  can be obtained from this linear regression.

A correlation of  $\eta_{sp}$  with concentration and molecular weight can now be achieved using an  $[\eta] = KM^a$  relation and replacing  $[\eta]$  in eq. (5) by its molecular

weight dependent form to give

$$\eta_0 = \eta_s (c \cdot K \cdot M^a + c^2 K^2 M^{2a} K_H + c^n K^n M^{n \cdot a} \cdot B_n + 1). \quad (6)$$

Thus, to derive an  $\eta_0 - M - c$  relationship it is necessary to know:

- $K_H$ , the Huggins constant,
- $B_n$  and  $n$ , from a linear regression analysis at high  $c \cdot [\eta]$  values of the plot  $\log \eta_{sp}$  vs.  $\log (c \cdot [\eta])$ , and
- the  $[\eta] - M$  relationship for the polymer-solvent system.

### 3.3. $\eta_0 - M - c$ relationship for PS in toluene and *t*-decalin

The experimental zero-shear viscosities obtained for different molecular weights and concentrations in toluene and trans-decalin are plotted as  $\log \eta_{sp}$  against  $\log c \cdot [\eta]$  in figure 5. The data used in this figure are listed in tables 1 and 2. The data sets of each solvent are fitted by a single curve, which can be described to a good approximation by the three terms proposed in eq. (5). Additionally, experimental values of PS in toluene obtained by Zakin et al. [19] at 30 °C are plotted in figure 5 and are observed to be in good agreement with the data at 25 °C. For the polystyrene solutions in toluene, the data beyond  $c \cdot [\eta] = 12$  were

used in a linear least-square-regression analysis to estimate  $B_n$  from the intercept and  $n$  from the slope. As indicated by the correlation coefficient of 0.982, the experimental points are well described by a straight line in this range of  $c \cdot [\eta]$ . The  $[\eta] - M$  relationship for polystyrene in toluene was presented recently as [1]:

$$[\eta] = 8.62 \cdot 10^{-3} M_w^{0.736}$$

where the units of  $[\eta]$ , the intrinsic viscosity, are  $\text{cm}^3 \cdot \text{g}^{-1}$ . The Huggins constant  $K_H$  was estimated to be about 0.40. The data required for evaluating eq. (6) are:

$$\begin{aligned} \eta_s &= 0.558 \text{ mPa} \cdot \text{s}, \\ K &= 8.62 \cdot 10^{-3}, \\ a &= 0.736, \\ K_H &= 0.40, \\ n &= 4.55, \\ B_n &= 2.474 \cdot 10^{-3}. \end{aligned}$$

The resulting  $\eta_0 - M - c$  relationship with  $\eta_0$  expressed in  $\text{mPa} \cdot \text{s}$  is then

$$\eta_0 = 4.81 \cdot 10^{-3} \cdot c \cdot M_w^{0.736} + 1.658 \cdot 10^{-5} \cdot c^2 \cdot M_w^{1.472} + 5.579 \cdot 10^{-13} \cdot c^{4.55} \cdot M_w^{3.35} + 0.558. \quad (7)$$

The zero-shear viscosities measured in toluene solution are listed in table 1 together with the values of  $\eta_0$  (theor.) calculated from eq. (7). The percentage deviation of the theoretical from the measured viscosities is given in column 8.

The same procedure was also applied to polystyrene in trans-decalin at the same temperature of 25 °C.

The values for calculating the  $\eta_0 - M - c$  relation for PS in trans-decalin are:

$$\left. \begin{aligned} \eta_s &= 2.42 \text{ mPa} \cdot \text{s}, \\ K &= 6.7 \cdot 10^{-2} \\ a &= 0.52 \\ K_H &= 0.50 \\ n &= 6.30, \\ B_n &= 1.08 \cdot 10^{-3}. \end{aligned} \right\} \text{taken from [37],}$$

The resulting relation is

$$\eta_0 = 0.162 \cdot c \cdot M_w^{0.52} + 5.432 \cdot 10^{-3} \cdot c^2 \cdot M_w^{1.04} + 1.051 \cdot 10^{-10} \cdot c^{6.3} \cdot M_w^{3.28} + 2.42. \quad (8)$$

The values of  $\eta_0$  are presented in table 2 and plotted in figure 5.

The differences between the calculated and experimental viscosities for PS in toluene given in table 1 are remarkably low considering the relatively large range of viscosities and values of  $(c \cdot [\eta])$ . The viscosities of PS in *t*-decalin calculated from eq. (8) deviate from the experimental data more than those for the PS-toluene

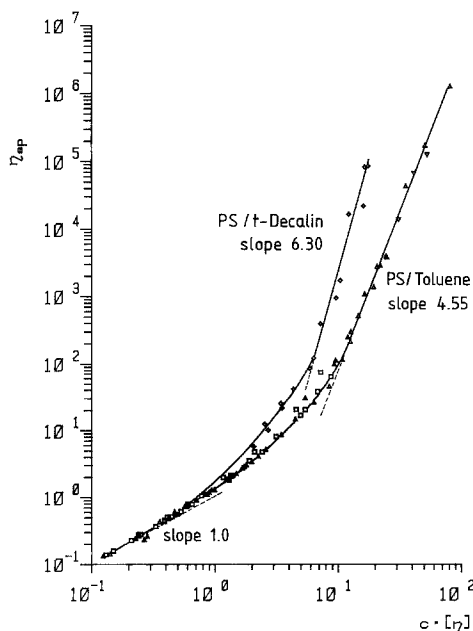


Fig. 5. Specific viscosity,  $\eta_{sp}$ , as a function of the product  $c \cdot [\eta]$  for polystyrene in toluene and *t*-decalin at 25 °C.

