Star branched polystyrenes: an evaluation of solvent and temperature influences on unperturbed chain dimensions

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Temperature coefficients of unperturbed dimensions of three high molecular weight polystyrene stars have been evaluated from intrinsic viscosity measurements in six theta solvents and two solvent/nonsolvent mixtures over a temperature range of 10 to 70°C. Larger values of unperturbed dimensions were found in cyclic aliphatic solvents than in chloroalkanes at similar temperatures. Negative values of the temperature coefficient of unperturbed dimensions were found in both solvent series, values which were in essential agreement with those found for linear polystyrene. The values of the branching index, g', were found to be independent of both temperature and solvent type.

(Keywords: star polystyrenes; theta temperature; intrinsic viscosities; unperturbed dimensions; branching index)

INTRODUCTION

Recent experimental work[1-3] has indicated that the temperature coefficient of unperturbed dimensions, κ, for a 13-arm polystyrene star ($M_w = 2.5 \times 10^6$) was considerably larger ($\sim 10\times$) than that of its linear equivalent. This finding implies that the various shrinkage factors (g, g') used to describe branching in model star polymers should also show a similar dependence upon temperature. The various theories[4-26] offering descriptions of the dilute solution behaviour of star-shaped homopolymers have not taken such an effect into account. Consequently, this work describes an investigation into the magnitude of κ and g' values for star polystyrenes under theta or near-theta conditions. To this end we have utilized high molecular weight polystyrene stars with functionalities ranging from 10 to 18 arms.

EXPERIMENTAL

The synthesis of the star polystyrenes was accomplished using vacuum line techniques[27] with purified sec-butyllithium as the initiator. The polymerization solvent was benzene. Two of the stars were prepared by reacting the styryl active centre with several units of butadiene followed by linking with a dodeca- or octadecachlorosilane[28,29]. The remaining star was prepared[30] using a commercial divinylbenzene (DVB)–ethylvinylbenzene (EVB) mixture[31] (18 mol% *p*-DVB, 39% *m*-DVB, 10% *p*-EVB and 33% *m*-EVB via ^{13}C n.m.r. This spectrum is shown in *Figure 1*). The DVB/EVB mixture was dried by sequential exposure to calcium hydride and dibutylmagnesium. There was no attempt to separate the divinylbenzene isomers from those of the ethylvinylbenzene. The linking reaction was carried out for 24 h at 45°C. The DVB/active centre ratio was seven, and the polymer concentration was $\sim 8\%$ (w/v). Termination was done using degassed methanol.

Sample fractionations were done from dilute (~ 0.1 w/v %) solutions using toluene and methanol as

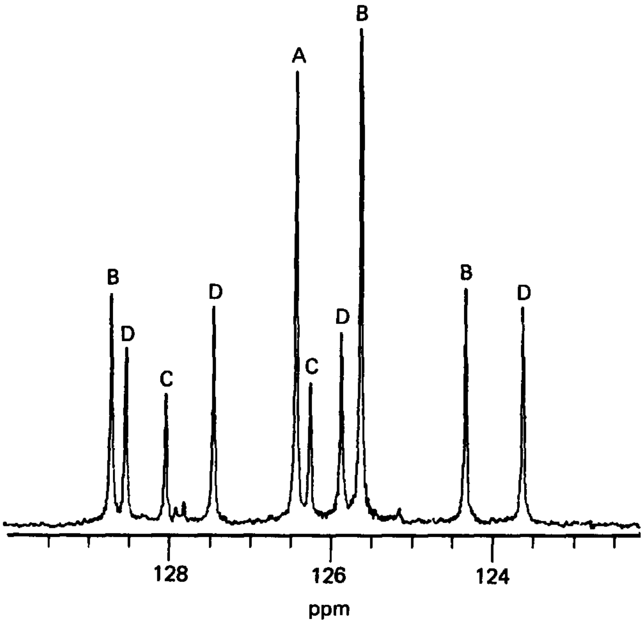

Figure 1 ^{13}C n.m.r. spectrum of the purified divinylbenzene/ethylvinylbenzene mixture *p*-DVB(A); *m*-DVB(B); *p*-EVB(C); *m*-EVB(D)

