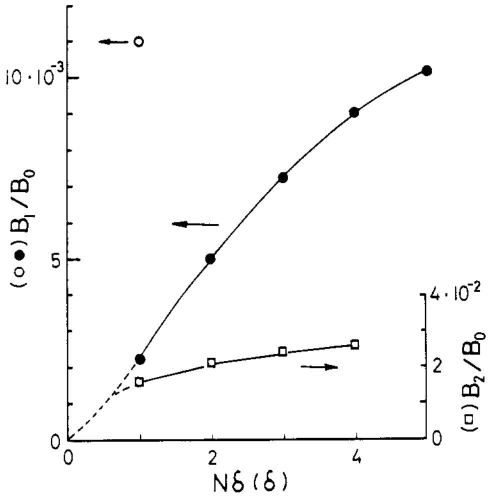

**Figure 4.** Intensity associated with a chemical relaxation. Computations were made for $N$ = 50 (● and ○) and $N$ = 10 (○) at $\gamma^2$ = 1. (○) $\alpha_i = \alpha(1 + i\delta)$ with $N\delta = 1$, (●) $\alpha_i = \alpha(1 + i\delta)$ with $1 \leq N\delta \leq 5$ and (□) $\alpha_i = \alpha[1 + \delta \sin(\pi i/N)]$ with $1 \leq \delta \leq 4$.

scattering study. Main reasons for this come from experimental difficulties in separating the weak contributions of chemical relaxation modes from the high intensity associated with the center-of-mass motion. We must therefore work under the condition of $DK^2 \leq \tau_L^{-1} \ll \tau_p^{-1}$ ($\tau_L$: the coherence time of laser light, typically 100 msec.). In that condition, the scattered light associated with the diffusive motion will act as a reference signal in the heterodyne detection and only the broadening associated with chemical relaxation modes will be observed. A depolarized light-mixing technique may also be useful in order to eliminate the strong contribution from the center-of-mass motion,[31] although this technique has inherent difficulties. Because of a collective behavior of a coupled reaction, very fast reaction kinetics may be followed. For example, if $A = B = 10^6$ sec$^{-1}$ is assumed, the $\tau^{-1}$ value will become $10^3$ sec$^{-1}$ for $N$ = 100 (from eq 26). This value of $\tau_1$ is in a favorable range of measurements by the present method.

We are trying to detect the *in vivo* interaction between actin and myosin in the presence of ATP,[32] where both proteins are hard to diffuse randomly.[33]

The following is noteworthy: Throughout this investigation, we assumed $D_i = D$ for all $i$'s. When $D_i \neq D_j$ (and/or $P_i(\mathbf{K}) \neq P_j(\mathbf{K})$), the intensity associated with the chemical reaction, $B_P$, does not equal zero even for $\alpha_i = \alpha$. As has been pointed out,[9] $D_i \neq D_j$ may be important in detecting a chemical relaxation in the case of small $N$. However, a possible existence of sample polydispersity might make the analysis difficult for the case of large $N$.

**Acknowledgment.** The facilities of the Computing Center of Nagoya University were utilized in this work.

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# Viscosity and Normal Stresses of Linear and Star Branched Polystyrene Solutions. I. Application of Corresponding States Principle to Zero-Shear Viscosities[1a]

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ABSTRACT: The zero-shear solution viscosities, $\eta_0$, of linear, 4- and 6-star branched, monodispersed polystyrenes in diethylbenzene, $c$ = 25.5 g/dl, were measured by a capillary and cone-and-plate method. As for each type of polymer the molecular weights vary by a factor of at least 30, the $\eta_0$'s varied at least by a factor of $10^3$. It was demonstrated that the corresponding states principle (CSP) applied to these systems predicts a superposition of data plotted as $(\eta_0 - \eta_s)/[\eta]'_\Theta$ *vs.* $[\eta]_\Theta$. Using experimental $[\eta]_\Theta$'s a remarkable superposition was found. Replacing $[\eta]_\Theta$ by $(M_w g)^{1/2}$, where $g$ has the value computed from Zimm and Stockmayer relation, still a good superposition was achieved. It was also found that the numerical value of the coefficient $(\partial \ln \eta_0/\partial \ln c)_{M,T}$ calculated from the master curve agreed numerically with the experimental value computed from the data published in 1953 by Bueche. For samples with molecular weights larger than the critical entanglement molecular weight the temperature dependence of the viscosity in the range 20–40° can be expressed by an Arrhenius-type equation. The average activation energy of flow $E_\eta$ equals 5.9 ± 1.1 kcal/mol and is independent of the molecular weight and the structure of the polymer.

In many industrial applications one of the most often discussed parameters is the chain branching of polymer macromolecules. Unfortunately, in spite of numerous papers published on this subject,[2-7] no quantitative prediction can be made in regard to the effect of branching on rheological behavior of polymers. The main reasons for this lie in the diversity of branching and in the heterogeneity of polymer samples as far as branching length, branching density, and molecular weight are concerned. Furthermore, very often the rheological studies are limited to the viscous properties or to the low rate of shear re-

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(1) (a) Part of this work was presented at the 55th Annual Meeting of the Chemical Institute of Canada, Quebec, Canada, June 5-7, 1972. (b) Department of Chemical Engineering, McGill University, Montreal, Canada. The shear-dependent properties were measured at the Gulf Oil Canada, Research Center in Ste-Anne-de-Bellevue, Quebec, Canada. (c) Division of Chemistry, National Research Council of Canada, Ottawa KIA OR9, Canada.

