Synthesis and dilute solution characterization of comb polystyrenes

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Four new series of comb polystyrenes were prepared and characterized. The observed θ temperature depression of the combs can be described by Benoit's three parameter theory with $\Psi_1 = 0.32$ and $(1/3 - \chi_2) = 0.045$. Also, the dimensions of the combs at θ agree reasonably with the theory. Intrinsic viscosity measurements were used to investigate m in $g' = g_{th}^m$. A decrease of m from 3/2 to about 0.6 is found on decreasing g_{th} at θ_{A_2}. At constant g_{th}, m is slightly dependent on the comb structure. In a good solvent m varies less, an average $m = 0.75$ is found for the combs studied. The gel permeation chromatograms of the combs obey the universal calibration based on the hydrodynamic volume parameter. The glass transition temperatures of the combs depend on the number of end groups per unit volume, the branch points having a small T_g raising effect.

INTRODUCTION

Long-chain branching occurs very frequently in commercial high polymers. But the extent of branching and the effect of the branches on the physical properties of commercial polymers are extremely difficult to elucidate. The study of model branched polymers will be very useful in this regard. The synthesis of regular star polymers with up to twelve arms has been perfected and the study of their properties has yielded valuable insight into the effect of branching[1–6]. However, because regular star type branching is not normally found in commercial polymers, studies on other model branched polymers are desirable.

Model comb polystyrenes in which narrow molecular weight distribution branches (M_{br}) are placed randomly along a narrow molecular weight distribution backbone (M_{bb}) have been studied repeatedly[7–11]. It was found that comb polystyrenes exhibit lower θ_{A_2} temperatures as do star polystyrenes[7–10]. However, analysis in terms of two interaction parameters Ψ_1 and $(1/3-\chi_2)$ representing binary and triple contact interactions was only successful for the star polymers[2,8]. This is the more puzzling because the polymer segment densities in the comb polymers are seldom as high as in low molecular weight star polystyrenes. The radii of gyration of comb polymers are always higher than calculated from random-flight statistics but not well accounted for[7–10]. Intrinsic viscosities of comb polymers are routinely measured and are lower than those of linear polymers with the same molecular weight. However, despite attempts, no correlation is apparent between the intrinsic viscosity and the radius of gyration of a comb polymer[9,10].

Clearly, the properties of model comb polymers are not yet understood to the same extent as those of regular star polymers. Improvements in the synthesis and characterization are desirable. The effect of the presence of foreign groups on the properties of combs needs investigation[12]. In this paper, the synthesis of four sets of comb polystyrenes is described and their properties investigated in the light of the aforementioned problems. In a subsequent paper, the concentrated solution and melt properties of these comb polymers will be described.

EXPERIMENTAL

The backbone polystyrenes were made with sec-butyllithium in benzene at room temperature. The resulting narrow molecular weight distribution polystyrenes were chloromethylated to about 50 (C3 series), 25 (C5 series), and 30 (C6 and C7 series) chlorine atoms per chain[13]. The branch prepolymers were also prepared with sec-butyllithium in benzene. They were terminated with CO_2, acidified and converted to the potassium salt. The comb polymers were prepared by coupling backbone and branches using dicyclohexyl-18-crown-6 as catalyst[14]. The reaction was monitored by g.p.c. An example is shown in *Figure 1*. Excess branch material was removed by a double fractionation in dilute benzene-methanol. A small head and tail fraction (~5%) was also removed from each comb sample.

The i.r. absorption of the carboxyl groups in the comb polymer was measured with an Infracord, the concentration

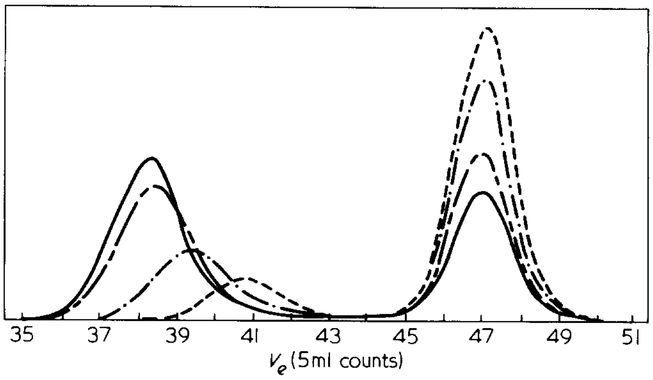

Figure 1 G.p.c. monitoring of the synthesis of comb C752. The single branch elutes at 47 counts. At 47 counts from the top: initial, after 4 hrs., after 1 day, after 6 days

