

Effect of branching on the sedimentation behaviour in moderately concentrated polystyrene solutions

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Sedimentation velocity measurements on moderately concentrated solutions of linear and four-branched star polystyrenes at both good (benzene) and theta (cyclohexane) solvent conditions are reported. The branched polystyrenes show a different sedimentation behaviour than the linear ones. If, for instance, s_0/s is plotted *versus* $c[\eta]$ the resulting curves for the branched polystyrenes are significantly steeper than the corresponding curves for the linear samples, both at good and theta solvent conditions. The difference in sedimentation behaviour between linear and branched polymers is further elucidated by utilizing the permeability concept and the scaling law hypothesis.

INTRODUCTION

The dynamics of solutions of branched polymers are not well documented, even for dilute macromolecular solutions¹⁻⁹. However, the effect of branching on viscoelastic properties in concentrated macromolecular solutions has attracted great interest recently and was found to influence the rheological properties^{8,10-12}. In view of this, it is likely that parameters such as sedimentation coefficient, which are closely related to the hydrodynamics of the polymer-solvent system, should be affected by branching.

A fair amount of work on the sedimentation behaviour of linear macromolecules under both poor and good solvent conditions has recently been reported¹³⁻²³. The detailed sedimentation process in moderately concentrated macromolecular solutions showed different features depending on the nature of the polymer-solvent system considered. Furthermore, it was found that the concentration dependence of the sedimentation coefficient is a function of the shape of the sedimenting molecule even over an extended concentration region¹⁴.

Quite recently, the sedimentation behaviour of a branched and a linear polymer-solvent system, namely poly[2-(triphenylmethoxy)ethyl methacrylate] (PTEMA)/toluene and poly(methyl methacrylate) (PMMA)/toluene, respectively, was investigated²¹. The branched polymer PTEMA showed a significantly different sedimentation behaviour from the linear polymer PMMA. However, there are some factors which complicate an unambiguous analysis of the observed difference in sedimentation behaviour.

First, it was not possible to prepare a linear homologue of PTEMA, and therefore a linear polymer (PMMA) with similar properties was used as reference. Secondly, the branched structure of PTEMA is not uniquely defined; furthermore, PTEMA can be expected to display a higher rigidity than PMMA because of the incorporation of a bulky substituent into the side-chain. Thirdly, the polymer PTEMA was found to be fairly monodisperse ($\bar{M}_w/\bar{M}_n \leq 1.2$), but PMMA was more polydisperse.

In order to investigate systematically and effectively the influence of branching on the sedimentation process, well-characterized model polymers have been studied. These are four-branched star polystyrenes (PSDT) with narrow molecular weight distribution and sharp polystyrene (PS) fractions of practically the same molecular weight. The sedimentation behaviour of these polymers have been studied over an extended concentration interval, and at both good and theta solvent conditions. The main interest in this paper is the difference in sedimentation behaviour between the polymers PSDT and PS. In order to elucidate this difference more thoroughly the permeability concept¹³ and the 'scaling law' hypothesis²⁴ have been utilized.

EXPERIMENTAL

Materials and preparation of solutions

Linear polystyrene samples with narrow molecular weight distribution from Pressure Chemical Co., Pittsburgh, Pa, USA, were used as received. The weight-average molecular weights (\bar{M}_w) and the dispersity indices (\bar{M}_w/\bar{M}_n), according to the manufacturer's specifications, and intrinsic viscosity data²⁵ for the samples are given in *Table 1*.