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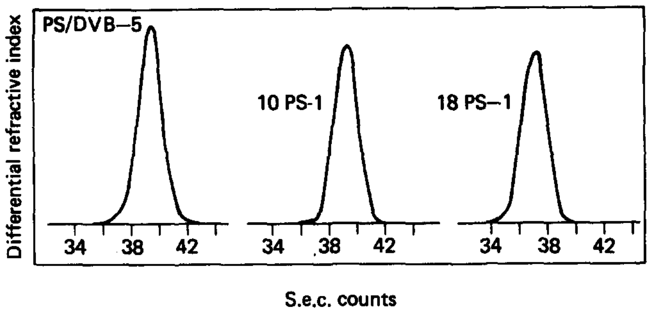

Figure 2 Size exclusion chromatographs of fractionated polystyrene stars (μ-Styragel® columns)

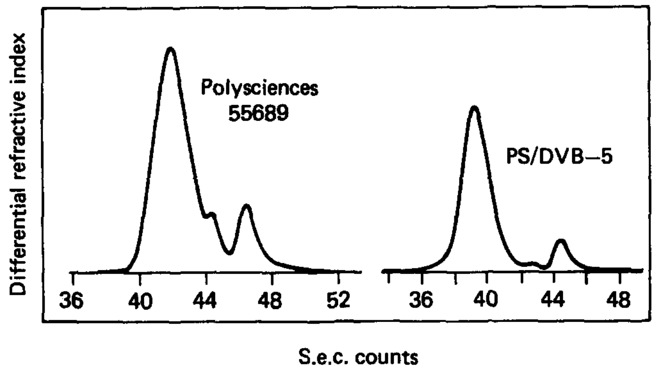

Figure 3 Size exclusion chromatographs of unfractionated divinylbenzene-linked stars (μ-Styragel® columns)

the solvent/nonsolvent system. As many as four fractionations were required to eliminate residual arms and in the case of the DVB-linked star, coupled linear doublet material (ca. 4 wt% of the unfractionated material).

A Waters 150C size exclusion chromatography (s.e.c.) instrument was used for the star analysis. Six μ-Styragel® columns having a porosity range of 10^6–10^2 Å were used. Tetrahydrofuran was the mobile phase at 30°C. The chromatograms of the fractionated stars, shown in *Figure 2*, were obtained at a flow rate of 0.1 ml min^{-1} to benefit from the improved resolution obtainable under these conditions.[32] The chart speed was 6 cm h^{-1}. A single elution count corresponds to an elution volume of 1 ml. These chromatograms demonstrate the absence of 'parent' arm polystyrene and, in the case of PS/DVB-5, the absence of coupled linear product.

Additional s.e.c. characterization was done in one case using a Waters instrument equipped with six ultra-Styragel® columns with nominal porosities of 10^2, 500 and 10^3 Å. To enhance resolution two columns of each porosity were used with tetrahydrofuran at 30°C as the mobile phase. A flow rate of 1.0 ml min^{-1} was maintained. As before, one elution count denotes an elution volume of 1 ml.

Chromatographs of the unfractionated PS/DVB-5 sample and commercially available[33] (Polysciences Inc.) DVB-linked polystyrene 'stars' are given in *Figures 3–5*. These chromatographs share a common feature in that all samples contain coupled linear chains in addition to the presence of unlinked arm. Also, the sample analysed by the ultra-Styragel® column arrangement (*Figure 5*) displays the presence of not only linear singlet and doublet materials (counts 43 and 39.5) but also a considerable amount of what is probably 3-armed star at count 37. The fractionation of DVB-linked stars must be done to remove such components.