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**Table I**
**Characteristics of Polymer Samples**

| No. | Code | $M_w \times 10^{-3}$ [a] | $f$ [b] | $M_w/M_n$ [a] | $[\eta]_0$ [c] | $k_1$ [c] | $\eta_0$ |
|---|---|---|---|---|---|---|---|
| | | | Linear Polystyrenes | | | | |
| 10 | MSI-3 | 34.0 | | 1.17 | 0.1515 | 0.618 | 0.343 |
| 11 | S 102 | 84.0 | | 1.05 | 0.241 | | 1.24 |
| 12 | PS-100 | 117 | | 1.01 | 0.279 | 0.567 | 2.23 |
| 13 | S 105 | 153 | | 1.04 | 0.325 | | 4.38 |
| 14 | S 109 | 193 | | 1.06 | 0.359 | | 7.22 |
| 15 | S 108 | 238 | | 1.08 | 0.440 | | 16.5 |
| 16 | MSI-2 | 465 | | 1.03 | 0.575 | | 129.8 |
| 17 | PS-800f2 | 675 | | | 0.684 | 0.52 | 365 |
| 18 | PS-1000f2 | 1790 | | | 1.245 | 0.50 | |
| 19 | PS 150 | 216 | | | 0.383 | 0.578 | |
| | | | Four-Branched Polystyrenes | | | | |
| 40 | S 131A | 50.7 | 3.92 | 1.11 | 0.141 | 0.764 | 0.276 |
| 41 | S 121A | 93.5 | 3.92 | 1.06 | 0.191 | 0.754 | 0.660 |
| 42 | S 111A | 154 | 4.06 | 1.05 | 0.256 | 0.608 | 1.61 |
| 43 | S 161A | 351 | 3.86 | 1.07 | 0.384 | 0.584 | 8.22 |
| 44 | S 141AA | 525 | 3.84 | 1.13 | 0.448 | 0.628 | 23.5 |
| 45 | S 221A | 897 | (4.05) | | 0.589 | 0.59 | 103 |
| 46 | S 181A | 1050 | (4.12) | | 0.635 | 0.667 | 209 |
| 47 | S 191AA | 1390 | (4.14) | | 0.740 | 0.605 | 586 |
| 48 | S 091A | 193 | | | 0.278 | 0.644 | |
| 49 | S 101AAA | 454 | | | 0.420 | 0.557 | |
| | | | Six-Branched Polystyrenes | | | | |
| 60 | HS 071A | 65.3 | 5.61 | $1.01_5$ | 0.136 | 0.635 | 0.34 |
| 61 | HS 061A | 110 | 5.83 | 1.03 | 0.177 | 0.658 | 0.641 |
| 62 | HS 011A | 237 | 6.19 | 1.02 | 0.269 | 0.607 | 2.01 |
| 63 | HS 101B | 317 | 5.68 | 1.02 | 0.302 | 0.667 | 3.46 |
| 64 | HS 041A | 509 | (6.04) | | 0.374 | 0.638 | 8.62 |
| 65 | HS 111A | 591 | (5.90) | | 0.405 | 0.659 | 12.0 |
| 66 | HS 051A | 1090 | (5.63) | | 0.557 | 0.658 | 71 |
| 67 | HS 091B | 1650 | (6.00) | | 0.680 | 0.619 | 292 |
| 68 | HS 121A | 1820 | (6.09) | | 0.723 | 0.635 | |

[a] $M_w$ from light scattering (L Sc) in cyclohexane at 35°, $M_n$ from osmotic pressure in toluene at 35°. [b] $f = M_n(\text{star})/M_n(\text{prepolymer})$ except the values in parentheses $(f) = M_w(\text{prepolymer})/M_n(\text{prepolymer})$. [c] In cyclohexane at 35°.

**Table II**
**Rheological Data from Cone-and-Plate Viscometer for $Et_2Ph$ Solutions at 30.0°**

| Sample No. | $\eta_0$ (P) | $E_\eta$ (kcal/mol) |
|---|---|---|
| 15 | 18.6 | 9.7 |
| 17 | 362 (365)[a] | 4.9 |
| 18 | 13,100 | 5.3 |
| 43 | 7.5 | 5.2 |
| 45 | 95 | 6.7 |
| 47 | 569 | 4.4 (6.7)[a] |
| 66 | 79 | 5.2 |
| 68 | 347 | 5.1 |
| | | $\bar{E}_\eta = 5.9 \pm 1.1$ |

[a] Two independent sets of data.

gion, and cannot supply sufficient information necessary for industrial scientists.

In the first part of this paper the results on the zero-shear viscosity, $\eta_0$, measurements of 25.5-g/dl solutions in diethylbenzene ($Et_2Ph$) of monodispersed linear, 4- and 6-star branched polystyrenes are reported. Eight of the total twenty-six samples were investigated at temperatures 20–40°, whereas the remaining at 30° only. The results were compared with the data reported for linear polystyrenes.[8-10] In the second part of this paper the shear dependent properties of these polymers will be discussed.

The main objective of this work was to examine the comparative solution viscosity behavior of linear and star branched polymers and to establish a method which would allow calculation of $\eta_{0,\text{br}}$ for branched samples from the value of $\eta_0$ of linear homologue and some characteristic parameter of the branched polymer.

In addition, it was of interest to analyze the applicability of the corresponding states principle for viscosity[11-16] (CSP) to these branched polymer solution data.

## Experimental Section

**Polymers and Solvents.** The characteristics of polymer samples are shown in Table I. The methods of their preparation and characterization are published elsewhere.[17,18] Reagent grade $Et_2Ph$ was fractionated from $CaH_2$ and a middle cut consisting of equal amounts of meta and para isomers (density, $d^{30}$ = 0.8563 g/cm$^3$; viscosity, $\eta_s^{30}$ = 0.8009 cP) was used.

The solutions (25.5 g/dl) in $Et_2Ph$ were made up in evacuated and sealed glass ampoules. These were regularly inverted to speed up the dissolution process. It took from 1 to 3 weeks to dissolve the polymer at 25.0°.