The four-branched star polystyrenes were a gift from Dr C. Strazielle, Centre de Recherches sur les Macromolécules, Strasbourg, France. The preparation, fractionation and

Table 1 Characteristic data for linear and four-branched star polystyrenes

Sample	$\bar{M}_w \times 10^{-5}$	\bar{M}_w/\bar{M}_n	$[\eta]$ ($\text{m}^3 \text{kg}^{-1}$)	
			Benzene (25°C)	Cyclohexane (35°C, θ -conditions)
PS (lot No. 3b)	3.92	≤ 1.10	0.131	0.054
PS (lot No. 14a)	17	≤ 1.20	0.377	0.112
PSDT III	3.12	≤ 1.15	0.074	0.0317
PSDT IX	22.1	~ 1.2	0.322	0.084

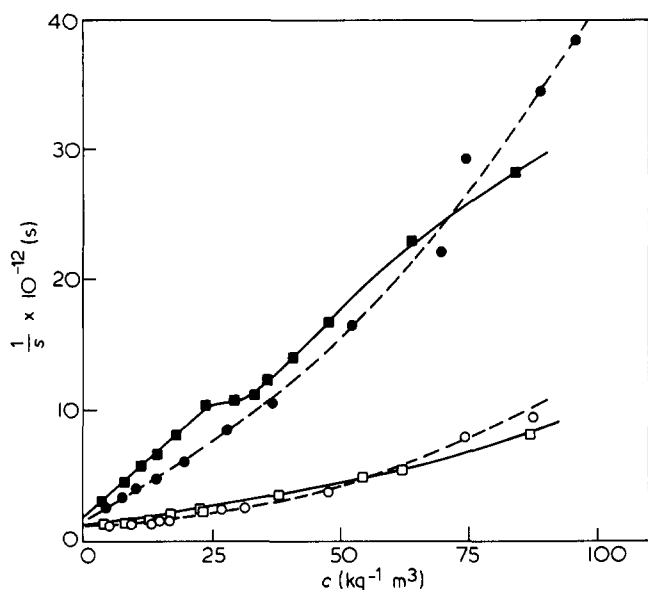


Figure 1 Concentration dependence of the reciprocal sedimentation coefficient for the systems indicated: ■, PS ($\bar{M}_w = 392\,000$)/benzene at 25°C; ●, PSDT III ($\bar{M}_w = 312\,000$)/benzene at 25°C; □, PS ($\bar{M}_w = 392\,000$)/cyclohexane at 35°C (θ -conditions); ○, PSDT III ($\bar{M}_w = 312\,000$)/cyclohexane at 35°C (θ -conditions)

characterization of these samples have been exhaustively described²⁶. The characteristic data for the samples used in this work are collected in Table 1.

The solvent benzene (Merck AG, spectroscopic grade) was used without further purification. Cyclohexane (Merck AG, spectroscopic grade) was dried over anhydrous P_2O_5 and fractionally distilled prior to use.

All solutions were prepared by weighing. Great care was exercised in the preparation to obtain homogenous solutions.

Sedimentation velocity

The sedimentation measurements were carried out in benzene at 25° and in cyclohexane at 35°C, using an MSE analytical ultracentrifuge (Centriscan 75) equipped with a temperature controlling unit and a schlieren system of the photoelectric scanning type²⁷ to record the position of the sedimenting boundary. The cells consisted of (depending upon solution concentration) 5, 10 and 20 mm single sector aluminium centre pieces provided with quartz windows. The speed of revolution of the rotor was 54 000 rpm in all the experiments.

The sedimentation experiments and the evaluation of sedimentation coefficients were performed in accordance with the principles discussed previously²⁸.

RESULTS AND DISCUSSION

Before the results are presented and discussed some fundamental aspects of the sedimentation behaviour in concentrated macromolecular solutions will be reviewed as a background for the subsequent discussion.

In sufficiently dilute solution the macromolecules will behave as individual units and the sedimentation process is mainly characterized by the intrinsic properties of the solute molecules. However, when the concentration increases the intermolecular interactions become more important and at a certain concentration c^* the domains of the polymer molecules begin to overlap. Simha *et al.*²⁹ con-

sidered solutions of flexible macromolecules, and estimated for spherical impenetrable coils that the concentration corresponding to incipient overlap to be $c^* = 1/[\eta]$. It should be noted that this model does not take into account a possible change in coil dimensions with increasing concentration.