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Table 1 Characteristics of backbone, branch and comb polystyrenes

Sample	$M_w \cdot 10^{-5}$ (Light scattering) cyclohexane	M* (Equation 1 or 2)	$M_{n_{br}} \cdot 10^{-3}$	$\bar{p}$** (Equation 3)	g_{th} (Equation 6)
C5*bb*	1.53	–	–	–	–
C522	1.78 (1.72)	1.69	1.0	25	0.862
C512	2.23 (2.30)	2.19	3.0	23	0.699
C502	3.68	3.57	10.0	21	0.463
C3*bb*	1.51	–	–	–	–
C352	2.06	–	1.0	55	0.737
C342	3.01	3.15	3.0	50	0.517
C332	10.4	10.4	18.7	48	0.189
C6*bb*	2.75	–	–	–	–
C612	4.75	4.7	6.5	31	0.597
C622	6.24	6.3	11.7	30	0.473
C632	9.13	(6.9)	25.7	25	0.353
C642	16.3	16.5	47.0	29	0.241
C652	31.3	31.4	98.0	29	0.175
C7*bb*	8.60	–	–	–	–
C712	10.5_5	10.7	6.5	30	0.819
C722	11.9	11.7	11.7	28	0.732
C732	15.3	16.0	25.7	26	0.583
C742	22.3	22.4	47.0	29	0.426
C752	36.2	36.5	98.0	28	0.300

* from equation 2 for C5 and C3; from equation 1 for C6 and C7

** from i.r. analysis of acetylated backbone. C5: 28; C3: 53; C6:30 and C7:30

(c) of the polymer in CCl_4 being adjusted to obtain an optical density (o.d.) in the range where Beer's law is applicable. Calibration was performed with completely acetylated and 2-phenylpropionated back bone samples[14].

Light scattering measurements were performed with a Fica 50 instrument using vertically polarized light of wavelength 4358 Å. The refractive index increment of polystyrene in cyclohexane is 0.181 and in toluene is 0.113 at 35°C. The Rayleigh ratio of benzene is taken as 50.8 x 10^{-6}. The temperature variation of the second virial coefficient (A_2) was used to determine θ_{A_2}, i.e. the temperature at which $A_2 = 0$, for each comb polymer. The angular alignment of the Fica 50 was checked with benzene and cyclohexane standards and daily instrument corrections (<1.5% at the 30° angle) were applied to the measured intensities. The zero-concentration angular scattering of the comb polymers was found in good agreement with calculated intramolecular scattering functions[15]. The radii of gyration of the comb polymers were obtained from a matching of the scattered light intensities at 13 angles with the calculated scattering curves.

Intrinsic viscosities were measured in Ubbelohde viscometers with solvent flow times between 150 and 200 seconds.

Gel permeation experiments were performed with a Waters 301 g.p.c. equipped with 9 columns between 60 Å and 3 x 10^6 Å. Toluene at 35°C was the solvent and the flow rate was 1 ml/min.

The glass transition temperatures were determined by differential scanning calorimetry (Perkin–Elmer DSC-1B) at 10°C/min heating rates.

RESULTS AND DISCUSSION

Synthesis and polymer characterization

The structure of the comb polymers will be unambiguously established when their molecular weight characteristics agree with those expected from the stoichiometry of the coupling reaction. The final weight fraction of the comb relative to the initial weight fraction of backbone in the coupling reaction mixture can be used to calculate the molecular weight of the comb polymer:

$$M_{comb} = M_{bb}\frac{\text{final weight \% comb}}{\text{initial weight \% backbone}} \qquad (1)$$

I.r. analysis of the carboxyl group allows one to calculate the number-average molecular weight from

$$M_{comb} = M_{bb}\left(\frac{\text{o.d.}}{c}\right)_{bb-acetyl}\left(\frac{c}{\text{o.d.}}\right)_{comb} \qquad (2)$$

The former method is more suitable when there is a large molecular weight increase on forming the comb as in the C6 and C7 combs. The latter method is more sensitive for combs with a large number of small branches as in the C3 and C5 series of combs. The results are given in *Table 1*. The agreement with the weight-average molecular weights measured by light scattering is satisfactory. The experimental number of branches per backbone is calculated from

$$\bar{p} = \frac{M_{w_{comb}} - M_{w_{bb}}}{M_{n_{br}}} \qquad (3)$$

Values of $\bar{p}$ are also given in *Table 1*. They differ from the more rigorous

$$p_n = \frac{M_{n_{comb}} - M_{n_{bb}}}{M_{n_{br}}} \qquad (4)$$

because of the finite polydispersity of the backbone and branches and the random placement of the branches on the

