

Viscosity-Temperature Relationships for Linear and 12-Arm Star Polystyrenes in Dilute Solution

MARIA LIOUNI, COSTAS TOULOUPIIS, and NIKOS HADJICHRISTIDIS, *University of Athens, Division of Chemistry, Athens (106 80), Greece*, and JIMMY W. MAYS,* *Hercules Incorporated, Research Center, Wilmington, Delaware 19894*

Synopsis

The actual viscosities (cP) of dilute solutions of linear and 12-arm star polystyrenes were measured in benzene, a good solvent, and cyclohexane, a poor to moderate solvent, as a function of temperature. The equations of Moore, previously established for solutions of linear polymers, were also found to be valid for star polystyrenes. A branching parameter b was defined which is essentially the same as $g' = [\eta]_{br}/[\eta]_l$. The values of b found in benzene are close to the value of g' for 12-arm star polystyrene in toluene, another thermodynamically good solvent. It thus appears that Moore's relationships have at least limited utility in studying branching in polymers.

INTRODUCTION

Moore and co-workers¹⁻⁸ have demonstrated that the Arrhenius expression

$$\eta = A \exp(Q/RT) \quad (1)$$

where Q is the apparent activation energy of flow and A is a preexponential term with an activation entropy significance, is valid for dilute solutions of linear polymers. Flexible and stiff polymers in poor, moderate, and good solvents have been found to conform to Moore's treatment.

In this work, we analyze the actual viscosity behavior of linear and 12-arm star-branched polystyrenes in both benzene, a good solvent, and cyclohexane, a poor to moderate solvent. This work constitutes the first report of actual viscosity behavior of dilute solutions of branched polymer.

EXPERIMENTAL

Linear polystyrenes used in this study were purchased from Pressure Chemical Company (Pittsburgh, PA) and Waters Associates (Milford, MA). The synthesis of the 12-arm star polystyrene has been described previously.⁹ The stars were subjected to solvent/nonsolvent fractionation to remove unlinked arm material. All samples, linear and branched, were found to have

*Present address: Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294.

TABLE I
Molecular Characteristics of Linear and 12-Arm Star Polystyrenes

Sample	Linear polystyrenes		
	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
LPS-1	0.97	—	—
LPS-2	2.10	1.96	1.07
LPS-3	3.70	3.59	1.03
LPS-4	5.10	4.95	1.03
LPS-5	10.4	9.62	1.08
LPS-6	17.3	16.4	1.05
LPS-7	25.4	23.5	1.08
LPS-8	41.3	37.9	1.09
LPS-9	65.5	—	—

Sample	Star polystyrenes			
	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	f^a
PS 9-12	6.10	5.79	1.05	12.1
PS 6-12	16.4	15.8	1.04	11.7
PS 4-12	50.6	48.5	1.04	12.1
PS 5-12	80.5	—	—	11.6
PS 7-12	112	—	—	12.4

^a $f = \overline{M}_n(\text{star})/\overline{M}_n(\text{arm})$ or $\overline{M}_w(\text{star})/\overline{M}_n(\text{arm})$, where $\overline{M}_n(\text{star})$ was not available.

polydispersity ratios, $\overline{M}_z/\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$, less than 1.1 by size exclusion chromatography (SEC) analysis.

Weight-average molecular weights (\overline{M}_w) were measured for the linear polystyrenes in toluene at 25°C using a Chromatrix KMX-6 low-angle laser light scattering unit operating at 633 nm. The refractive index increment (dn/dc) was taken as 0.107 mL g⁻¹.^{10,11} \overline{M}_w was measured for the star polymers in cyclohexane at 35°C using a Sofica PGD instrument at 436 nm. The Sofica was calibrated with benzene ($R_\theta = 50.79 \times 10^{-6}$);¹² dn/dc was found to equal 0.181 mL g⁻¹ at 436 nm using a Brice-Phoenix differential refractometer. The values of \overline{M}_w used in this work are in agreement with \overline{M}_w values reported by Huber et al.⁹ for the same samples.