Further increase in concentration leads to the formation of intermolecular entanglements which assume increasing importance the higher the concentration. Eventually the polymer coils interlace with each other so extensively that an interlocked network composed of physically entangled molecules is formed, and the distribution of segments will be more or less homogeneous over the volume available. In this concentration régime the 'porous plug' model¹³, in which the sedimentation of the polymer is closely related to the permeability of this 'plug', provides the conceptual basis for the discussion of the sedimentation process. The details of this concept have been elaborated elsewhere¹³.

In Figure 1 the concentration dependence of the reciprocal sedimentation coefficient for PS ($\bar{M}_w = 392\,000$, linear) and PSDT III ($\bar{M}_w = 312\,000$, branched) at both good and theta solvent conditions is illustrated (see Table 1). The curve for the system PS/benzene exhibits an anomaly at the onset of the region where a more or less homogeneous segment distribution prevails (semi-dilute solution); a similar observation has also been reported for linear polystyrenes in toluene¹⁵. At higher concentrations the curve has a slight tendency to become concave downwards. These peculiar features are probably associated with changes in coil dimensions. A number of findings³⁰⁻³² indicate that the coil dimensions in good solvents shrink rapidly towards their theta solvent values when the concentration increases. Above a certain concentration the shrinkage is much less pronounced or almost negligible; the dimensions are then close to the theta solvent value. This contraction of the coils may influence the concentration dependence of the sedimentation coefficient in such a way that an inflection region is not unlikely. In contrast, the curve representing the system PSDT III/benzene does not show an anomaly; the curve is concave upwards over the concentration interval considered.

Studies^{6,7,33-35} have shown that the molecules of a branched polymer display a more compact conformation (i.e. a smaller radius of gyration) than the corresponding linear polymer of the same molecular weight, and that the average segment density in the coils of a branched polymer is far higher than that for the linear analogue. These structural differences may lead to a different development of the state of entanglements for branched polymers as compared with linear ones. Because of the relatively small coil dimensions and the high average segment density of branched polymers the coils cannot overlap extensively when the concentration increases but must be in contact with each other at the periphery. Eventually entanglements will occur. In addition, it is likely that branched polymer coils in good solvents do not contract as extensively as linear ones when the concentration increases. These factors taken together may lead to different sedimentation behaviour when branched and linear polystyrenes are compared.

The curves representing theta solvent conditions (see Figure 1), however, display only a modest increase with concentration, and there exists no pronounced difference between the linear and the branched polystyrene. It is interesting to note the significant difference between the curves representing good and theta solvent conditions: the former exhibit a marked rise whereas the latter only display a modest increase. This considerable distinction in sedimentation behaviour between good and theta solvent systems