**Measurements.** The zero-shear viscosities were measured in calibrated Cannon-Ubbelohde viscometers at 30.0°. The maxi-

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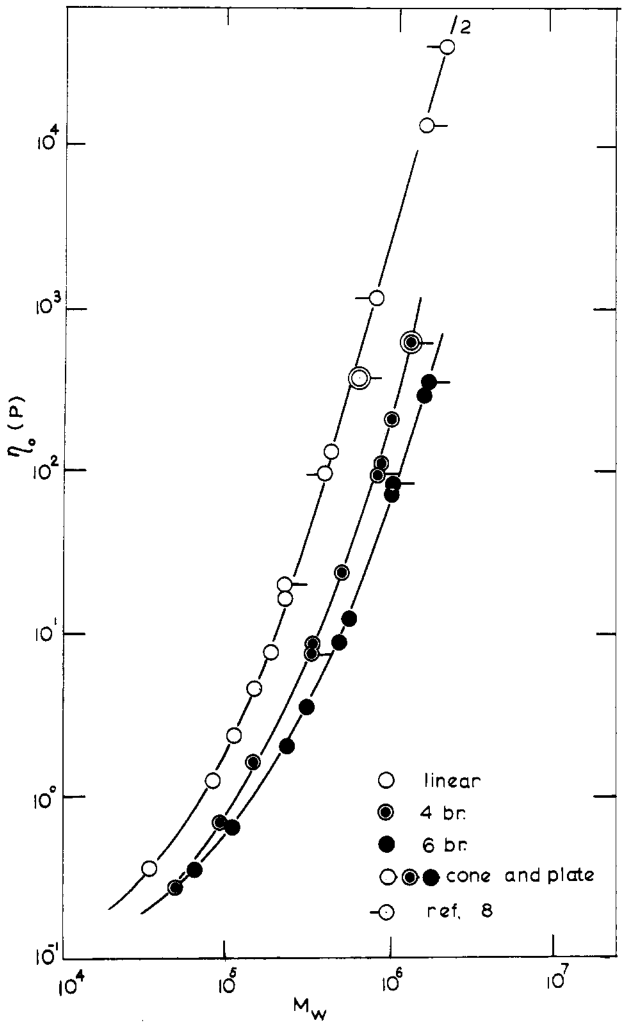

**Figure 1.** Zero-shear viscosity, $\eta_0$, as a function of weight-average molecular weight, $M_w$, for diethylbenzene solution ($c$ = 25.5 g/dl) of linear, 4-star branched, and 6-star branched, polystyrenes at 30.0°. The points with pip right are from cone-and-plate instrument.

mum shear rate varied between $\dot{\gamma}$ = 50 sec$^{-1}$ and $\dot{\gamma}$ = 0.1 sec$^{-1}$ for the lowest and highest viscosity samples, respectively. The published results on viscosity behavior of linear polystyrene solutions[8,9] indicate that under these conditions the viscosities are independent of $\dot{\gamma}$. Similar conclusion was reached on the basis of our own cone-and-plate measurements for the investigated solutions.

The rheological measurements were carried out with the cone-and-plate Weissenberg rheogoniometer, Model R18, equipped with a new modified normal force servo system. Two pairs of platens were used: 5- and 7.5-cm diameter, both having 2° cone angle. Three torsion bars with the following spring constants $K_T$ = 92.4, 877, and 10,080 (dyn cm) per $\mu$ were employed. These values are the averages of three sets of $K_T$'s determined by three different methods in our laboratory. They are up to 18% in variance with the values supplied by the manufacturer. Where necessary ($\dot{\gamma} \geq$ 30 sec$^{-1}$), the centrifugal force and shear heating effect corrections were used.[19]

The experiments were carried out at constant temperature ($T$ ± 0.2°). The data were inter- or, as in some cases, extrapolated to 30.0°.

It was found that, due to evaporation of $Et_2Ph$, the viscosity of the solutions increased with time ($t$): $\eta' = (\partial \ln \eta_0/\partial t)_{\dot{\gamma},T}$ = 0.06–0.6 hr$^{-1}$. Consequently, $\eta'$ was determined first in the Newtonian region and then the viscosity *vs.* $\dot{\gamma}$ curves were extrapolated to zero-shearing time. Owing to this effect each sample was sheared for less than 15 min.

## Results

The zero-shear viscosities at 30.0° of 25.5-g/dl polymer solutions in $Et_2Ph$ are presented in Tables I and II. The $\eta_0$'s are plotted *vs.* the weight-average molecular weight ($M_w$) in Figure 1. The solvent contribution to the solution viscosity: $(1 - \varphi)\eta_s$ = 0.0056 P ($\varphi$ is the polymer volume fraction), is always less than 2% and is neglected. In Figure 1, Graessley *et al.*[8,9] results for narrow distribution linear polystyrenes in $n$-butylbenzene at 30° are also shown.

In Table II the activation energies of viscous flow, $E_\eta$ are given. In the temperature range 20–40°, the Arrhenius plot for both linear and star branched polymers indicate a simple activated flow and no systematic variation of the slopes with branching was observed. The mean average $\bar{E}_\eta$ = 5.9 ± 1.1 kcal/mol is calculated. Alternatively rejecting the unreasonably large value of $E_\eta$ = 9.7 of sample 15, for which we do not have an explanation, the average $\bar{E}_\eta$ = 5.4 ± 0.3 kcal/mol is found instead.