The effectiveness of the fractionation can be analysed by ultracentrifugation. This was done on two polystyrene stars in cyclohexane at 35°C using a Spinco Model E analytical ultracentrifuge. Solutions of 0.25% (w/v) were examined at rotor speeds of 3.0×10^4 rev/min (10PS-1) and 3.6×10^4 rev/min (PS/PVB-5). An intercomparison of these results, *Figures 6* and *7*, and those elsewhere[34] indicate that the chlorosilane-linked polystyrene stars possess narrower molecular weight distributions than PS/DVB-5, a not unexpected finding considering the different identity of the linking events. Nonetheless, this analysis further demonstrates that the fractionated PS/DVB-5 does not contain either low functionality branched polymer or linear chains.[35]

The weight-average molecular weights for PS/DVB-5 and 10PS-1 were measured at room temperature using a Chromatix KMX-6 low-angle laser light scattering photometer ($\lambda = 633$ nm) with toluene as the solvent. The

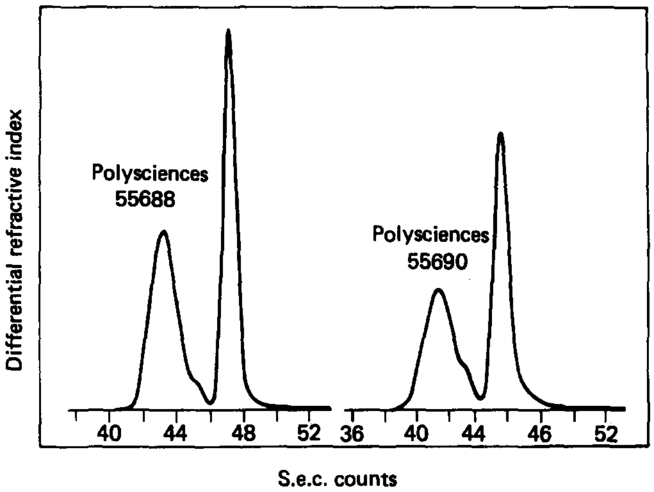

Figure 4 Size exclusion chromatographs of unfractionated divinylbenzene-linked stars (μ-Styragel® columns)

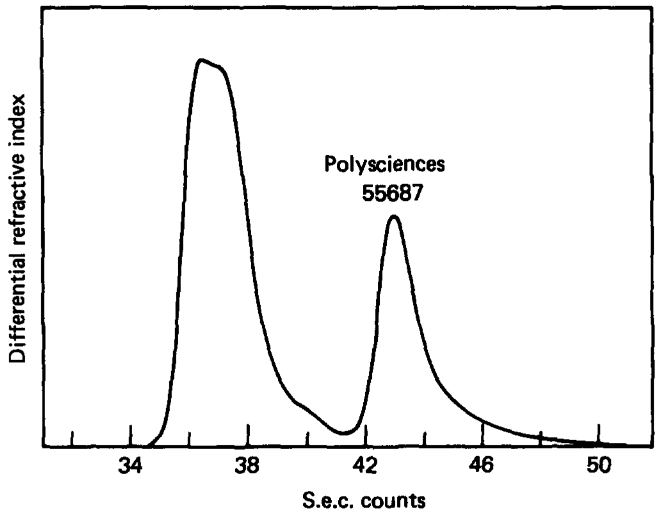

Figure 5 Size exclusion chromatograph of unfractionated divinylbenzene-linked star (ultra-Styragel® columns)

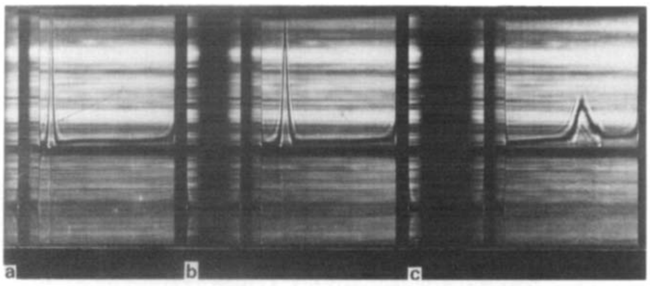

Figure 6 Ultracentrifugation sedimentation patterns of 10PS-1 in cyclohexane at: (a) 35°C, 9 min; (b) 21 min; (c), 77 min