Table 2 Radii of gyration and expansion coefficient at the Flory θ temperature

Sample	$M_w \cdot 10^5$	$\langle S^2\rangle_\theta \cdot 10^{-4}$ (Å^2)	g_{exp}	α^2_θ	α^2 (Equation 8)
C332	10.4	2.76		1.85	1.86
C612	4.75	2.6_3	0.729	1.22	1.12
C622	6.24	2.7_9	0.588	1.24	1.20
C632	9.13	3.2_7	0.472	1.34	1.35
C642	16.3	4.2_0	0.338	1.4_3	1.6_5
C652	31.3	6.3_5	0.267	1.5_3	1.9_5
C712	10.5	7.1	0.886	1.08	1.06
C722	11.9	7.4_5	0.825	1.13	1.07
C732	15.3	7.7_7	0.669	1.15	1.13
C742	22.3	9.1_2	0.538	1.2_6	1.2_5
C752	36.2	11.8	0.429	1.4_3	1.4_6

backbone. According to Orofino[16].

$$\bar{p} = p_n \left(\frac{x_w}{x_n} + \frac{y(x_n - p_n)}{x_n(x_w + p_n y)}\right) \tag{5}$$

where x and y are the degrees of polymerization of backbone and branches respectively. The first term in the brackets is nearly one for anionically prepared polystyrene. The second term in the brackets is less than 0.031 for the comb polymers studied here. The uncertainty in $\bar{p}$ due to experimental errors in the molecular weight determination is probably as large as the difference between $\bar{p}$ and p_n.

Values of $\bar{p}$ agree with the chlorine analysis of the backbone polymer and i.r. analysis of the acetylated backbone. Also, $\bar{p}$ values within a comb series show little variation.

It is instructive to check the g.p.c. traces of the combs even when one cannot calculate the molecular weight distribution. Each g.p.c. trace was found to be as narrow as for an anionically prepared linear polystyrene with the same elution volume. Especially, no high molecular weight component could be detected that would indicate the occurrence of backbone–backbone coupling. The presence of such molecules would be difficult to detect by other molecular weight determination methods, but would be particularly troublesome in the determination of the structure-property relations.

Dimensions at the Flory θ-temperature

The determination of the molecular weight of each comb polymer leads immediately to $\bar{p}$, the number of branches in the comb, and λ, the weight fraction of backbone in the polymer. Both parameters are used in the calculation of g_{th}, the ratio of the mean-square radius of gyration of a branched polymer to that of the linear polymer with the same molecular weight. Theoretically, for heterogeneous comb polymers[17]

$$g_{th} = \frac{\langle S^2\rangle_{0\,comb}}{\langle S^2\rangle_{0\,lin}} = \lambda + \frac{3}{\bar{p}}(1-\lambda)^2 + \frac{(1-\lambda)^3}{\bar{p}^2} \tag{6}$$

Equation 6 is based on the random-flight model for the chain conformation of each subchain in the comb. The values for $\langle S^2\rangle_{0_{comb}}$ are calculated with $\langle S^2\rangle_{0_{lin}} = 7.6 \times 10^{-18} M\,(\text{cm}^2)$[2,18]. The radii of gyration determined in cyclohexane at the Flory θ-temperature, $\langle S^2\rangle_\theta$, are given in *Table 2*. In all cases the values are larger than $\langle S^2\rangle_{0_{comb}}$ predicted by equation 6. The comb polymers are therefore expanded at the θ-temperature

$$\frac{\langle S^2\rangle_\theta}{\langle S^2\rangle_0} = \alpha_\theta^2 \tag{7}$$

Benoit *et al.* have attributed this expansion to the increased likelihood of triple contacts due to the higher segment density in branched polymers than in linear polymers. While at the θ-temperature double contacts have disappeared, triple contacts still contribute to coil expansion. The extra term introduced in Flory's dilute solution theory is at θ

$$\alpha_\theta^8 - \alpha_\theta^6 = \frac{2C'_M(1/3 - \chi_2)}{3g_{th}^3} \tag{8}$$

where

$$C'_M = \frac{3^{5/2}\bar{v}_2^3}{2^4\pi^3 N_a^2 V_1}\left(\frac{M}{\langle S^2\rangle_0}\right)^3$$

Values of α_θ^2 calculated with $(1/3 - \chi_2) = 0.045$ in equation 8 are compared with the experimental values in *Table 2*. The agreement is fair indicating that the expansion of the comb polymers at θ can be accounted for on thermodynamic grounds with the same triple contact parameter previously derived from the θ_{A_2} values of low molecular weight star polymers[2].