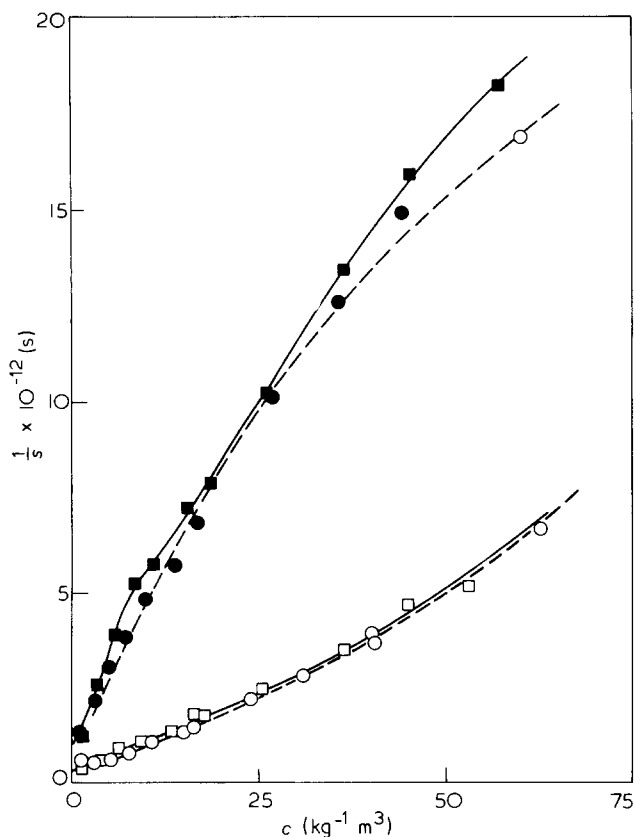


Figure 2 Concentration dependence of the reciprocal sedimentation coefficient for the systems indicated: ■, PS ($\bar{M}_w = 1.7 \times 10^6$)/benzene at 25°C; ●, PSDT IX ($\bar{M}_w = 2.21 \times 10^6$)/benzene at 25°C; □, PS ($\bar{M}_w = 1.7 \times 10^6$)/cyclohexane at 35°C (θ -conditions); ○, PSDT IX ($\bar{M}_w = 2.21 \times 10^6$)/cyclohexane at 35°C (θ -conditions)

indicates that the thermodynamics are substantially different. It is also plausible that the state of entanglement at higher concentration is quite different. At theta conditions the entangled chains may cling together more tightly and perhaps form multimolecular aggregates or bundles^{30,37} of polymer molecules before entanglements in the classical sense occur. In addition, it has been reported³⁸ that the polymer coils at theta solvent conditions have constant dimensions over the entire concentration region.

Figure 2 constitutes an analogous plot to that in Figure 1 for higher molecular weights. The main features are similar to those in Figure 1, except that the curves representing good solvent conditions are both somewhat concave downwards at higher concentrations. Furthermore, the curve for the system PS ($\bar{M}_w = 1.7 \times 10^6$)/benzene displays a much less clear (although discernible) 'anomaly' than the lower molecular weight polystyrene (see Figure 1). The findings from a previous investigation¹⁵ also indicate that the anomaly is more indistinguishable at higher molecular weights.

The dimensionless 'hydrodynamically normalized' plot¹⁴ of s_0/s versus $c[\eta]$, where the parameter $c[\eta]$ measures the degree of coil overlap in a solution if changes in coil dimensions are neglected, is sensitive to details in the transport process (s and s_0 denote the sedimentation coefficients at concentration c and at infinite dilution, respectively, and $[\eta]$ is the intrinsic viscosity). This plotting procedure has among its merits, especially at higher concentrations, its sensitivity even to small differences in the molecular shape¹⁴. The curves are steepest for the most compact spherical particle structures and tend to become more horizontal the

more elongated the particle. Another merit is that it may reduce or even eliminate the molecular weight dependence of the sedimentation process¹⁸.

In Figure 3, s_0/s is plotted versus $c[\eta]$ for linear and four-branched star polystyrenes in good solvent conditions. The clearest feature is the divergence (which is especially significant for the lower molecular weight samples) between the curves representing linear and branched polystyrenes. The small separation of the curves for the higher molecular weight samples may be associated with a smaller relative difference in segment density of the coils of branched and linear polystyrenes as compared with the lower molecular weight samples. Furthermore, the curves representing the linear polystyrenes at good solvent conditions display an inflection at $c[\eta] \sim 5$ which is in the region where a uniform segment distribution prevails, and where the molecular dimensions are approaching these at theta solvent conditions (see Discussion above).

An analogous plot for these polymers at theta solvent conditions is depicted in Figure 4. The characteristic feature, namely steeper curves for branched polymers observed in Figure 3 remains, indicating that in theta solvents there also exist topological differences between the molecules of branched and linear polystyrenes.

From these findings it appears probable that the steeper curves, in a 'hydrodynamically-normalized' plot, for branched polymers as compared with linear homologues can ultimately be attributed to the augmented segment density (within the polymer coils) of the branched molecules. The main features observed in Figures 3 and 4 are consistent with those reported for the systems PMMA/toluene and PTEMA/toluene²¹ (see above).