Number-average molecular weights (\overline{M}_n) were measured, where molecular weight allowed, using the Hewlett-Packard 502 high speed membrane osmometer. Toluene was used as solvent at 37°C; S & S08 regenerated cellulose membranes were employed. The combined results of light scattering and osmometry fortify the SEC findings regarding the near monodisperse nature of these polymers. Molecular weights and polydispersities are given in Table I. The number of arms, f , is also listed in Table I and is found to equal 12 for each of the stars.

The actual viscosities (η) were measured for dilute benzene and cyclohexane solutions of polymer, where concentration was varied between 0.1 and 0.4 g dL⁻¹. Sealed, automatic capillary viscometers with negligible kinetic energy corrections were used.¹³ Measurements in cyclohexane were conducted

at five temperatures between 35 and 59°C. For benzene solutions, six temperatures between 20 and 60°C were used.

The solvents used in this work were purified by drying and distillation prior to use.

RESULTS AND DISCUSSIONS

Figures 1 and 2 show typical plots of $\ln \eta$ vs. $1/T$ for 12-arm star and linear polystyrenes, respectively, in benzene. Comparable results were obtained for all other samples in benzene and in cyclohexane. All plots were strictly linear over the ranges of temperature and concentration used in this work. Values of A and Q were obtained via linear regression analysis.

The dependencies of A and Q on molecular weight are given by

$$Q = Q_0 + K_e \cdot M \cdot c \quad (\text{flexible and stiff chains}) \quad (2)$$

$$A = A_0 + K_\beta \cdot M^\beta \cdot c \quad (\text{flexible chains}) \quad (3)$$

$$A = A_0 \cdot \exp(K_\gamma \cdot M^\gamma \cdot c) \quad (\text{stiff chains}) \quad (4)$$

where Q_0 and A_0 refer to the solvent; K_e , K_β , K_γ , β , and γ are constants for a given polymer-solvent system, M is molecular weight, and c is concentration.

Plots of $K_e \cdot M$ versus \bar{M}_w are shown in Figure 3. The plots are linear and pass through the origin. The values of the entropy parameter K_e are given in Table II. Positive values are found in benzene, while negative values are observed in cyclohexane. Previously, positive K_e values have been associated with low chain flexibility and high chain extension, i.e., excluded

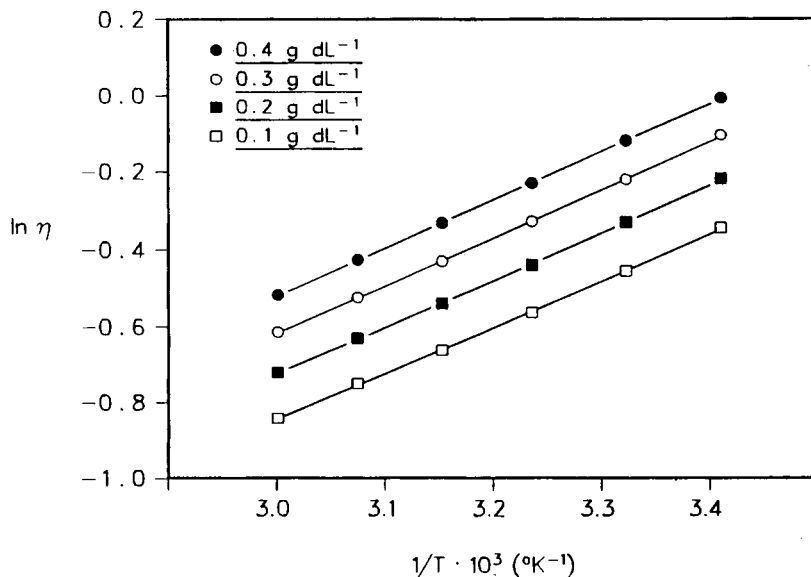


Fig. 1. Plots of $\ln \eta$ vs. reciprocal absolute temperature for PS 7-12 star polystyrene in benzene at various concentrations. (g dL⁻¹): (●) 0.4; (○) 0.3; (■) 0.2; (□) 0.1.