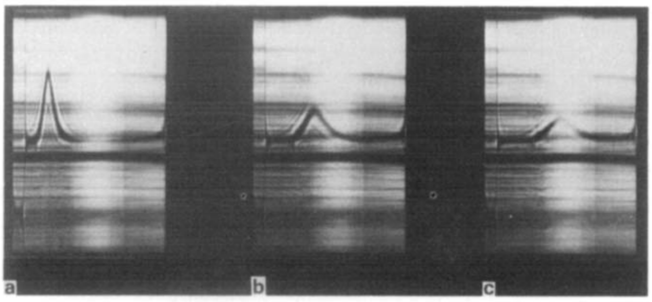

Figure 7 Ultracentrifugation sedimentation patterns of PS/DVB-5 in cyclohexane at: (a) 35°C, 17 min; (b) 38 min; (c) 49 min

value of d*n*/d*c* was taken as 0.105 ml g^{-1} (contrary to the claim[36] that differences exist in d*n*/d*c* values of linear and star-shaped polystyrenes, other findings[37,38] show that such differences are non-existent). The molecular weight of the 18PS-1 sample was taken as the average of available literature values[34,38].

The intrinsic viscosities were measured in Cannon–Ubbelohde dilution viscometers. Solutions and solvent were filtered using Gelman TF-5000 Teflon filters having 5 μm pore size. Kinetic energy corrections were not applied since solvent flow times were in excess of 120 s. Thermal control of the water bath was maintained with a Haake E-3 unit to ±0.02°C. The η_{sp}/c *versus* concentration plot was based on a minimum of four concentrations which were chosen so that η_r did not exceed 1.4 for the highest concentrations, i.e. well below c^*. No curvature, within experimental error, was detected. An analysis of the reproducibility of the flow time data demonstrated that the values of $[\eta]$ were accurate within less than one percent error. The Huggins coefficients and intrinsic viscosities were derived from unweighted linear regression analysis. The characterization results for the star polystyrenes are given in *Tables 1* and *2*.

It can be seen that the average functionality of the 10PS-1 star is 10.2 rather than the anticipated value of 12. The incomplete nature of the linking event has been observed and discussed previously[34]. The characterization results for this sample demonstrate that it is suitable for the purposes outlined in this work.

The choice of solvents and temperatures for the intrinsic viscosity measurements was based on published information[39]. The purity of the solvents used in this work was found by gas chromatography (g.c.) to be ⩾99.9%, with the exception of 1-chloro-n-dodecane, which was 99% pure. The values of the branching index, g', were derived from the ratio of the intrinsic viscosity values in *Table 2* and values calculated from the appropriate theta and near-theta condition Mark–Houwink–Sakurada equations for linear polystyrene available in Table 6 of ref. 39 and those determined in this work.

In addition to cyclohexane, Sun *et al.*[1] used two different solvent/nonsolvent mixtures to simulate theta conditions at 25°C (dioxane/methanol, 71.4:28.6, v/v)[40] and 45°C (toluene/methanol, 72.8:27.2, v/v)[41]. We have evaluated the influence of these solvent/nonsolvent systems at 25°C using the mixtures given in the literature[39,40] for that temperature. G.c. analysis of the two mixtures showed that the respective concentrations (v/v) were 71.0:28.9 for the dioxane/methanol mixture and 77.0:22.9 for the toluene/methanol system. These values are in agreement, within experimental error, with those used elsewhere[40,41]. Both solvent/nonsolvent mixtures were found to contain 0.1% water.

RESULTS AND DISCUSSION

The theta temperature depression exhibited by star molecules is now recognized to be both a function of the extent of branching and arm molecular weight[42–49]. Our use of the near-theta conditions used previously[39] for linear polystyrenes is justified on the basis that the samples used in this work were of high molecular weight, e.g. Bauer *et al.*[49] reported a theta temperature depression of ca. 1.5°C for an 8-arm polyisoprene star with an arm molecular weight of 5 × 10^4, while Huber *et al.*[38] measured the second virial coefficient (A_2) for a 12-arm polystyrene star with an arm M_w of 1.4 × 10^5. This sample showed a theta temperature within 1°C of that of linear polystyrene (where the theta temperature was

Table 1 Molecular characteristics of star polystyrenes

Sample	Arm $\bar{M}_w \times 10^{-4}$ [a] (g mol^{-1})	Star $\bar{M}_w \times 10^{-4}$ (g mol^{-1})	f_w [b]
PS/DVB-5	19.0	320	16.8
10PS-1	26.5	270	10.2
18PS-1	50.0	880[c]	17.6