Table 1. Characterization data and viscosities,  $\eta_0$ , of polystyrene in toluene at 25 °C. Theoretical viscosities,  $\eta_0$  (theor.), were calculated from eq. (7). In the last column  $\Delta$  means the relative deviation of  $\eta_0$  (theor.) from  $\eta_0$  (exp.)

$M_w$	$[\eta]$ (cm <sup>3</sup> /g)	$c$ (g/cm <sup>3</sup> )	$c \cdot [\eta]$	$\eta_{sp}$	$\eta_0$ (exp) (mPa · s)	$\eta_0$ (theor) (mPa · s)	$\Delta$ (%)
48 000	23.9	0.0052	0.124	0.133	0.632	0.631	- 0.1
		0.0100	0.233	0.266	0.706	0.705	- 0.1
		0.0149	0.356	0.432	0.799	0.787	- 1.5
		0.0197	0.471	0.609	0.898	0.872	- 2.9
117 000	46.6	0.0049	0.228	0.242	0.693	0.696	+ 0.4
		0.0102	0.476	0.558	0.869	0.871	+ 0.2
		0.0151	0.704	0.902	1.061	1.058	- 0.3
		0.0201	0.937	1.282	1.273	1.272	- 0.1
266 000	83.3	0.0050	0.417	0.475	0.823	0.835	+ 1.5
		0.0100	0.833	1.101	1.172	1.192	+ 1.7
		0.0150	1.250	1.867	1.600	1.632	+ 2.1
		0.0200	1.667	2.746	2.090	2.161	+ 3.7
		0.1436	11.96	248.0	138.9	162.0	+ 16.6
333 000	99.2	0.0050	0.496	0.554	0.867	0.893	+ 3.0
		0.0100	0.992	1.298	1.282	1.341	+ 4.6
		0.0150	1.488	2.267	1.823	1.906	+ 4.6
		0.0200	1.984	3.411	2.461	2.600	+ 5.6
390 000	112.3	0.0460	5.400	30.50	17.58	11.87	- 32.5
		0.1080	12.60	214.0	120.0	160.0	+ 33.4
701 000	172.5	0.0050	0.863	1.099	1.171	1.208	+ 3.2
		0.0100	1.725	2.875	2.162	2.208	+ 2.1
		0.0150	2.588	5.205	3.462	3.615	+ 4.4
		0.0200	3.450	8.592	5.352	5.556	+ 3.8
		0.0540	9.315	99.00	55.80	61.72	+ 10.6
		0.1420	24.50	3 924	2 190	3 118	+ 42.4
1 019 000	235.5	0.0270	6.360	26.20	15.18	17.88	+ 17.8
		0.0360	8.480	45.50	25.95	40.33	+ 55.4
		0.0460	10.83	115.5	65.00	92.49	+ 42.3
1 860 000	353.3	0.0004	0.141	0.141	0.637	0.642	+ 0.8
		0.0008	0.283	0.262	0.704	0.734	+ 4.3
		0.0012	0.424	0.497	0.835	0.836	+ 0.1
		0.0016	0.565	0.723	0.961	0.947	- 1.5
		0.0020	0.707	0.923	1.073	1.066	- 0.6
		0.0270	9.539	113.0	63.61	67.31	+ 5.8
		0.0360	12.72	300.4	168.2	195.6	+ 21.4
		0.0465	16.43	1 074	600.0	556.1	- 33.6
		0.1000	35.33	43 010	24 000	16 129	- 39.0
		0.1434	50.66	170 200	95 000	82 213	- 25.6
3 200 000	541.0	0.0270	14.61	513.3	287.0	306.1	+ 6.7
		0.0360	19.48	1 375	767.8	1 025	+ 33.5
		0.0460	24.89	3 780	2 110	2 993	+ 41.9
9 150 000	1 147	0.0270	31.00	13 977	7 800	8 743	+ 12.0
		0.0360	41.30	67 463	37 630	31 917	- 15.2
		0.0460	52.80	127 060	70 900	96 781	+ 36.5
23 600 000	2 245	0.0001	0.225	0.240	0.692	0.698	+ 0.9
		0.0004	0.898	1.185	1.219	1.262	+ 3.5
		0.0006	1.347	2.026	1.689	1.760	+ 4.4
		0.0008	1.796	3.041	2.255	2.364	+ 5.3
		0.0010	2.245	4.119	2.856	3.086	+ 8.9
		0.0020	4.490	14.73	8.780	9.317	+ 10.0
		0.0092	20.65	2 741	1 530	1 630	+ 4.5
		0.0098	22.00	2 866	1 600	2 149	+ 30.6
		0.0360	80.82	1 254 000	699 732	754 913	+ 7.9