The analogy between the sedimentation coefficient and the permeability of a 'porous plug' has recently been elaborated by Mijnlief and Jaspers¹³, who derived, using irreversible thermodynamics, the following relation between the

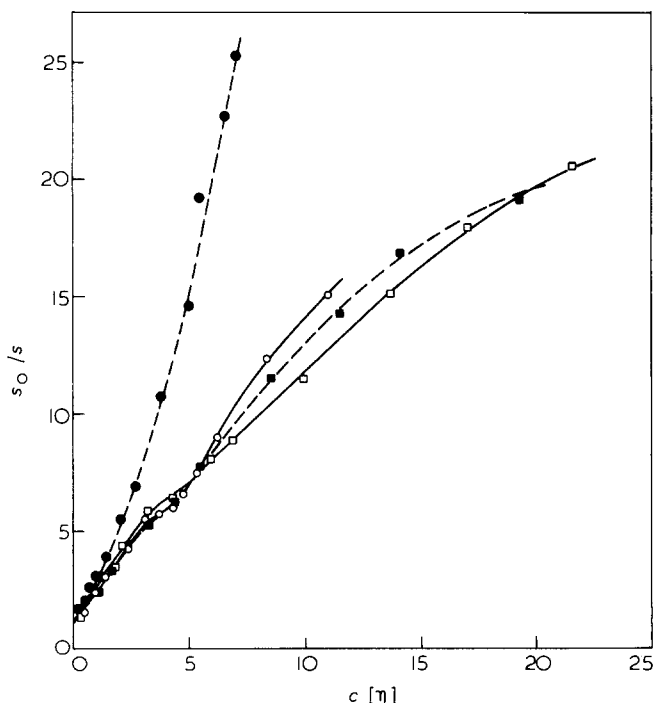


Figure 3 Plot of s_0/s versus $c[\eta]$ for linear and four-branched star polystyrenes in benzene at 25°C: ●, PSDT III ($\bar{M}_w = 3.12 \times 10^5$); ○, PS ($\bar{M}_w = 3.92 \times 10^5$); ■, PSDT IX ($\bar{M}_w = 2.21 \times 10^6$); □, PS ($\bar{M}_w = 1.7 \times 10^6$)