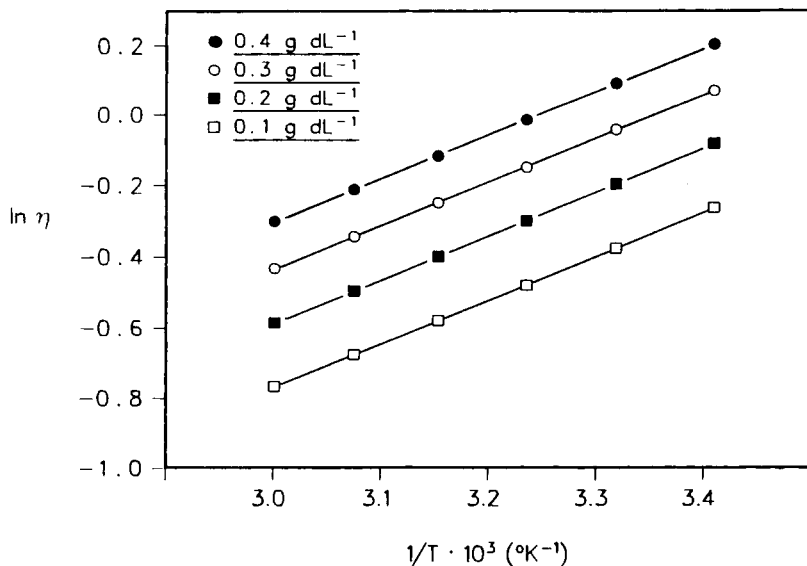


Fig. 2. Plots of $\ln \eta$ vs. reciprocal absolute temperature for LPS-9 linear polystyrene in benzene at various concentrations. (g dL⁻¹): (●) 0.4; (○) 0.3; (■) 0.2; (□) 0.1.

volume.^{1,2,4,5,7,8,13-16} It seems clear that, at least with regard to our results, chain extension plays the more dominant role.

Larger values of K_e are found for linear than for star polystyrenes in both solvents. This is to be expected in view of the smaller size of star polystyrenes.

Figures 4 and 5 show typical plots of A vs. c and $\ln A$ vs. c according to eqs. (3) and (4), respectively, for star polystyrenes in benzene. Both equations appear to fit the experimental data equally as well.

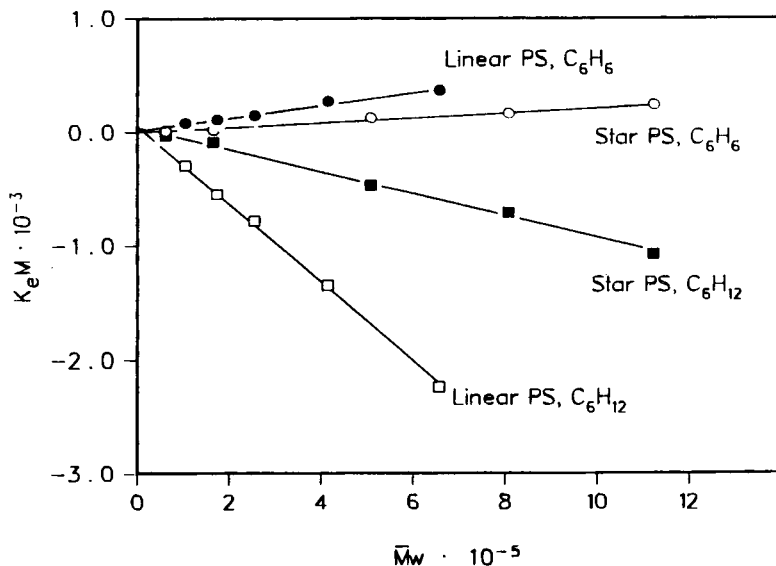


Fig. 3. Plots of $K_e M$ vs. \bar{M}_w for star and linear polystyrenes in benzene and cyclohexane.