[a] SEC measurements yielded $\bar{M}_z/\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ ratios of 1.07 or less

[b] f_w = star $\bar{M}_w$/arm $\bar{M}_w$

[c] Average value based on data in refs 34 and 38

Table 2 Intrinsic viscosities and Huggins coefficients for star polystyrenes[a]

	PS/DVB-5	10PS-1	18PS-1
$[\eta]^{10°C}_{CDE}$	49.8	58.5	72.8
k_H	0.84	1.01	1.08
$[\eta]^{33°C}_{CUD}$	47.7	57.8	70.5
k_H	0.99	0.82	1.03
$[\eta]^{58°C}_{CDD}$	46.6	54.7	66.5
k_H	0.87	0.93	0.74
$[\eta]^{34.5°C}_{CHX}$	53.5	65.2	81.6
k_H	0.72	0.86	0.75
$[\eta]^{68°C}_{MCH}$	49.0	58.5	72.1
k_H	0.99	0.67	0.82
$[\eta]^{70°C}_{ECH}$	48.1	57.5	69.9
k_H	0.86	0.98	0.96

[a] $[\eta]$ in ml g^{-1}; Symbols for solvent identification: CDE = 1-chloro-n-decane; CUD = 1-chloro-n-undecane; CDD = 1-chloro-n-dodecane; CHX = cyclohexane, MCH = methylcyclohexane; ECH = ethylcyclohexane

defined as that at which $A_2 = 0$). Based on these observations, our decision to use the theta or near-theta conditions reported elsewhere[39] is appropriate.

The influence of temperature on the unperturbed dimensions of branched polymers can be calculated from intrinsic viscosities measured under theta conditions following Flory's approach[50] where:

$$\kappa = \frac{2}{3}\frac{\mathrm{d}\ln[\eta]}{\mathrm{d}T} \qquad (1)$$

Table 3 gives the values of the temperature coefficients for the star polystyrenes in the chloroalkane and cyclohexane solvent series. As has been demonstrated[39] for linear polystyrenes, the use of a homologous series of chemically similar theta solvents will minimize or eliminate specific solvent effects[51,52] insofar as chain dimensions are concerned. For linear atactic polystyrene an average value of the temperature coefficient of $-1.1 \times 10^{-3}\,\mathrm{deg}^{-1}$ has been found experimentally[39,53] and theoretically[54,55]. These results are in fair agreement with the average value of $-1.7 \times 10^{-3}\,\mathrm{deg}^{-1}$ found for the polystyrene stars (*Table 3*).

Table 3 Temperature dependence of unperturbed dimensions for star polystyrenes

	$\kappa \times 10^3$ (deg^{-1})		
	PS/DVB-5	10PS-1	18PS-1
Solvent family			
Cyclohexanes	−1.9	−2.3	−2.7
Chloroalkanes	-0.9_2	-0.9_4	−1.3

Table 4 Influence of temperature on intrinsic viscosities in cyclohexane of 18PS-1

Temperature (°C)	$[\eta]$ (ml g^{-1})	k_H
34.0	78.7	0.92
34.5	81.6	0.75
35.0	83.5 (86.5)[a]	0.76
36.0	87.5	0.82

[a] Ref. 34

It is apparent that somewhat larger values of κ were found in the cyclohexane family relative to the chloroalkane series, with the latter yielding results in excellent agreement with those obtained for linear polystyrene. The hazards inherent in a 'one-point' approach to the determination of κ involving a series of solvents can be pronounced in view of the fact that slight deviations in temperature in the vicinity of theta can lead to pronounced changes in $[\eta]$ due to the potential sensitivity of chain dimensions to temperature (see *Table 4*). Thus, the relatively high values of κ found in the cyclohexane family may be due to deviations from the theta temperature for the higher temperature measurements involving methyl- and ethylcyclohexane, where some slight discrepancies exist regarding the true theta temperatures for polystyrene in those solvents.