The θ_{A_2} temperature

The temperature at which the second virial coefficient of the comb polystyrenes becomes zero (θ_{A_2}) was also investigated. First, it was ascertained that the presence of foreign groups, i.e. the sec-butyl end group and the carboxyl group at the branch point do not affect the θ_{A_2} value in linear polystyrene[12]. For this purpose the chloromethylated C3 backbone was completely converted to C3*bb*—CH$_2$—(methyl-2-butyrate). It was found that the θ_{A_2} temperature of this polymer was unchanged from that of linear polystyrene ($\theta_{A_2} = \theta = 34.5°\text{C}$; $dn/dc = 0.179$; $M_w = 1.53 \times 10^5$). Obviously, the effect of the sec-butyl and carboxyl groups on the θ-temperature cancel each other[12]. The variation of A_2 around the θ-temperature was also unaffected by the substituents[12]. In the following discussion it will be assumed that these groups do not influence θ_{A_2} when they are part of a comb polystyrene.

From the θ_{A_2} results for the lower molecular weight comb polystyrenes in *Table 3* it can be seen that there is a maximum θ_{A_2} temperature depression within each series of

Table 3 θ_{A_2} of comb polystyrenes with small branches

Sample	$M_w\,10^5$	θ_{A_2}	θ_{A_2} (Equation 9)*
C522	1.78	30.5	32.6
C512	2.23	29.2	31.6
C502	3.68	30.7	30.6
C352	2.06	27.6	30.8
C342	3.01	25.3	24.5
C332	10.4	32.3	30.2
C612	4.75	33.2	33.2

* $\Psi_1 = 0.321$ and $1/3 - \chi_2 = 0.045$

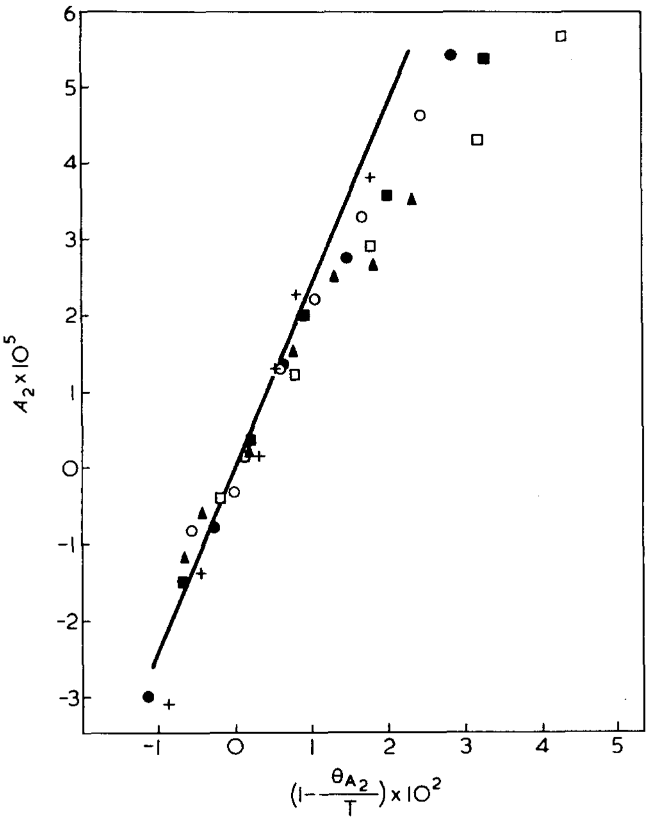

Figure 2 Temperature dependence of the second virial coefficient of comb polystyrene in cyclohexane: ○, C352; □, C342; ●, C522; ■, C512; ▲, C502; +, C3bb–CH$_2$–(2-methyl-butyrate). The line represents the asymptote at $(1 - \theta/T)$ for linear polystyrene

comb polystyrenes. This maximum θ_{A_2} depression is found at relatively small branch lengths and is largest in the combs with the smallest spacing between the branches. The comb polymers of the C6 and C7 series are not listed in *Table 3* as their θ_{A_2} values are experimentally indistinguishable from θ. Previously published results indicated that comb polymers with similar structure had somewhat larger θ_{A_2} depressions than found in this work[7]. This is probably caused by the abundance of sec-butyl end groups and the in-chain $-CH_2-CH-O-Si-(CH_3)_2-$ linking groups in these comb polystyrenes both of which are expected to improve the solubility of polystyrene in cyclohexane. The trend of smaller θ_{A_2} depressions on increasing the branch molecular weight above 10 000, observed with the earlier comb polystyrenes is also observed with the combs studied here.