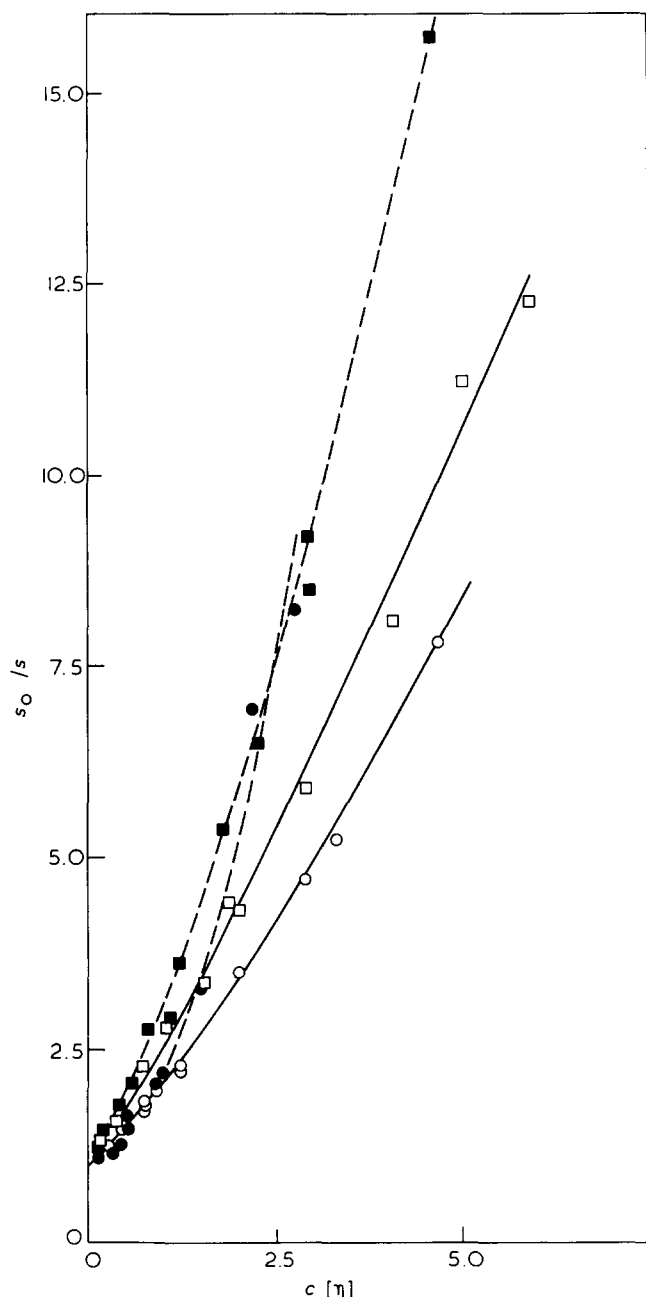


Figure 4 Plot of s_0/s versus $c[\eta]$ for linear and four-branched star polystyrenes in cyclohexane at 35°C (θ -conditions). ■, PSDT III ($\bar{M}_w = 2.21 \times 10^6$); ●, PSDT IX ($\bar{M}_w = 3.12 \times 10^5$); □, PS ($\bar{M}_w = 1.7 \times 10^6$); ○, PS ($\bar{M}_w = 3.92 \times 10^5$)

sedimentation coefficient, s , and the permeability coefficient, k :

$$k = \frac{\eta_0 s}{c(1 - \bar{v}_2/\bar{v}_1)} \quad (1)$$

Here η_0 is the solvent viscosity, and \bar{v}_1 and \bar{v}_2 are the partial specific volumes of solvent and solute, respectively. The concentration dependence of k is shown in Figure 5 for linear and four-branched polystyrenes under both good and theta conditions. The curves representing the permeability coefficient at theta solvent conditions are significantly higher, over the entire concentration region, than those at good solvent conditions. These higher values of k have been attributed to local clustering of repeating units of the polymer,¹³ which could result in wider pores between the

clusters, thus leading to the higher values. The slight divergence between the curves representing linear and four-branched polystyrenes, both at good and theta solvent conditions, may be ascribed to the enhanced segment density in the coils of branched polymers relative to the linear polymers.

In order to elucidate the transport properties further in moderately concentrated solutions the concentration dependence of the sedimentation and permeability coefficients, respectively, is described utilizing the scaling law hypothesis²⁴. This concept is based upon an analogy between the magnetic problem and the problem of polymer solutions^{31,39,40} from which scaling laws characterizing static and dynamical properties of macromolecular solutions emerged. The existence of these laws has been confirmed from experimental studies^{31,41-43}.

The concentration dependence of the coefficients k and s in the semi-dilute régime can be represented by the following power laws²⁴:

$$k \sim \begin{cases} c^{-1.5} & \text{(good solvent conditions)} & (2) \\ c^{-2.0} & \text{(theta solvent conditions)} & (3) \end{cases}$$

$$s \sim \begin{cases} c^{-0.50} & \text{(good solvent conditions)} & (4) \\ c^{-1.0} & \text{(theta solvent conditions)} & (5) \end{cases}$$

The exponents (a_p and a_s) listed in Table 2 have been calculated from the slopes above c^* in lg–lg plots of k and s , respectively, vs. c . There is no fully unambiguous trend in the value collected in Table 2. However, certain interesting