## Discussion

**Molecular Weight Dependence of the Zero-Shear Viscosity.** The theoretical or semitheoretical relations between zero-shear viscosity coefficient (hereafter referred to as the viscosity, $\eta_0$ in poise), molecular weight ($M$) and concentration ($c$ in g/dl) can be divided into three groups: (I) theories[2,20] based on Bueche's work[21] which predict a sharp change of slope

$$a = (\partial \log \eta_0/\partial \log M)_{c,T}$$

($T$ is the absolute temperature) at the entanglement point ($\eta_{0e}$, $M_e$); (II) theories[22,23] which assuming a thermodynamic coupling mechanism arrive at a monotonicly increasing function $a = a(M)$; and (III) the CSP approach[11-16] which, avoiding any explicit mathematical formulation of $\eta_0 = \eta_0(c,M,T)$ dependence, provides means to generate $\eta_0$ values from the master curve expressed in the reduced variables form $\tilde{\eta} = \tilde{\eta}(\tilde{c})$.

The experimental data $\eta_0 = \eta_0(M, c = \text{constant}\ T = \text{constant})$ of linear and star branched polystyrenes reported in this paper will be analyzed in the framework of these three types of theoretical approach. The values of $M$ used in the following part are the weight averages $M_w$.

(I) The most popular $\eta_0 = \eta_0(M)$ dependence was written[2] in the form

$$\eta_0 = F(X)\zeta \tag{1}$$

where

$$F(X) = (N_A/6)X_e(X/X_e)^a$$
$$a = 1 \text{ for } X \leq X_e$$
$$a = 3.4 \text{ for } X \geq X_e$$
$$X = \langle s_0^2\rangle\varphi/v_0 m_a$$

where $\zeta$ is the friction coefficient per chain atom, $N_A$ is Avogadro's number, $\langle s_0^2\rangle$ is the mean-square radius of gyration of the unperturbed chain, $v_0$ is polymer specific volume, and $m_a$ is the molecular weight of the polymer per backbone atom. $X_e$ is the value of $X$ at the entanglement point given by the intersection of the two straight-

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line dependencies in the log $\eta_0$ *vs.* log $M_w$ plot, predicted by eq 1. For branched molecules, eq 1 should also be valid,[2,21] provided that $\langle s_0^2 \rangle$ is replaced by the unperturbed dimension of a branched polymer

$$\langle s_0^2 \rangle_{\mathrm{br}} = \langle s_0^2 \rangle g \qquad (2)$$

where $g$ is the ratio defined by this equation and the symbols with and without the subscript "br" are referring to the properties of branched and linear molecules, respectively. For star branched molecules[24]

$$g = g_z = (3f - 2)/f^2 \qquad (3)$$

where $f$ is the number of branches per molecule, and the subscript $z$ refers to the values of $g$ calculated from eq 3.

It should be noted that even for linear polymers eq 1 approximates only the $\eta_0$ *vs.* $M_w$ dependence.[13,14] For polymer solutions and for $\eta_0$ of polydisperse polymer melts it became exceedingly difficult to draw the two straight lines on the log $\eta_0$ *vs.* log $M_w$ plot, predicted by this relation, as the exponent a changes continuously with $M$. Furthermore,[13] for $X < X_e$, experimentally $a = 0.23$–$1.4$ instead of 1; whereas for $X > X_e$, $a = 1.88$–$5.8$ instead of 3.4, and more recently[25] the value $a = 7$ was reported. This indicates that eq 1 cannot be applied to all cases even if it is useful for most flexible chain polymers at a limited range of $X > X_e$ where $a = 3.5 \pm 0.1$ is indeed observed.[2,13] According to ref 2 the eq 1 should be used at $\xi$ = constant. However, as the authors noted, in the range of $X > X_e$, which is of particular interest to us, the corrections needed to compensate for variation in $\xi$ are negligibly small.

If eq 1 were valid for our linear and branched sample data, than it would be possible[2,21] to calculate $\eta_{0,\mathrm{br}}$ from $\eta_0$ and the parameter $g$

$$\eta_0/\eta_{0,\mathrm{br}} = K[\langle s_0^2 \rangle / \langle s_0^2 \rangle_{\mathrm{br}}]^a \qquad (4)$$

where

$$K = (\xi/\xi_{\mathrm{br}})(X_{\mathrm{e,br}}/X_{\mathrm{e}})^{a-1}(v_{0,\mathrm{br}}/v_0)^a \qquad (5)$$

Equation 4 is derived assuming that $a = a_{\mathrm{br}}$ over the whole range of $X$. Furthermore, the parameter $K$ given by eq 5 cannot be calculated without a previous knowledge of the ratios $\xi/\xi_{\mathrm{br}}$, $X_e/X_{e,\mathrm{br}}$, $V_0/V_{0,\mathrm{br}}$ entering this parameter. In the past, for $X \gg X_e$, the value $K = 1$ was assumed.[21d]

The three curves of Figure 1 indicate that the parameter $a$ varies with the molecular weight and no sharp indication of entanglement can be found. The experimental values of $a$ calculated from the limiting portion of each of these curves at the highest range of $M_w$ are 3.5, 4.1, and 3.1 for linear, 4-branched, and 6-branched polymers, respectively. It is worth noting that for star branched polystyrenes of $\bar{f} \cong 3.4$ the value of $a = 4.5$ was reported,[7] for long branched polyethylenes $a = 6.56$ was found,[26] whereas, for trichain polybutadiene[27] of $M_w > 10^5$ the value of $a = 9$ was quoted.

**Table III**
**Test of Applicability of Equation 1 to Linear and Star Branched Polystyrenes at $T$ = 303°K, c = 25.5 g/dl, and $M_w > M_e$**

| No. | Parameter | Linear | 4 Branched | 6 Branched |
|---|---|---|---|---|
| 1 | $a$ (eq 1) | 3.4 | 3.4 | 3.4 |
| 2 | $a$ (experimental) | 3.5 | 4.1 | 3.1 |
| 3 | $g_z$ (eq 3) | 1 | 0.625 | 0.444 |
| 4 | $g$ L Sc[17,18] | 1 | 0.640 | 0.464 |
| 5 | $([\eta]_{0,\mathrm{br}}/[\eta]_0)^2$ (ref 17, 18) | 1 | 0.58 | 0.40 |
| 6 | $\eta_0/\eta_{0,\mathrm{br}}$ (eq 4) | 1 | 4.94 | 15.75 |
| 7 | $\eta_0/\eta_{0,\mathrm{br}}$[a] | 1 | 10 | 39 |

[a] At the highest molecular weight range of the branched polymers (see Figure 1).