The results in *Table 3* for star polystyrenes can be compared with the value[1,2] of κ of $-1.2 \times 10^{-2}\,\mathrm{deg}^{-1}$; this is an order of magnitude larger than the theoretical[54,55] and experimental[39,53] values available for linear polystyrene. Our results were obtained under conditions which should eliminate or at least minimize specific solvent effects on polystyrene chain dimensions whereas previous work[1,2] used, in addition to cyclohexane at 35°C, dioxane/methanol[40] (25°C) and toluene/methanol[41] (45°C) mixtures to achieve theta condition environments.

The data in *Table 5* show that the branching parameter:

$$g' = [\eta]_{(\mathrm{star})}/[\eta]_{(\mathrm{linear})} \qquad (2)$$

is essentially constant for a given sample in different theta solvents. In essence g' is neither a function of temperature, as was claimed elsewhere[1,2], nor of solvent type. In this regard the star-shaped polystyrenes are identical to their linear counterparts where κ was shown[39] to be essentially independent of the solvent family identity.

These findings, though, leave unresolved the question as to whether specific solvation effects were present in the toluene/methanol and dioxane/methanol mixtures used by Sun *et al.*[1,2] (such effects would have to be more pronounced in the star polymers than in the

Table 5 Branching indices for star polystyrenes

		g'		
Solvent	Temperature (°C)	10PS-1	PS/DVB-5	18PS-1
1-Chloro-n-decane	10	0.44	0.35	0.31
1-Chloro-n-undecane	33	0.45	0.34	0.31
1-Chloro-n-dodecane	58	0.45	0.35	0.30
Cyclohexane	34.5	0.47	0.36	0.33
Methylcyclohexane	68	0.46	0.35	0.31
Ethylcyclohexane	70	0.45	0.34	0.30
Av. values		0.45 (0.45)[a]	0.35 (0.34)[b]	0.31 (0.31[c], 0.32[d])
Theory (ref. 4)[e]		0.24	0.16	0.15
Theory (ref. 5)[f]		0.52	0.45	0.43

[a] Interpolated value for this functionality; ref. 56

[b] DVB-linked polyisoprene star ($p_w = 16.1$) in dioxane; ref. 56

[c] Ref. 57

[d] Ref. 56

[e] $g' = p^{3/2}[2 - p + 2^{1/2}(p-1)]^{-3}$

[f] $g' = (2/p)^{3/2}[0.390(p-1) + 0.196]/0.586$

Table 6 Intrinsic viscosity and Huggins coefficient values for linear and star polystyrenes in dioxane/methanol and toluene/methanol mixtures

		Dioxane/methanol		Toluene/ methanol	
Sample[a]	$\bar{M}_w \times 10^{-4}$ ($g\,mol^{-1}$)	$[\eta]$ ($ml\,g^{-1}$)	k_H	$[\eta]$ ($ml\,g^{-1}$)	k_H
PS-37	3.7	16.8	0.54	18.0	0.39
PS-111	11.1	32.4	0.51	33.1	0.45
PS-254	25.4	51.5	0.49	49.0	0.54
PS-392	39.2	66.7	0.46	62.9	0.53
PS-950	95.0	119	0.46	105.0	0.34
10PS-1	270	97·9	0.66	80.5	0.69
PS/DVB-5	320	79·6	0.58	70.2	0.70
18PS-1	880	126	0.98	97.9	0.75

[a] Linear polystyrene samples are those used in ref. 39

Table 7 Branching indices for star polystyrenes in solvent/nonsolvent mixtures at 25°C

	g'	
Sample	Dioxane/methanol	Toluene/methanol
10PS-1	0.45	0.45
PS/DVB-5	0.33	0.36
18PS-1	0.29	0.29

corresponding linear chains). We therefore evaluated the solution behaviour of the polystyrene stars in these two solvent/nonsolvent mixtures. This required the determination of the Mark–Houwink–Sakurada parameters for linear polystyrenes in these two solvent/nonsolvent mixtures at 25°C. This approach allowed a more definitive comparison of the star behaviour relative to the linear counterparts. The intrinsic viscosity results for the linear and star polystyrenes are given in *Table 6*.