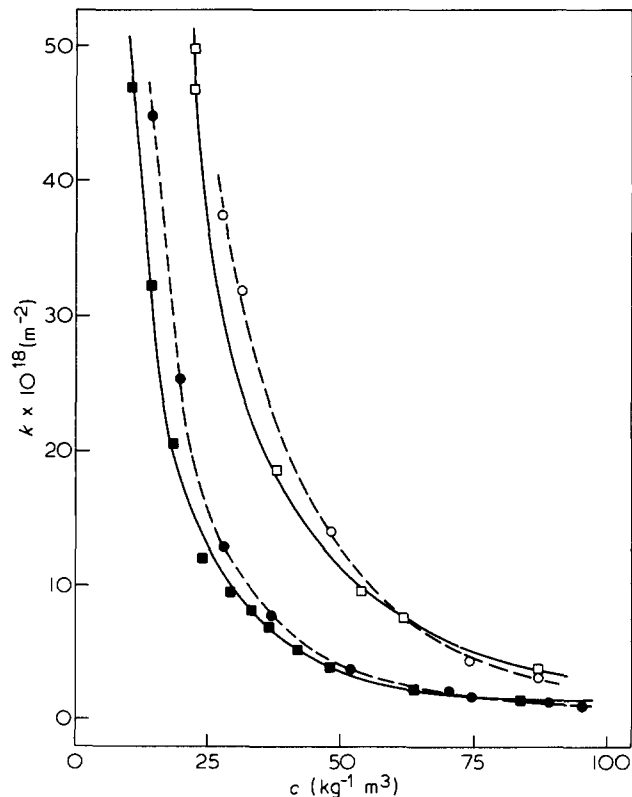


Figure 5 Concentration dependence of the permeability coefficient for the systems indicated: ■, PS ($\bar{M}_w = 392\,000$)/benzene at 25°C; ●, PSDT III ($\bar{M}_w = 312\,000$)/benzene at 25°C; □, PS ($\bar{M}_w = 392\,000$)/cyclohexane at 35°C (θ -conditions); ○, PSDT III ($\bar{M}_w = 312\,000$)/cyclohexane at 35°C (θ -conditions)

Table 2 Exponents (a_p and a_s) describing the concentration dependence of the sedimentation coefficient (s) and the permeability coefficient (k) for linear and four-branched star polystyrenes under both good and theta solvent conditions. a_p and a_s indicate the slopes (above c^*) in lg–lg plots of k and s , respectively, versus concentration

Polymer	$\bar{M}_w \times 10^{-5}$	Benzene (25°C)		Cyclohexane (35°C; θ -condition)	
		a_p	a_s	a_p	a_s
PS	3.92	-1.81	-0.89	-1.92	-0.90
PS	17	-1.72	-0.71	-1.86	-0.90
PSDT III	3.12	-2.00	-0.98	-2.13	-1.15
PSDT IX	22.1	-1.75	-0.78	-2.12	-0.97

features should be observed. Firstly, the experimentally obtained values are higher than those predicted by theory (see equations 2–5). Secondly, there is a tendency for the absolute values of the exponents for the branched polystyrenes to be larger, both at good and theta solvent conditions, than those for the linear ones. Similar observations have been reported in a previous work⁴³ where exponents for several polymer–solvent systems under various thermodynamic conditions were compiled.

In this work only four-branched star polystyrenes and their linear analogues have been studied. In order to obtain a more resolved picture of the sedimentation behaviour in moderately concentrated solutions, other branched polymers, e.g. comb-shaped and randomly branched polymers, should be studied together with their linear homologues.