**Table IV**
**Parameters of Equation 6 Computed for Linear, 4-Branched, and 6-Branched Polystyrene Solutions in $Et_2Ph$ at 30.0°**

| Parameter | Linear | 4 Branched | 6 Branched |
|---|---|---|---|
| $A_{1\xi} \times 10^{-9}$ | 6.10 | 8.95 | 14.7 |
| $A_2$ | 11.3 | 5.84 | 4.36 |
| $(B/kT) \times 10^3$ | 10.7 | 7.83 | 6.13 |

The difference in $a$ value of linear and branched systems indicates that eq 4 is not obeyed. However, as a parameter is a derivative property sensitive to experimental uncertainties the relative position of $\eta_0$ and $\eta_{0,\mathrm{br}}$ curves should provide an additional test. Here $K = 1$ has to be assumed. The ratios $\eta_0/\eta_{0,\mathrm{br}}$ calculated from eq 4 using $a = 3.4$ and $g = g_z$ computed from eq 3 are quoted in Table III. In this table, the experimental values of $g$ and of the ratio $\eta_0/\eta_{0,\mathrm{br}}$ are also given. On the basis of discrepencies between experimental and theoretical values of $a$ and $\eta_0/\eta_{0,\mathrm{br}}$ eq 1 must be judged not to be suitable for the interpretation of linear and star branched polystyrene solution viscosity data.

(II) A continuous increase of $a$ with $M$ and/or $\varphi$ is predicted by Imai's equation[22]

$$\eta_0 = A_1 \xi BM[(1 + A_2 Y)/(1 + Y)^{7/2}] \exp\{Y\} \qquad (6)$$

where

$$Y \equiv BM^{1/2}/kT$$

and

$$B \equiv (27/\pi)^{3/2}(\epsilon_0/M_0)(\langle s_0^2 \rangle / M)^{3/2}$$

In these relations $A_1$ and $A_2$ are integration constants, $k$ is the Boltzmann constant and $(\epsilon_0/M_0)$ is an interaction parameter computed per one polymer segment.

For small $Y$, eq 6 can be written as

$$\eta_0 = A_1 \xi BM \qquad (7a)$$

equivalent to eq 1 for $X < X_e$, whereas for large $Y$

$$\ln \eta_0 = A + BM^{1/2}/kT \qquad (7b)$$

The last relation for $B/kT$ = constant takes the form of Flory's empirical dependence[28] proposed for polyester melts. Unfortunately, the range of molecular weights of the samples employed in this study precludes a use of eq 7a or 7b.

An effort was made to compute the three parameters of eq 6: $A_1\xi$, $A_2$, and $B/kT$, by the curve-fitting technique. The steepest descent least-square method was used. The iterations were terminated when the improvement of standard deviation was less than $10^{-5}$. The results are presented in Table IV.

It can be seen that all three parameters systematically change from one polymer to another, which, for a practical reason, precludes any use of eq 6 for calculation of $\eta_{0,\mathrm{br}}$.

It is to be expected that $\xi$, being a measure of the

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hydrodynamic interactions between segments, will increase with $f$, but this increase should be small.[2] Consequently, the increase of $(A_1\xi)$ should be assigned to the variations in $A_1$.

If the interaction parameter $(\epsilon_0/M_0)$ in eq 6 is purely thermodynamic in its origin, then its values computed for the three discussed systems should be nearly the same.[17,18] Furthermore, the ratio

$$(B/kT)_{\text{br}}/(B/kT)$$

should equal $g^{3/2}$. Experimentally, from the plot log $(B/kT)$ *vs.* log $g_z$, the ratio was found to be proportional to $g_z^{0.68}$, instead. This may indicate that the interaction parameter $(\epsilon_0/M_0)$ originates in both the thermodynamic and hydrodynamic effects.

To the same group of relations predicting a continuous increase of $a$ with $M_w$ belongs the recently derived[23] equation

$$\eta_0 = a_0 + \sum_{i=0}^{n} a_{i+1} M_w^{2i+1} \tag{8}$$

usually truncated at $i = 2$. The $a_i$'s are empirical parameters and eq 8 provides a better fit to the experimental data than eq 1 or eq 7 by using a larger number of adjustable parameters of purely empirical nature.

(III) The corresponding states principle[11-16] (CSP) does not require a specific mathematical relation between $\eta_0$ and such independent variables as $c, M, T$, quality of a solvent, characteristics of a polymer, etc., but specifies the method of computing $\eta_0$ from an experimental master curve

$$\tilde{\eta} = \tilde{\eta}(\tilde{c}, \tilde{T}) \tag{9}$$

where

$$\tilde{\eta} \equiv (\eta_0 - \eta_s)/\eta_s c[\eta]$$
$$\tilde{c} \equiv c/\gamma, \; \gamma = \gamma(M,T)$$
$$\tilde{T} \equiv T/T_c(M_0)$$

$\eta_s$ is the solvent viscosity, $[\eta]$ the intrinsic viscosity, $\gamma$ the concentration reducing parameter[11-15] found to be proportional to critical mixing volume fraction, $v_{2c}$, or to the entanglement concentration, $c_e$, and finally $T_c(M_{0r})$ is the critical mixing temperature of the reference polymer with molecular weight $M = M_{0r}$.[16]

The CSP was applied to generate the master curves for 16 different polymer–solvent pairs of various range of $M$ and $c$ and for two couples of various $M$, $c$ and $T$. The method was found to be successful in all cases. However, deviations were observed in a range of lowest molecular weight, which appears to depend on the type of polymer.[14]

It is of interest to apply the same principle to the systems investigated at the present time. Here $c$ and $T$ are constant, solvent and polymer segments are the same but the polymer molecular weight and its geometry vary.