The three parameter theory for dilute solutions of branched polymers was also applied to the θ_{A_2} results, although the smaller branches would not be expected to have a Gaussian conformation. The θ_{A_2} temperature is given by[8]

$$\frac{\theta}{\theta_{A_2}} - 1 = \frac{3^{3/2}C'_M(1/3-\chi_2)\,H(K')}{2^4 C_M \Psi_1 M^{1/2} g_{th}^{3/2}\alpha^3_{\theta A_2}} \tag{9}$$

where

$$C_M = \frac{3^{3/2}}{2^4\pi^{3/2}}\frac{\bar{v}_2^2}{N_a V_1}\left(\frac{M}{\langle S^2\rangle_0}\right)^{3/2},$$

$$K' = \frac{2C'_M(1/3-\chi_2)}{g_{th}^3\,\alpha^6_{\theta A_2}}$$

and $H(K')$ is given in reference 8.

The value of Ψ_1 can be obtained from the slope at $T = \theta_{A_2}$ in plots of A_2 vs $[1-(\theta_{A_2}/T)]$ (reference 2).

$$A_2 = \frac{\bar{v}_2^2}{V_1}\Psi_1\left(1-\frac{\theta_{A_2}}{T}\right)G(K_1K') + \frac{\pi^{3/2}N_a\left(\frac{\langle S^2\rangle_0}{M}\right)^{3/2}C'_M}{M^{1/2}\alpha^3 g_{th}^{3/2}}\left(1-\frac{\theta_{A_2}}{T}\right)J(K') \tag{10}$$

if $G(K_1K')$ goes to one at θ_{A_2} and the second term in equation 10 is small compared to the first one. The first condition is approximately met since K and K' have opposite effects at θ_{A_2} [2]. The second condition holds because the second term depends on $M^{-1/2}$. *Figure 2* shows experimental data of A_2 plotted vs $[1-(\theta_{A_2}/T)]$ for low molecular weight comb polymers. The data indicate that Ψ_1 for these comb polystyrenes is unchanged from that of linear polystyrene as was also found for four and six-arm star polystyrenes[2]. The value of $\Psi_1 = 0.32$ was used.

In order to apply equation 10 to low molecular weight comb polystyrenes, values of $\alpha_{\theta A_2}$ have to be calculated by putting $T = \theta_{A_2}$ and solving for α in[8]

$$\alpha^5 - \alpha^3 = 2C_M\Psi_1\left(1-\frac{\theta}{T}\right)\frac{M^{1/2}}{g^{3/2}} + \frac{2}{3}C'_M\frac{(1/3-\chi_2)}{\alpha^3 g^3} \tag{11}$$

using $(1/3-\chi_2) = 0.045$ in equations 11 and 9 yields the calculated θ_{A_2} values given in *Table 3*. The agreement with the experimental data is not perfect but the major trends are reproduced. In the case of the C_6 and C_7 comb polymers experimental $\alpha_{\theta A_2}$ are available (*Table 2*). Calculated θ_{A_2} values vary from 33.2°C for C612 to 31.8° for C652 and from 33.9°C for C712 to 33.4°C for C752, while experimentally their θ_{A_2} is indistinguishable from the Flory θ-temperature.

It can therefore be concluded that the three parameter theory for branched polymers accounts reasonably well for the θ_{A_2}-temperature depression and θ-temperature expansion of the comb polystyrenes with Ψ_1 and $(1/3-\chi_2)$ parameter derived from linear and star-branched polystyrenes. There is evidence that for combs with many closely spaced branches Ψ_1 and $(1/3-\chi_2)$ are no longer constants[8].

Behaviour in a good solvent

Table 4 summarizes the radii of gyration and second virial coefficients obtained for the C6 and C7 comb polystyrenes in toluene at 35°C. Rigorously, the expansion of the comb polymers in toluene is defined by

$$\alpha^2 = \frac{\langle S^2\rangle}{\langle S^2\rangle_{0comb}} \tag{12}$$

where $\langle S^2\rangle_{0comb}$ is calculated with equation 6 [8]. The comb polymers are found to be more expanded in toluene than linear polystyrene of the same molecular weight. According to equation 11, only the first term on the right will be important and $\alpha^5 - \alpha^3$ will depend on $M^{1/2}g^{-3/2}$. Such behaviour is however not found for the comb polymers studied.