TABLE II
Values of Entropy Parameter K_e for Linear and Star Polystyrenes

Polymer type	Solvent	K_e (cal dL g ⁻¹)
Linear PS	Benzene	5.58×10^{-4}
Linear PS	Cyclohexane	-3.39×10^{-3}
Star PS	Benzene	2.17×10^{-4}
Star PS	Cyclohexane	-9.96×10^{-4}

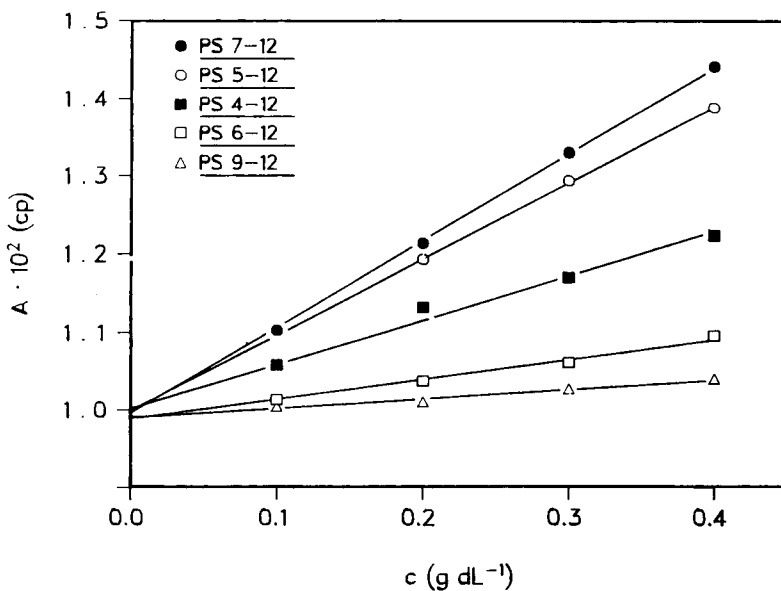


Fig. 4. Plot of A vs. c for star polystyrenes in benzene.

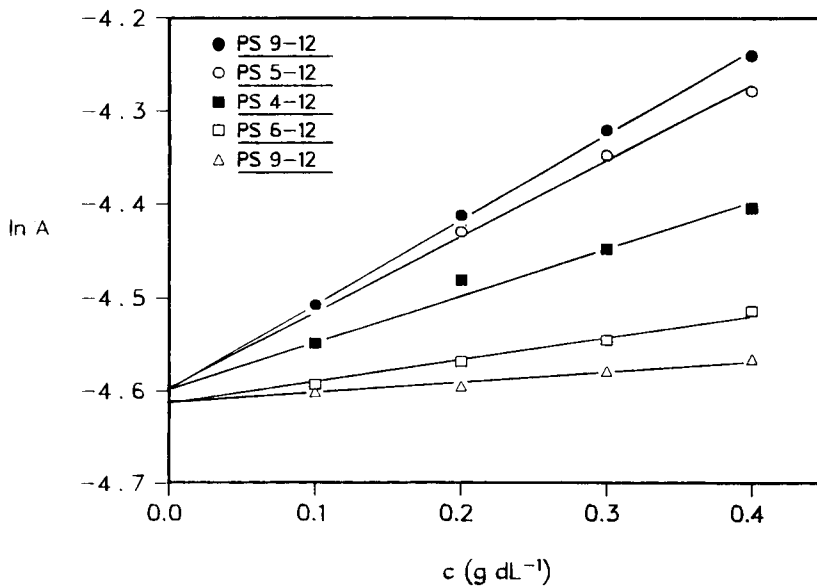


Fig. 5. Plot of $\ln A$ vs. c for star polystyrenes in benzene.

TABLE III
Parameters for Linear Polystyrene in Benzene

Polymer	\bar{M}_w $\times 10^{-4}$	$Q = Q_0 + K_e Mc$		$A = A_0 \exp(K_\gamma M^\gamma c)$		$A = A_0 + K_\beta M^\beta c$	
		Q_0	$K_e M$	$A_0 \times 10^3$	$K_\gamma M^\gamma$	$A_0 \times 10^3$	$K_\beta M^\beta$
LPS-1	0.97	2442	34.2	9.68	0.069	9.68	0.00069
LPS-2	2.10	2447	6.8	9.76	0.163	9.76	0.00165
LPS-3	3.70	2426	44.3	10.1	0.173	10.1	0.00183
LPS-4	5.10	2449	7.0	9.74	0.275	9.72	0.00288
LPS-5	10.4	2400	74.0	10.0	0.493	10.0	0.00545
LPS-6	17.3	2420	105	10.0	0.545	10.0	0.00610
LPS-7	25.4	2408	141	10.1	0.792	10.0	0.00976
LPS-8	41.3	2320	266	10.4	1.123	10.0	0.0155
LPS-9	65.5	2320	363	10.0	1.488	9.3	0.0215