Under isothermal conditions eq 9 can be expressed as[11]

$$\tilde{\eta} = 1 + \sum_i k_i([\eta]c)^i \tag{10}$$

where $k_i$'s are parameters defined by this equation. Truncating eq 10 at $i = 1$, one generates the Huggins' relation for dilute solution viscosity. From CSP and eq 10 it follows that $1/k_i^{1/i}[\eta]$ must be proportional to the concentration reducing parameter $\gamma$. Since for the systems investigated here $c$ = constant, the equality $\tilde{\eta} = \tilde{\eta}_{\text{br}}$ can hold only if

$$k_i[\eta]^i = (k_i[\eta]^i)_{\text{br}} \quad \text{for all } i \tag{10a}$$

For the particular systems under discussion the eq 10a can be checked for the product $k_1[\eta]_\Theta$ using the data of Table I. The dependence of $k_1[\eta]_\Theta$ *vs.* $M_w$ is shown in Figure 2. The two straight lines are drawn with the previously observed[11] slope 0.476. They limit the range of variation ±15% in $k_1[\eta]_\Theta$. At a constant $M_w$ the values of the product for 6-branched systems are slightly lower from those of 4-branched samples which in turn fall below the data points of linear polymers. This effect may be due to narrower molecular weight distribution of the branched samples than of the linear polymers.[11] In the same Figure $k_1[\eta]$ values for toluene solutions at 35.0° for the same polystyrenes[17,18] are also shown. Two observations can be made. (1) The superposition of all three sets of data is better than for cyclohexane solutions, nevertheless again the data points for linear samples tend to be approximately 5% higher whereas those for 6-branched samples slightly lower than those for 4-branched polymers. (2) The data points for the highest and the lowest molecular weights are slightly above the straight line dependence drawn through the remaining data. A similar "upturn" of the limiting data points was observed[11-13,16] both for $k_1[\eta]$ and for $1/\gamma$.

From the results presented in Figure 2 it follows that at least for $i = 1$ the required identity (eq 10a) is observed both in Θ solvent and in a very good solvent. It is to be expected that the same identity does exist for Et$_2$Ph solutions.

In general $\gamma \propto [\eta]^{-\alpha}$ and experimentally[13] $\alpha$ varied from 0.73 to 1.26. The lines drawn in Figure 2 for cyclohexane and toluene solutions allow calculation of $\alpha = 0.96$ and 0.91, respectively. Generally[11] near Θ conditions $\alpha \cong 1$ and $k_i$'s become nearly independent of molecular weight. In other words, under these conditions, an approximation $\gamma \cong 1/[\eta]_\Theta$ can be valid. For such a system in which in addition $c$ and $\eta_s$ are being constant $\eta \propto (\eta_0 - \eta_s)/[\eta]_\Theta$ and eq 10 can be modified to read

$$(\eta_0 - \eta_s)/[\eta]_\Theta = f([\eta]_\Theta) \tag{11}$$

Equation 11 requires a simultaneous knowledge of $\eta_0$ and $[\eta]_\Theta$ for each sample. If $[\eta]_\Theta$ is not known one can employ the Zimm–Kilb relation[29] which is approximately valid also for the investigated polymers as can be seen from the data of line 5 in Table III[17,18]

$$[\eta]_{\Theta,\text{br}} = [\eta]_\Theta g^{1/2} \tag{12}$$

where from using the well-known proportionality $[\eta]_\Theta \propto M_w^{1/2}$

$$M_{w,\text{br}}^{1/2} = (M_w g)^{1/2} \tag{13}$$

From eq 11 and 13 the master plot is expected to take the form

$$(\eta_0 - \eta_s)/g^{1/2} = f_1(M_w g) \tag{14}$$

Equations 11 and 14 are strictly valid for the systems near Θ condition only. Et$_2$Ph is not a Θ solvent for polystyrene,[10] but within the high concentration range the thermodynamic effect of solvent should be less pronounced. Furthermore, in the case discussed here the deviation from the Θ condition are expected to occur parallely in the same range of reduced molecular weight for all three types of polymer and the error in using these relations should be similar within the similar range of variables for each of the three types of polymer.

In Figure 3 the data of Table I, presented in Figure 1,

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(29) B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19 (1959).

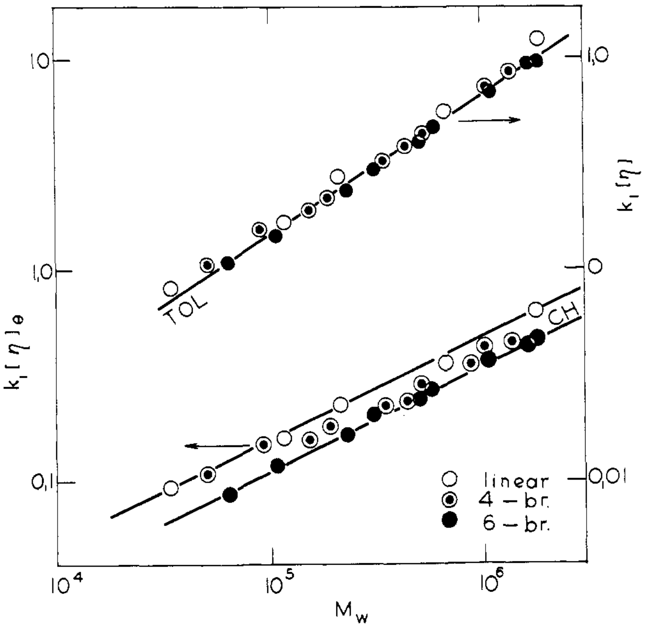

**Figure 2.** The $k_1[\eta]$ *vs.* $M_w$ dependence for linear,[17] 4-branched,[17] and 6-branched[18] polystyrenes in cyclohexane (CH) and toluene (TOL) at 35.0°.

are replotted according to eq 11 and according to eq 14 employing the $[\eta]_\Theta$ of Table I and $g_z$ values quoted in Table III, respectively. In both cases, the continuous lines are drawn through the data points of linear polystyrene samples.