Table 4 Properties of comb polystyrenes in toluene

Sample	$\langle S^2\rangle \times 10^{-4}$ (Å^2)	$A_2 \times 10^4$ (ml/g)	Ψ	g_{exp} (Equation 13)
C6*bb*	4.18	3.4	0.239	–
C612	4.79	2.3	0.369	0.647
C622	5.77	2.07	0.442	0.563
C632	7.75	1.62	0.515	0.458
C642	10.77	1.14	0.683	0.329
C652	17.05	0.8	0.867	0.246
C7*bb*	14.8	2.6	0.255	–
C712	16.9	2.2	0.265	0.887
C722	17.7	1.9	0.271	0.815
C732	21.0	1.7	0.330	0.696
C742	25.6	1.4	0.422	0.549
C752	34.3	1.0	0.545	0.401

Alternatively, the radii of gyration of the combs in toluene can be compared with those of the linear polymer of the same molecular weight

$$g_{exp} = \left(\frac{\langle S^2\rangle_{comb}}{\langle S^2\rangle_{lin}}\right)_M \tag{13}$$

The values of g_{exp} given in *Table 4* were calculated using $\langle S^2\rangle_{lin} = 1.66 \times 10^{-18} M_w^{1.18}$ (cm^2)[18–20]. These toluene g_{exp} values are within experimental error equal to those found in cyclohexane at θ, indicating that the excess expansion of the comb polymers at θ persists in the good solvent. Smaller g_{exp} values in good solvents than at θ have been observed with regular comb polystyrenes[9].

The second virial coefficients for the comb polymers in toluene are decreased from the values for linear polystyrene of the same molecular weight (*Table 4*). Our light scattering data for linear polystyrene fit $A_2 = 6.5 \times 10^{-3} M^{-0.235}$. The second virial coefficient is related to the radius of gyration by a function of the form

$$A_2 M^2 = 4\pi^{3/2} N_a \langle S^2\rangle^{3/2} \Psi \tag{14}$$

where Ψ is a measure of the non-interpenetration of the polymer coils[21]. From *Table 4* it can be seen that Ψ values for the comb polymers increase from that of linear polymers (0.25 ± 0.01) indicating that the increased segment density in the combs makes them less penetrable.

Intrinsic viscosities

The intrinsic viscosities of the comb polymers were determined at their individual θ_{A_2} temperatures in cyclohexane and in toluene at 35°C. From *Table 5* it can be seen that the intrinsic viscosity of a comb polymer can be smaller than that of its parent backbone. This phenomenon was not observed in our earlier study in which the intrinsic viscosities of the combs were compared with their vinyl acetate group containing parent backbones at 35°C[7]. It was later experimentally verified that the vinyl acetate units in polystyrene increase its θ_{A_2} [12].

There has been a great theoretical and experimental interest in establishing a relation between g' and g where g' is defined as $([\eta]_{br}/[\eta]_{lin})_M$. In the evaluation of g' we used $[\eta]_{lin} = 8.3 \times 10^{-4} M_w^{1/2}$ for cyclohexane at θ and $[\eta]_{lin} = 1.02 \times 10^{-4} M_w^{0.728}$ for toluene at 35°C[1].

Direct application of Flory's relation for linear polymers

$$[\eta] = \phi' \frac{\langle S^2\rangle^{3/2}}{M} \tag{15}$$

to branched polymers suggests that $g' = g^{3/2}$. Zimm and Kilb found an approximate relation for certain star polymers, $g' = g_{th}^{1/2}$ which they suggested would be a general approximation for all types of branched polymers[22]. Stockmayer and Fixman suggested $g' = h^3$ where h is the ratio of the translational friction constant of branched and linear polymers[23]. For the combs described here h can be calculated to a good approximation[24]. No one of these suggestions matches the experimental g' values. In fact g' data fall between $g_{th}^{1/2}$ and h^3 much in the same way as was found for star polymers[1–3]. In toluene, a good solvent, g' values are slightly lower than at θ_{A_2} as also observed in the star polymers[1–3]. It was also argued qualitatively that in a relation