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REFERENCES

- Zimm, B. H. and Kilb, R. W. *J. Polym. Sci.* 1959, **37**, 19
- Kurata, M. and Fukatsu, M. *J. Chem. Phys.* 1964, **41**, 2934
- Altare, T., Wyman, D. P., Allen, V. R. and Meyersen, K. *J. Polym. Sci. (A-2)* 1965, **3**, 4131
- Wales, M. and Coll, H. *Ann. NY Acad. Sci.* 1969, **164**, 102
- Noda, J., Horikawa, T., Kato, T., Fujimoto, T. and Nagasawa, M. *Macromolecules* 1970, **3**, 795
- Berry, G. C. *J. Polym. Sci. (A-2)* 1971, **9**, 687
- Candau, F., Rempp, P. and Benoit, H. *Macromolecules* 1972, **5**, 627
- Small, P. A. *Adv. Polym. Sci.* 1975, **18**, 1
- Bywater, S. *Adv. Polym. Sci.* 1978, **30**, 89
- Berry, G. C. and Fox, T. G. *Adv. Polym. Sci.* 1968, **5**, 261
- Fujimoto, T., Naruekawa, H. and Nagasawa, M. *Macromolecules* 1970, **3**, 57
- Kajiura, H., Ushiyama, Y., Fujimoto, T. and Nagasawa, M. *Macromolecules* 1978, **11**, 894
- Mijnlieff, P. F. and Jaspers, W. J. M. *Trans. Faraday Soc.* 1971, **67**, 1837
- Sundelöf, L. -O. and Nyström, B. *J. Polym. Sci. (Polym. Lett. Edn)* 1977, **15**, 377
- Nyström, B., Porsch, B. and Sundelöf, L. -O. *Eur. Polym. J.* 1977, **13**, 683
- Nyström, B. and Bergman, R. *Eur. Polym. J.* 1978, **14**, 431
- Nyström, B. and Roots, J. *Eur. Polym. J.* 1978, **14**, 551
- Nyström, B., Roots, J. and Bergman, R. *Polymer* 1979, **20**, 157
- Roots, J., Nyström, B., Porsch, B. and Sundelöf, L. -O. *Polymer* 1979, **20**, 337
- Sundelöf, L. -O. and Nyström, B. *Chem. Scripta* 1977, **4–5**, 162
- Nyström, B., Sundelöf, L. -O., Bohdanecký, M. and Petrus, V. *J. Polym. Sci. (Polym. Lett. Edn)* 1979, **17**, 543
- Nyström, B. *Abstract of Dissertation*, University of Uppsala (1978)
- Nyström, B. and Roots, J. *Makromol. Chem.* 1979, **180**, 2419
- Brochard, F. and de Gennes, P. G. *Macromolecules* 1977, **10**, 1157
- 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut) 2nd Edn, Wiley, New York, 1975, section IV
- Strazielle, C. and Herz, J. *Eur. Polym. J.* 1977, **13**, 223
- Spragg, S. P., Travers, S. and Saxton, T. *Anal. Biochem.* 1965, **12**, 259
- Nyström, B. and Sundelöf, L. -O. *Chem. Scripta* 1976, **10**, 16
- Weissberg, S. G., Simha, R. and Rothamn, S. *J. Res. Nat. Bur. Stand.* 1951, **47**, 298; see also Simha, R. and Utracki, L. A. *Rheol. Acta* 1973, **12**, 455
- Cotton, J. P., Decker, D., Benoit, H., Farnoux, B., Higgins, J., Jannink, G., Ober, R., Picot, C. and des Cloiseaux, J. *Macromolecules* 1974, **7**, 863
- Daoud, M., Cotton, J. P., Farnoux, B., Jannink, G., Sarma, G., Benoit, H., Duplessix, R., Picot, C. and de Gennes, P. G. *Macromolecules* 1975, **8**, 804
- Hayashi, H., Hamada, F. and Nakajima, A. *Makromol. Chem.* 1977, **178**, 827
- Stockmayer, W. H. and Fixman, M. *Ann. NY Acad. Sci.* 1953, **57**, 334
- Decker, P. D. *Makromol. Chem.* 1969, **125**, 136
- Khokhlov, A. R. *Polymer* 1978, **19**, 1387
- Kargin, V. A. *Pure Appl. Chem.* 1966, **12**, 135
- Tager, A. A., Dreval, V. E., Lutsky, M. S. and Vinogradov, G. V. *J. Polym. Sci., Part C* 1968, **23**, 181
- Hayashi, H., Hamada, F. and Nakajima, A. *Polymer* 1977, **18**, 638
- de Gennes, P. G. *Phys. Lett. (A)* 1972, **38**, 339
- des Cloiseaux, J. *J. Phys. (Paris)* 1975, **36**, 281
- Cotton, J. P., Farnoux, B. and Jannink, G. *J. Chem. Phys.* 1972, **57**, 290
- Adam, M. and Delsanti, M. *Macromolecules* 1977, **10**, 1229
- Roots, J. and Nyström, B. *Polymer* 1979, **20**, 148