The superposition predicted by eq 11 is excellent, in the whole range of variables. The two data points for the lowest molecular weight 6-branched samples deviate from the common dependence by ~10%.

The superposition predicted by eq 14 is somewhat less satisfactory. This can be expected, considering the simplifications and assumptions made in the course of its derivation. Nevertheless, as long as the Zimm–Kilb relation holds, eq 14 provides an easy and fast method of calculating $\eta_{0,\mathrm{br}}$ for any $M_{\mathrm{w,br}}$ from theoretical value of $g_z$ and $\eta_0$ of linear sample having

$$M_\mathrm{w} = M_{\mathrm{w,br}}/g_z$$

Equation 11 was also examined using $\eta_0$ of Table I and $[\eta]$ values in toluene.[17,18] As expected, no superposition was achieved and the three curves crossed in mid range.

The better superposition observed in Figure 3 for relation 11 than that of 14 is due to the fact that the first equation does not require any theoretical parameter (like $g_z$) nor quantity determinable with a large error (like $M_\mathrm{w}$); both $\eta_0$ and $[\eta]_\Theta$ can be measured with a good accuracy. The linear portion of curve 2 in Figure 3 applies for $[\eta]_\Theta \geq 0.4$ and can be approximated by

$$\eta_0 \propto [\eta]_\Theta^{\;6.2} \propto M_\mathrm{w}^{\;3.1}$$

Equation 5a of ref 13 can be written as

$$\epsilon_1 \alpha = (a/a^*) + (\alpha - 1)(1 - \eta_s/\eta_0) \qquad (15)$$

where $\epsilon_1 = (\partial \ln \eta_0 / \partial \ln c)_{M,T}$ and $a^*$ is the exponent from the Mark–Houwink–Sakurada equation $[\eta] = K^*M^{a^*}$. For $\alpha = 1$, $a^* = \frac{1}{2}$ and $a = 3.1$ determined from the curve 2 of Figure 3, the value $\epsilon_1 = 6.2$ is found in excellent agreement with the value 6.2 ± 0.1 determined from the actual plot of log $\eta_0$ *vs.* log $c$ of Bueche[10] data for linear fractions of polystyrene in the same solvent.

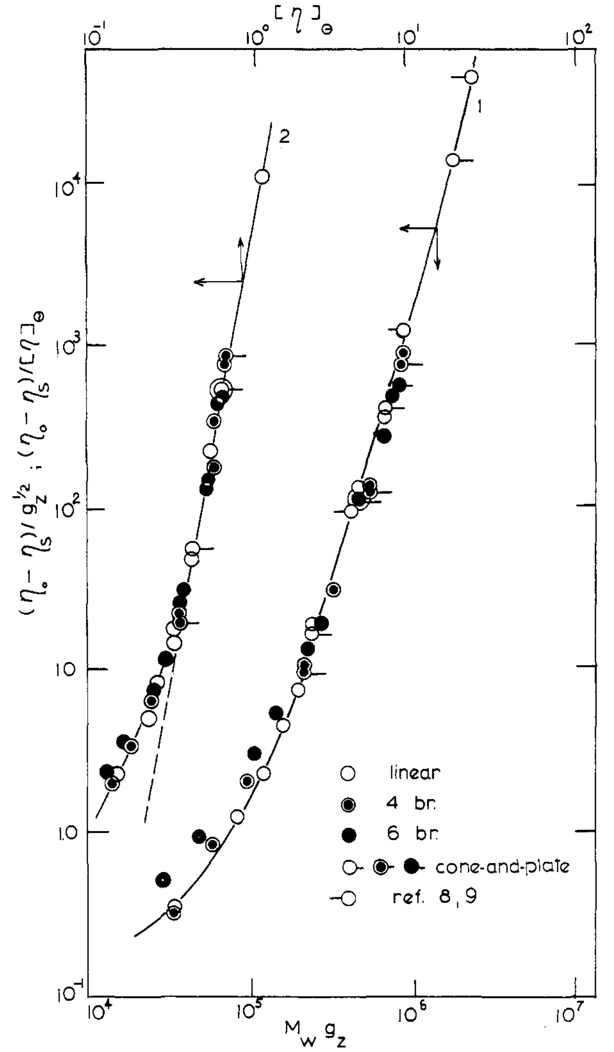

**Figure 3.** Superposition of $\eta_{0,\mathrm{br}}$ of branched polystyrenes on the $\eta_0$ *vs.* $M_\mathrm{w}$ dependence of linear polystyrenes as predicted by the corresponding states principle: curve 1, $(\eta_0 - \eta_s)/g_z^{1/2}$ *vs.* $g_zM_\mathrm{w}$; curve 2, $(\eta_0 - \eta_s)/[\eta]_\Theta$ *vs* $[\eta]_\Theta$. The solid lines represent the best fit to linear polymer data (see text).