$$g' = g_{th}^m \tag{16}$$

m would vary from 3/2 for combs with small branches on long backbones (limit for linear polymer when $g_{th} \to 1$) to ½ for combs with many long branches (limit for star polymers $g_{th} \to 0$)[25]. In fact it is not known whether m would be solely governed by g_{th} (or g_{exp}). Attempts, so far, to establish any order in observed g' values have failed[7,9,10]. In *Figure 3* the variation of m is shown as a function of g_{th} for comb polystyrenes with 20–30 branches and backbones with molecular weights between 1×10^5 and 2×10^5. It can be seen that the initial drop from 3/2 occurs for comb polymers with $0.8 < g < 1$ which have not previously been studied. At low g_{th} values where the combs become starlike, $m \approx 0.60$ for data obtained at θ_{A_2}. It is remarkable that for star polymers with four arms ($g_{th} = 0.625$) and six arms ($g_{th} = 0.444$), $m = 0.58$ can be calculated[1–3]. The exponent m is not a function of g_{th} of the branched polymer alone, as indicated by the different values for comb and star branched polymers. Also the m values for the C6 and C7 combs are somewhat lower than those shown in *Figure 3*. The difference becomes smaller as g_{th} decreases.

When experimental radii of gyration are available as is

Table 5 Intrinsic viscosity data for comb polystyrenes

Sample	$M_w \cdot 10^{-5}$	$[\eta]_{CH,\theta A_2}$	$[\eta]_{\text{Tol}\,35°\text{C}}$	m_{tol}
C5*bb*CH_2Cl	1.53	(0.315)	0.594	–
C522	1.78	0.286	0.582	1.02
C512	2.23	0.271	0.568	0.95
C502	3.68	0.263	0.606	0.83
C3*bb*	1.51	0.319	0.580	–
C352	2.06	0.273	0.583	0.84
C342	3.01	0.236	0.574	0.83
C332	10.4	0.269	0.720	0.74
C6*bb*	2.75	0.414	0.918	–
C612	4.75	0.377	0.925	0.782
C622	6.24	0.382	0.950	0.771
C632	9.13	0.389	1.04	0.765
C642	16.3	0.413	1.20_5	0.73_5
C652	31.3	0.489	1.56	0.72_8
C7*bb*	8.6	0.776	2.13	–
C712	10.5	0.753	2.15	0.731
C722	11.9	0.718	2.17	0.69_4
C732	15.3	0.700	2.16	0.78_8
C742	22.3	0.694	2.34	0.72_4
C752	36.2	0.721	2.72	0.70_3

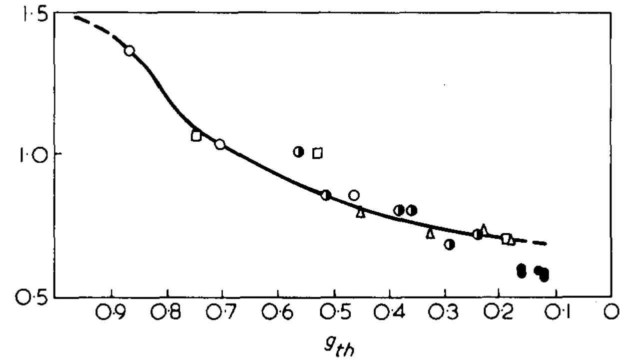

Figure 3 m vs g_{th} for comb polystyrenes with between 20 and 30 branches and M_{bb} between 1 and 2.10^5. ○, C5; □, C3; △, C0 (ref 7); ◑, ref 9; ●, ref 10. Cyclohexane θ_{A_2}