TABLE IV
Parameters for 12-Arm Star Polystyrenes in Benzene

Polymer	\bar{M}_w $\times 10^{-4}$	$Q = Q_0 + K_e Mc$		$A = A_0 \exp(K_\gamma M^\gamma c)$		$A = A_0 + K_\beta M^\beta c$	
		Q_0	$K_e M$	$A_0 \times 10^3$	$K_\gamma M^\gamma$	$A_0 \times 10^3$	$K_\beta M^\beta$
PS 9-12	6.10	2440	5.90	9.9	0.121	9.9	0.00125
PS 6-12	16.4	2439	13.8	9.9	0.260	9.8	0.00273
PS 4-12	50.6	2401	122	10.2	0.468	10.1	0.00533
PS 5-12	80.5	2375	157	10.0	0.784	10.0	0.00971
PS 7-12	112	2376	232	10.1	0.892	9.9	0.0113

TABLE V
Parameters for Linear Polystyrene in Cyclohexane

Polymer	\bar{M}_w $\times 10^{-4}$	$Q = Q_0 + K_e Mc$		$A = A_0 \exp(K_\gamma M^\gamma c)$		$A = A_0 + K_\beta M^\beta c$	
		Q_0	$K_e M$	$A_0 \times 10^3$	$K_\gamma M^\gamma$	$A_0 \times 10^3$	$K_\beta M^\beta$
LPS-1	0.97	2920	-37.2	6.57	0.093	6.54	0.00067
LPS-2	2.10	2912	-68.2	6.59	0.213	6.57	0.00153
LPS-3	3.70	2907	-99.3	6.61	0.334	6.60	0.0024
LPS-4	5.10	2900	-200	6.68	0.545	6.62	0.0043
LPS-5	10.4	2892	-300	6.76	0.757	6.65	0.0062
LPS-6	17.3	2937	-552	6.12	1.34	5.78	0.0115
LPS-7	25.4	2891	-791	6.75	1.75	6.04	0.0185
LPS-8	41.3	2908	-1357	6.40	2.85	4.30	0.0377
LPS-9	65.5	2963	-2243	6.08	4.31	0.035	0.0799

The results of linear regression fits of the data to eqs. (2)–(4) are given in Tables III–VI. The average value of Q_0 for benzene solutions of polystyrene is 2405 cal. This is only slightly smaller than the published value¹⁷ of 2428 cal. For cyclohexane we find $Q_0 = 2901$ cal, in excellent agreement with the literature value of 2905 cal.¹⁷ The values of A_0 are roughly constant for all polymers in benzene, and an average value of $A_0 = 9.9 \times 10^{-3}$ cP is obtained. This value is in excellent accord with the published value of 9.8×10^{-3} cP.¹⁷

TABLE VI
Parameters for 12-Arm Star Polystyrenes in Cyclohexane

Polymer	\bar{M}_w $\times 10^{-4}$	$Q = Q_0 + K_e Mc$		$A = A_0 \exp(K_\gamma M^\gamma c)$		$A = A_0 + K_\beta M^\beta c$	
		Q_0	$K_e M$	$A_0 \times 10^3$	$K_\gamma M^\gamma$	$A_0 \times 10^3$	$K_\beta M^\beta$
PS 9-12	6.10	2871	-36.0	6.98	0.16	6.97	0.0012
PS 6-12	16.4	2874	-94.7	6.94	0.336	6.92	0.00252
PS 4-12	50.6	2886	-473	6.80	1.058	6.57	0.00939
PS 5-12	80.5	2880	-721	6.90	1.534	6.90	0.0146
PS 7-12	112	2873	-1089	6.95	2.204	5.33	0.0276

Values of A_0 are also roughly constant for polystyrene in cyclohexane except at the highest molecular weights, where lower values are found.