Table 2. Characterization data and viscosities,  $\eta_0$ , of polystyrene in *t*-decalin at 25 °C. Theoretical viscosities,  $\eta_0$  (theor.), were calculated from eq. (8)

$M_w$	$[\eta]$ (cm <sup>3</sup> /g)	$c$ (g/cm <sup>3</sup> )	$c \cdot [\eta]$	$\eta_{sp}$	$\eta_0$ (exp) (mPa · s)	$\eta_0$ (theor) (mPa · s)	$\Delta$ (%)
266 000	44.4	0.0465	2.06	5.8	16.5	12.8	− 22.3
		0.0978	4.34	41.6	103.0	64.2	− 37.7
		0.1431	6.35	123.0	300.0	379.7	+ 26.6
		0.2172	9.64	949.4	2 300.0	4 477.5	+ 94.7
390 000	54.1	0.0500	2.71	10.2	27.0	19.3	− 28.6
		0.1090	5.90	85.8	210.0	256.5	+ 22.2
701 000	73.4	0.0465	3.43	25.4	64.0	31.1	− 51.4
		0.0974	7.18	396.0	960.0	747.6	− 22.1
		0.1418	10.40	1 735.4	4 200.0	7 256.5	+ 72.8
		0.2172	16.02	21 900.0	53 000.0	104 526.4	+ 97.2
742 000	75.6	0.0464	3.50	21.7	55.0	33.3	− 39.4
		0.2172	16.40	82 643.6	200 000.0	125 898.0	− 37.1
1 860 000	122.0	0.0464	5.70	346.0	840.0	207.8	− 75.3
		0.1000	12.20	16 528.0	40 000.0	19 514.0	− 51.2
		0.1432	17.50	85 536.2	207 000.0	180 495.0	− 12.8

system, probably because *t*-decalin behaves like a theta solvent at 25 °C.

The comparison of the solution behaviour of *PS* in both solvents, toluene and *t*-decalin, leads to the result that the limiting power of the molecular weight dependence of  $\eta_0$  (3.35 and 3.28 respectively) is in close agreement with the value of 3.4 observed in highly concentrated solutions and melts. The concentration dependence of  $\eta_0$ , however, is clearly different in each of the solvents:

$$\eta_0 \propto c^{4.55} M_w^{3.35} \quad \text{for } PS \text{ in toluene, } T = 25^\circ\text{C}, \quad (9)$$

$$\eta_0 \propto c^{6.30} M_w^{3.28} \quad \text{for } PS \text{ in } t\text{-decalin, } T = 25^\circ\text{C}. \quad (10)$$

The zero-shear viscosities of *PS* in the poorer solvent *t*-decalin depend on a higher exponent of  $c$  than in the better solvent toluene. Although it has been assumed in the literature [10] that  $\eta_0 \propto c^4 \cdot M^{3.5}$ , experimental investigations show higher exponents for  $c$  [38]. Since we consider it to be well established that  $\eta_0 \propto M^{3.4}$  in the high-molecular-weight region and at high concentrations [9], we suggest that an estimate of the exponent ( $n$ ) of  $c$  in the  $\eta_0$  equation be given by

$$n = 3.4/a \quad (11)$$

where  $a$  is the exponent in the Mark-Houwink equation. This means that  $n$  is approximately 6.8 for theta systems with  $a = 0.5$  with  $n$  decreasing as the solvent improves due to increasing  $a$ .

The careful work of Onogi et al. [14] on the effects of molecular weight and concentration on the flow properties of concentrated polymer solutions is consistent with the present investigation concerning the powers of the concentration and molecular weight dependence of the viscosity. They reported that the solution viscosities of polystyrene at 40 °C are given by  $\eta = K(c \cdot \rho)^{4.7} M^{3.4}$  for toluene and by  $\eta = K(c \cdot \rho)^{5.6} M^{3.4}$  for decalin, where  $\rho$  is the density of the solution. The exponents determined by Onogi et al. [14] agree very well with those determined in this study, because the influence of temperature on the viscosity is known to be small for polystyrene in toluene [1] and so the power of  $c$  is not expected to differ significantly between 25 °C and 40 °C. However, the higher temperature used by Onogi et al. for the decalin solution (40 °C) affects its solvent quality for polystyrene; that is the exponent  $a$  in the  $[\eta] - M$  relation increases. This explains why the power of  $c$  was found to be lower at 40 °C than at 25 °C.

The  $\eta_0 - M - c$  equations (7) and (8) determined in this study are valid over a very wide concentration range, but they are restricted to samples having molar masses greater than approximately 20 000 g/mol. Viscosity data for lower molecular weights show a more rapid increase in the  $\eta_{sp} - (c[\eta])$  plot than the general curve. This was also observed by Zakin et al. [19] for a narrow distributed polystyrene ( $M_w = 15 000$ ) in toluene at 30 °C.

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