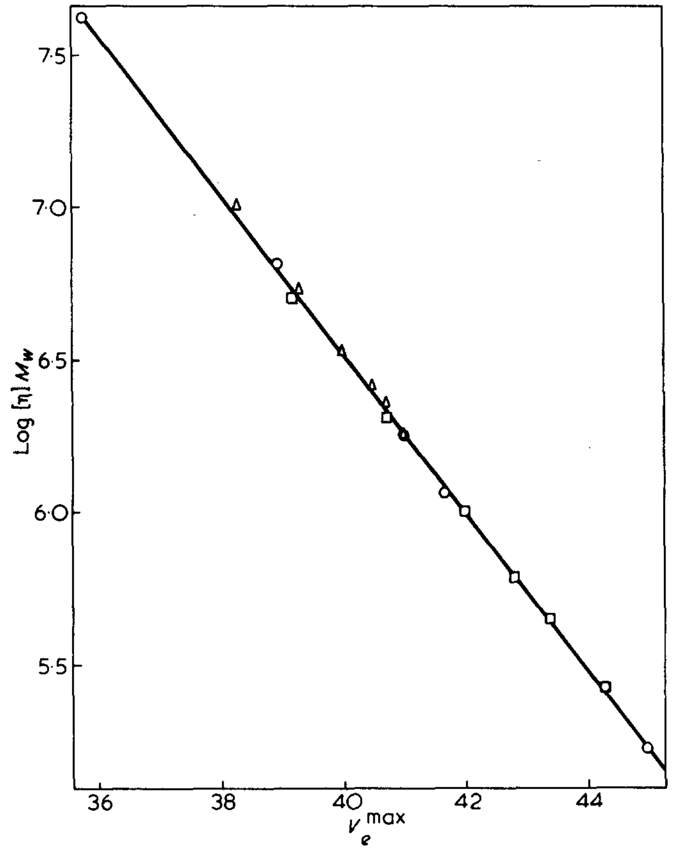

Figure 4 The universal calibration based on the hydrodynamic volume for the g.p.c. elution volume of comb polystyrenes. The data for linear polystyrene ○; C7, △; C6, □. The line refers to linear polystyrene

the case for the C6 and C7 comb polystyrenes a relation

$$g' = g_{exp}^{\mu} \qquad (17)$$

can be tested. At θ_{A_2}, it is found that μ varies between 1.20 and 0.83 with decreasing values of g. The higher values of μ compared to corresponding values of m originate from the inequality $g > g_{th}$.

Equations 16 and 17 can also be applied to the data in toluene. The values of m are given in *Table 5*. They vary between 1.0 and 0.7 with a small residual dependence not accounted for by the g_{th} parameter. From these data it seems advisable to use an average value 0.75 rather than 0.5 in the Drott–Mendelsohn method for characterizing branched polymers from their g.p.c elution volume and intrinsic viscosity in a good solvent[26]. Values of μ for C6 and C7 combs in toluene smoothly vary between 1.2 and 0.9 in going from high to low values of g_{exp}.

An alternative way of considering the relation between intrinsic viscosity and radii of gyration of comb polymers would be by making ϕ' in equation 15 an adjustable parameter. Using this treatment, ϕ' gradually increases from its value for linear polystyrene in each solvent as the branch length increases.

Gel permeation chromatography

Gel permeation chromatography is extensively used with branched polymers since it is the easiest way to characterize them. Use is made of the hydrodynamic volume as an empirical universal parameter[27].

$$V_e = f([\eta]\,M)$$

for which some theoretical justification has been given[28]. The elution data for the C6 and C7 combs are shown in *Figure 4*. They lie on the line obtained with narrow molecular-weight distribution polystyrenes. In particular it can be said that a correlation of the elution volume with $\langle S^2\rangle_{Tol}$ favoured by others for comb-shaped polystyrenes[29,30] does not hold. This follows immediately from the fact that there is no simple relation between $[\eta]$ and $\langle S^2\rangle$ as indicated by the variation of ϕ' in equation 15 for branched polymers.

Glass transition temperature

The results of d.s.c. measurements of the glass transition temperature of the lower molecular-weight comb polymers are shown in *Figure 5*. The line established for four- and six-branched polystyrenes is included for comparison[31]. A lowering of the glass transition temperature on branching is observed which depends on the number of end groups per unit volume. The decrease is not as strong as that found in the star polystyrenes, indicating that the many branch points in the comb have a glass transition temperature raising effect. The glass transition temperature of branch polymers will therefore depend on the chemical nature of the branch point and the chain ends. The glass transition temperature of C612 will be about 2°C lower than the limiting value for high molecular weight polystyrene. The other combs have

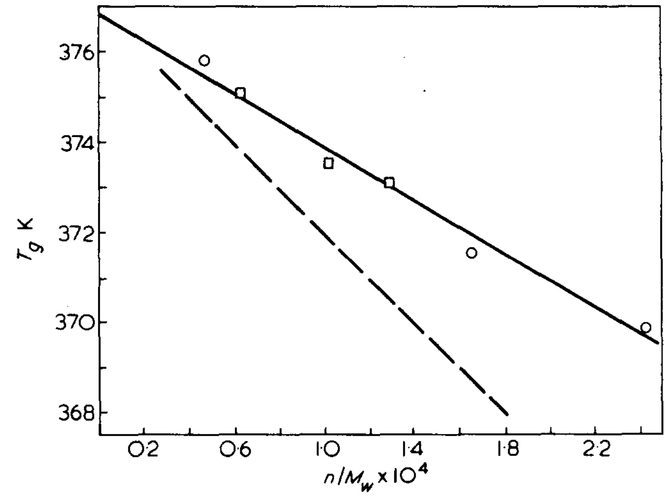

Figure 5 Glass-transition temperatures for comb polystyrenes as a function of the number of ends group per unit volume. ○, C3; □, C5. Dashed line for linear and star polystyrenes[31]

T_gs experimentally indistinguishable from that of high molecular weight polystyrene.

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