Equation 11 for $\eta_0 \gg \eta_s$ can be written as $\eta_0 = \eta_0([\eta]_\Theta)$, and as such belongs to the family of functions correlating the Newtonian viscosity of polymer solutions or melts with the intrinsic viscosity. Two of these correlations were used to analyze the data of Table I. Both Moore's equation,[30] rewritten by Bueche[31] for $M \gg M_c$ as

$$\log \eta_0 = \text{constant} + (3.5/a^*)[\eta]/\langle[\eta]\rangle \qquad (16)$$

($\langle[\eta]\rangle$ is an average value of $[\eta]$ over the range of measurements) and Peticolas'[32] relation:

$$\eta_{0,\mathrm{br}}/\eta_0 = ([\eta]_{\Theta,\mathrm{br}}/[\eta]_\Theta)^2 E n_\mathrm{w} \quad \text{for } M = M_\mathrm{br} \qquad (17)$$

($E$ is an entanglement parameter and $n_\mathrm{w}$ is the chain branching index) failed to predict the observed dependencies.

**Temperature Dependence of $\eta_0$.** The logarithmic plot of $\eta_0$ *vs.* $1/T$°K allows calculation of the activation energy of flow $E_\eta$ reported in Table II. The plots are linear in whole range of temperature.

If the entanglement theory is valid, then a constant value of $E_\eta$ is expected for $M_\mathrm{w} > M_\mathrm{e}$ (where $M_\mathrm{e}$ is the effective entanglement molecular weight). The relation be-

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(30) L. D. Moore, Jr., *J. Polym. Sci.*, **36**, 155 (1959).

(31) F. Bueche, *J. Polym. Sci.*, **41**, 551 (1959).

(32) W. L. Peticolas, *J. Polym. Sci.*, **58**, 1405 (1962).

tween $M_e$ and the critical entanglement molecular weight is

$$M_c = \varphi^{a^*} M_e \tag{18}$$

where the exponent where $a^*$ varies from ½ to 1 (see ref 13). Taking[33] $M_c = 3.51.10^4$, one finds $M_e$ = 73,000-151,000. All the linear samples used to determine $E_\eta$'s have $M_w > M_e$. The average value $\bar{E}_\eta = 5.9 \pm 1.1$ kcal/mol (or $\bar{E}_\eta = 5.4 \pm 0.3$ kcal/mol if the value $E_\eta = 9.7$ for sample 15 is neglected) and the absence of systematic variations indicate that our data are consistent with the assumption of the entanglement theory for viscosity. It is worth pointing out that $E_\eta = 4.5$ kcal/mol can be calculated from Bueche's data[10] for polydisperse samples of polystyrene $M_w = 7.2 \times 10^5$ dissolved *in* $Et_2Ph$ ($c = 0.26$ g/cm$^3$) and $E_\eta$ = 4.41–5.33 kcal/mol from the results of Graessley *et al.*[8]

## Conclusions

The experimental results indicate that the CSP provides a simple and accurate method of generalization of the solution viscosity data of linear and branched polymers. From the knowledge of $\tilde{\eta}_0 = \tilde{\eta}([\eta]_\Theta)$ evaluated for linear samples and the knowledge of either $[\eta]_\Theta$ or $M_{w,br}$ and $g$ it is possible to calculate the $\eta_{0,br}$ with the error ≤10% for 4- and 6-star branched polystyrenes.

The use of CSP demonstrated in this paper is a new one. Here we were looking for superposition of $\eta_0 = \eta_0(c =$ constant, $T$ = constant, $M$, structure) functions instead of $\eta_0 = \eta_0$ ($c, T, M$, structure = constant) as in the past.[11-16] For this reason the choice of $\gamma = \gamma(M,T)$ as the concentration reducing parameter may be less critical, provided it is done on the same basis for the linear and branched samples; *e.g.*, $\gamma \neq [\eta]$ for polystyrene[11] in cyclohexane or toluene, whereas here the systematic use of $[\eta]_\Theta$ as a measure of the relative polymer coil dimension provides an excellent superposition for all data.

The limitations of the CSP applied to the viscosity data of branched polymer molecules can be established only on the basis of experimental analysis of $\eta_0$ in whole range of variables. The applicability of CSP to low and middle range of concentration of linear polymer,[11-16] and an excellent superposition demonstrated in this paper suggest that the limitations if any should occur at the range of high concentration, and high viscosity.

Fortunately, Kraus and Gruver[27] reported melt viscosities of 3- and 4-star branched polybutadienes, stating that $\eta_{0,br} < \eta_0$ only for $M_{w,br} \leq M_e f^2$. The "crossover" point was interpreted as due to the existence of the branching which can be considered as a rigid entanglement point. Their data were recomputed according to eq 11 and 14. An excellent superposition of low molecular weight data was achieved in both cases, however the data for branched polymer did deviate from the linear polymer dependence for $[\eta] > 1$ in the first case, and for $M_w \cdot g_z > 2 \times 10^4$ in the second, which corresponds to $\eta_0 > 10^4$P and $\eta_0 < 10^2$P, respectively. In the calculation, instead of $[\eta]_\Theta$ the $[\eta]$'s in toluene at 25° had to be used.[27] Again the superposition predicted by eq 11 is obeyed in much wider range of variables than that specified by eq 14. This range of applicability of CSP should be extended if $[\eta]_\Theta$ were available. It is of interest to note that the data for 3- and 4-branched polybutadienes plotted according to eq 11 and eq 14 do superimpose on the same master curve in whole range of $\eta_0$ *even if at the higher range of* $\eta_0$ (*or* $M_w$) the $\eta_{0,br} = \eta_{0,br}$ ($M_{w,br}$) dependence is different from that followed by the linear samples.

The superposition of solution viscosity data of linear and branched polymers predicted by eq 11 and demonstrated in Figure 3 means that at least for the systems investigated the corresponding states do exist. Furthermore, the high concentration isothermal data indicate that the factors that influence the relation between the Θ-solvent intrinsic viscosities of branched and linear polymers are also responsible for the relation between high concentration viscosities of these polymers in a relatively good solvent.

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(33) R. S. Porter and J. F. Johnson, *Chem. Rev.*, **66**, 1 (1966).