Plots of $\ln K_\gamma M^\gamma$ and $\ln K_\beta M^\beta$ against $\ln \bar{M}_w$ are shown in Figures 6 and 7 for linear and star polystyrenes in benzene and cyclohexane, respectively. The values of β , γ , K_β , and K_γ were determined from these plots and are given in Table VII. The highest values of K_β and K_γ are found for linear polystyrene in benzene, and the lowest values are found for star polystyrenes in cyclohexane. Thus, it seems reasonable to associate higher K_β and K_γ values with greater chain extension (excluded volume). This is particularly true in light of the fact that K_β and K_γ are much greater for 12-arm star polystyrenes in benzene than for linear polystyrene in cyclohexane whereas at constant molecular weight the sizes of linear polystyrenes in cyclohexane and 12-arm star polystyrenes are similar.

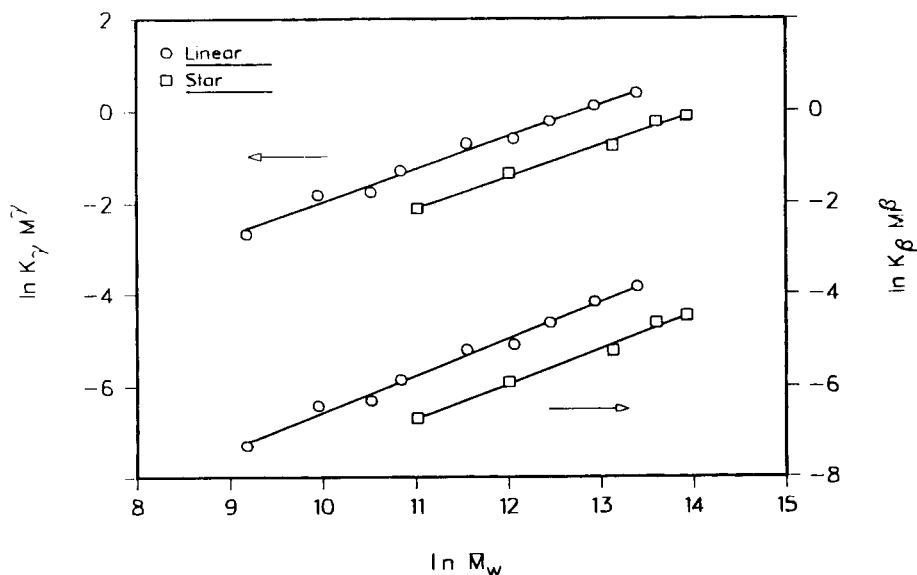


Fig. 6. Plots of $\ln K_\gamma M^\gamma$ and $\ln K_\beta M^\beta$ vs. $\ln \bar{M}_w$ for linear (○) and star (□) polystyrenes in benzene.

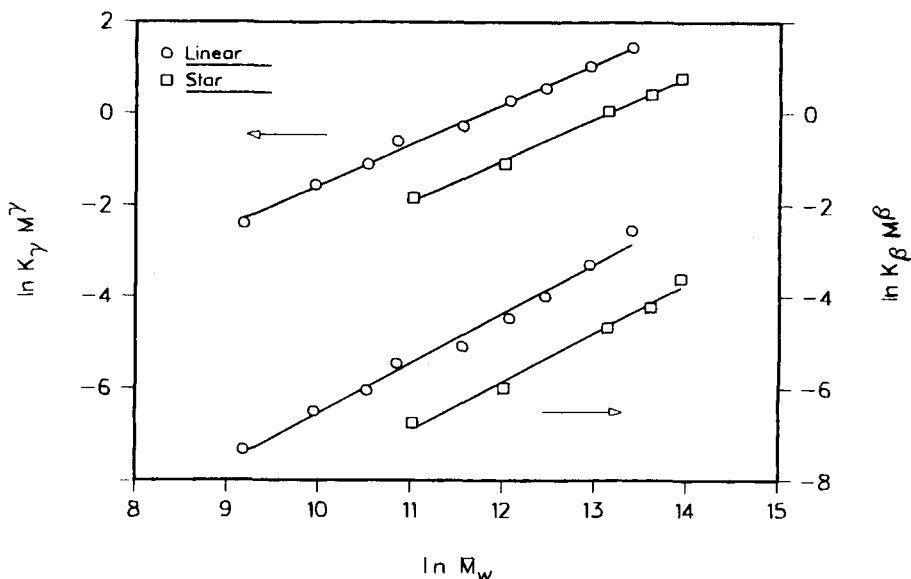


Fig. 7. Plots of $\ln K_\gamma M^\gamma$ and $\ln K_\beta M^\beta$ vs. $\ln \bar{M}_w$ for linear (○) and star (□) polystyrenes in cyclohexane.