The data of *Table 6* for the linear polystyrenes yield the following Mark–Houwink–Sakurada equations:

Dioxane/methanol (25°C)

$$[\eta] = 3.09 \times 10^{-2} M_w^{0.598}$$

correlation coefficient 0.9996 (3)

Toluene/methanol (25°C)

$$[\eta] = 6.30 \times 10^{-2} M_w^{0.537}$$

correlation coefficient 0.9994 (4)

These equations permit the determination of g' for the polystyrene stars examined in these solvent/non-solvent mixtures (*Table 7*). Therein it can be seen that within experimental error the g' values are in agreement with those of *Table 5*. Therefore, our conclusion is that these mixed solvent/nonsolvent systems do not yield under equivalent conditions abnormal values for the relative comparison of chain dimensions of star and linear polystyrenes.

Several comments can be made which serve as partial explanations for the differences in our findings and those of Sun *et al.*[1,2]. For example, in our experiments neither of the solvent/nonsolvent systems used yielded true theta condition environments. In particular, the dioxane/methanol mixture was found to be a mediocre solvent for polystyrene[58]. This was also demonstrated by the failure of this mixture to show a cloud point at temperatures as low as 0°C. Conversely, Sun *et al.*[2] reported that their linear and star polystyrenes, at a concentration of 0.75% (w/v), exhibited cloud points of 23°C, i.e. 2°C less than the reported[39] theta temperature of 25°C for this system. Our experience involving dioxane has shown that erratic results can be obtained regarding theta temperature behaviour unless freshly purified and dry material is used.

The toluene/methanol system[41,59] was found to be close to a theta condition environment at 25°C. A series of cloud point measurements (*Table 8*) at a concentration of 0.25% (w/v) led to a theta temperature of 17.5°C for linear polystyrenes. This may be contrasted with the findings that the cloud points of the three polystyrene stars (*Table 7*) seem to show that arm molecular weight controls the observed cloud point rather than the total molecular weight of the star, i.e. PS/DVB-5 exhibits a lower cloud point than 10PS-1 even though the former has both a higher functionality and total molecular weight than the latter. A continuation of this effect is observed for 18PS-1, which shows a cloud point higher than the estimated theta temperature for the linear chains under equivalent conditions. This may indicate that for the polystyrene stars specific solvation by toluene occurs leading to an elevated theta temperature relative to what is observed for the linear architecture.

Our results demonstrate that g' for a given degree of branching is not dependent on either temperature or solvent type. Although specific solvent and solvation effects influence polystyrene star chain dimensions, this influence does not affect the magnitude of g' since both the linear and branched polymer respond to a given solvent in an identical fashion insofar as the behaviour under theta conditions is concerned.

In conclusion the Huggins coefficients of the star polystyrenes in chloroalkanes (*Table 2*) are similar to those reported[39] for linear chains. Conversely, the star k_H values found for the cyclohexane family are marginally larger than those found[39] for the linear materials. However, the apparent near-theta conditions in the toluene/methanol mixture (*Table 6*) yield k_H values for the linear samples which are similar to those generally observed for thermodynamically good solvent environments whereas the star values are in general agreement with those found under theta or near-theta conditions.

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Table 8 Cloud point measurements of linear and star polystyrenes in toluene/methanol

Sample	Cloud point (°C)
PS-111	2
PS-254	7
PS-392	9
PS-950	12
PS/DVB-5	15
10PS-1	17.5
18PS-1	20

measurement involving the ultra-Styragel column arrangement. We also thank Mr E. G. Gregory, Hercules Inc., for the analysis of the star polystyrenes by ultracentrifugation and Dr M. J. Sullivan for ^{13}C n.m.r. analysis of the divinylbenzene–ethylvinylbenzene mixture.

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59 The data of Bianchi and Magnasco[41] in toluene/methanol and our results (*Table* 6) lead to K_θ values (via the Burchard–Stockmayer–Fixman approach) of 9.11×10^{-2} and 9.17×10^{-2} respectively. Thus, the differences in the apparent theta temperatures may be due to the quality of the methanol with water as the likely major impurity. It is of interest to mention that the K_θ values listed above and that of 8.08×10^{-2} for the dioxane/methanol system illustrate the influence of specific solvation effects on polystyrene chain dimensions in a fashion similar to that shown in ref. 39