Moore et al.⁵ have demonstrated that for flexible polymer chains $[\eta]$ is given as

$$[\eta] = K_e M / RT + K_\beta M^\beta / A_0 \quad (5)$$

In addition, Moore et al.⁵ have demonstrated that the second term of eq. (5) is much greater than the first term. This suggests that

$$[\eta] \approx K_\beta M^\beta / A_0 \quad (6)$$

In Table VIII we compare values of $[\eta]$ measured in benzene at 28°C for 12-arm star polystyrenes with values calculated from eq. (6). The calculated values range from within 3–13% of the measured values.

Based on these results and since A_0 is a constant, we can define a branching parameter, b , where

$$b = K_\beta M^\beta(\text{star}) / K_\beta M^\beta(\text{linear}) \quad (7)$$

TABLE VII
Values of β , γ , K_β , and K_γ for
Linear and 12-Arm Star Polystyrenes in Benzene and Cyclohexane

Polymer type	Solvent	β	γ	$K_\beta \times 10^9$ (dL g ⁻¹)	$K_\gamma \times 10^6$ (dL g ⁻¹)
Linear PS	Benzene	0.80	0.71	496	118
Linear PS	Cyclohexane	1.09	0.89	27.9	30.2
Star PS	Benzene	0.76	0.68	298	66.5
Star PS	Cyclohexane	1.16	0.91	2.71	6.72

TABLE VIII
Comparison of Measured and Calculated Values of $[\eta]$ for 12-Arm Star Polystyrenes in Benzene

Sample	$\bar{M}_w \times 10^{-4}$	28°C ^a ($[\eta]$ benzene)	$[\eta]^b$
PS 9-12	6.10	0.135	0.126
PS 6-12	16.4	0.266	0.279
PS 4-12	50.6	0.547	0.528
PS 5-12	80.5	0.861	0.971
PS 7-12	112	1.04	1.14

^a Measured values.

^b Values calculated from eq. (6).

and linear and star polymers of the same molecular weight are compared using results in thermodynamically good solvents. The parameter b is almost equivalent to the branching parameter $g' = [\eta]_{br}/[\eta]_l$. For results in benzene, we calculate $b = 0.38$ and $b = 0.35$ for $\bar{M}_w = 10^5$ and $\bar{M}_w = 10^6$, respectively. These results can be compared with the value of $g' = 0.35$ found for 12-arm star polystyrene in toluene,¹⁸ another thermodynamically good solvent for polystyrene.

The small molecular weight dependence of b can be attributed to the slightly different values of β given in Table VIII for linear and star polystyrenes in benzene. We attribute these differences to experimental errors. It is also appropriate to note that the values of β found in benzene are similar to values of α , the Mark-Houwink-Sakurada exponent, found for linear polystyrenes in benzene.^{19,20}

Values of β found in cyclohexane (Table VII) are larger than values found in benzene. Obviously these larger values of β can be attributed to changes in solvent quality of cyclohexane on going from 35°C (near- θ condition) to 59°C (moderate solvent quality). This change in solvent quality leads to chain expansion, which is greater for polymers of higher molecular weight. Consequently, the power law dependence on \bar{M}_w is greater under these conditions. In addition, because linear polymers undergo greater expansion than branched polymers with improving solvent quality, the values of b calculated from results in cyclohexane are much smaller than values obtained in benzene.

In conclusion, we have demonstrated that Moore's equations for actual viscosities of dilute solutions of linear polymer are also valid for star-branched polystyrenes in dilute benzene and cyclohexane solutions. We have defined a branching parameter [$b = K_\beta M^\beta(\text{star})/K_\beta M^\beta(\text{linear})$] derived from actual viscosity measurements and have shown that $b \approx g'$ for 12-arm star polystyrenes in benzene.

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