1196 *Macromolecules* **1984,** *17,* 1196-1200

Melt Rheology of H-Shaped Polystyrenes†

Jacques Roovers

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9. *Received August 22, 1983*

ABSTRACT: The viscoelastic properties of a series of H-polystyrenes were studied. Zero-shear viscosities of 0.255 g/mL solutions of H-polystyrenes were correlated with their Θ-temperature intrinsic viscosities. Zero-shear melt viscosities, η_0, of low molecular weight H-polymers are the same as those of linear polymers of the same size, but high molecular weight H-polymers exhibit enhanced viscosities. It is found that the enhancement of η_0 is larger in H-polymers than in three-arm or four-arm stars with the same number of entanglements per branch. The zero-shear recoverable compliance is approximately given by $J_e^0 = 0.4M/cRT$. The frequency dependence of the storage ($G'(\omega)$) and loss ($G''(\omega)$) moduli is discussed. $G''(\omega)$ has a maximum in the plateau region. The frequencies of this maximum, $\omega_{\max}$, are compared with those found in other types of branched polymers.

Introduction

The experimental characteristics of the linear melt rheology of narrow molecular weight distribution linear polymers are fairly well established.[1,2] Studies of the zero-shear viscosity, η_0, indicate that

$$\eta_0 = KM(M/M_c)^a \tag{1}$$

where $a = 0$ when $M < M_c$, $a = 2.4$ when $M > M_c$, K is the temperature (density) dependent constant, and M_c is a critical molecular weight for the changeover from a linear to a 3.4 power dependence of η_0 on M.[3] The zero-shear recoverable compliance, J_e^0, is given by

$$J_e^0 = \frac{2}{5}\frac{M}{\rho RT}\left(\frac{M}{M_c'}\right)^b \tag{2}$$

where $b = 0$ when $M < M_c'$, $b = -1$ when $M > M_c'$, ρ is the polymer density, R is the gas constant, T is the absolute temperature, and M_c' is another critical M for the changeover from a linear dependence of J_e^0 on M to J_e^0 independent of M.[2]

The low-M behavior of linear polymers in the melt is typically Rouse-like.[4] The high-M laws as given by eq 1 and 2 are presently best understood in terms of the reptation model, which considers high-M polymers embedded in tubes that are defined by the constraining presence of neighboring molecules (entanglements).[5] The consequences of this model for the viscoelastic properties of polymers were worked out by Doi and Edwards.[6] The theoretical deductions from the reptation model do not lead to perfect agreement with the experimental observations; notably the predicted M^3 dependence of η_0 is at variance with the experimental $M^{3.4}$ dependence.[7] This has resulted in various attempts of refinement of the theory.[8-11]

One particular advantage of the reptation model as introduced for linear polymers is that it can be extended to star polymers in a straightforward manner[12-15] and explains qualitatively a set of observations made on monodisperse stars described by[13,16-20]

$$(\eta_0)_{\text{star}} = g^a(\eta_0)_{\text{lin}}\Gamma \tag{3}$$

where $a = 1$, $\Gamma = 1$ when $2M < fM_c$ and $a = 3.4$, $\Gamma = \exp(\alpha 2M/fM_c)$ when $2M > fM_c$. In eq 3, $g = \langle s^2\rangle_{\text{br}}/\langle s^2\rangle_{\text{lin}}$ and is a measure of the smaller configuration of a branched polymer, a is either unity or 3.4, and $(\eta_0)_{\text{lin}}$ is given by eq 1. The exponential term in eq 3 accounts for the observation that high molecular weight stars have η_0 larger than linear polymers of the same size. This enhancement of η_0 is a consequence of the hindrance of reptation by the long arms in stars. The $2M/fM_c$ factor in the exponent of eq 3 is a measure of the number of entanglements per arm. The constant α is only weakly dependent on the number of arms (f) in the star. The extension of the reptation model to star-branched polymers also agrees with the observation that for stars[14]

$$J_e^0 = \frac{2}{5}g_2\frac{M}{cRT} \tag{4}$$

Indeed for stars J_e^0 is Rouse-like over the whole range of M and c investigated.[18,19,21] For stars $g_2 = (15f - 14)/(3f - 2)^2$.[22]

Table I

sample	$M_w \times 10^{-5}$	$[\eta]_\Theta$, dL/g	η_0,[a] P
H4A1A	1.11	0.21_8	
H2A1	2.37	0.31_8	4.73
H1A1	4.83	0.45_6	
H3A1A	6.74	0.54_5	80.6
H5A1	10.4	0.68_7	457.0
H6A1	16.9	0.88_9	

[a] Viscosity ($\eta_0 - \eta_{\text{solvent}}$) of 0.255 g/mL solutions in n-butylbenzene at 30 °C.

The melt properties of other types of branched polymers have also been studied experimentally. Unfortunately, these polymers are seldom of the monodisperse variety as stars and linear polymers can be. Work on comb polymers has shown that[23-28]

$$(\eta_0)_{\text{comb}} > g^a(\eta_0)_{\text{lin}} \tag{5}$$

indicating enhancement of η_0 occurs, but its dependence on the number of branches, their spacing along the backbone, and their length is not clear.[26] Similarly, J_e^0 of combs is higher than J_e^0 of linear polymers, even after correction by the appropriate g_2 factor.[27,28] Only a small number of fractions of randomly branched polymers have been carefully studied and generally, the observations summarized for the combs seem also to apply to the randomly branched polymers.[29-31]

We now report on a study of the melt properties of a series of H-shaped polystyrenes in which the five subchains are approximately of equal length. This type of polymer can be considered the smallest member of the comb polymers. It is also the simplest polymer with one chain between two branch points.

Experimental Section

The synthesis and characterization of the narrow molecular weight distribution H-polymers have been described previously.[32]

---

† Issued as NRCC No. 23335.

0024-9297/84/2217-1196$01.50/0

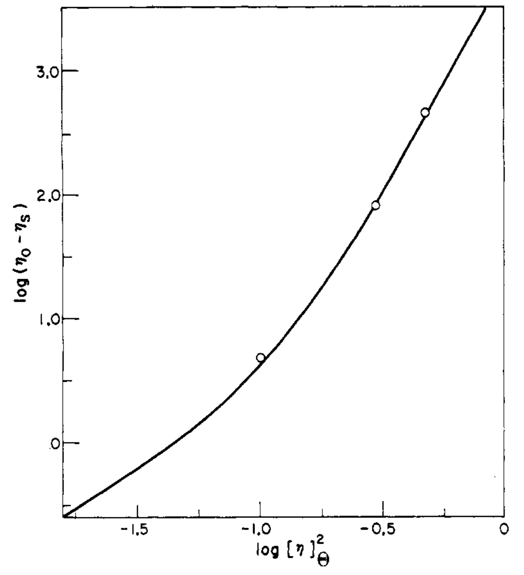

Figure 1. Zero-shear viscosities of 0.255 g/mL solutions of H-polymers in *n*-butylbenzene at 30.0 °C. The line is the master curve for stars and linear polymers.[34]

The properties relevant to this study are given in Table I. The viscosities of 0.255 g/mL solutions of the H-polymers in *n*-butylbenzene ($d_{30.0 °C}$ = 0.8524 g/mL; $\eta_s = 8.9 \times 10^{-2}$ P) were measured with calibrated semimicro Cannon-Ubbelohde viscometers at 30 °C. The flow times were about 1000 s or more. The procedure and results on linear and star-branched polymers have been reported previously.[33,34] Melt properties of the H-polymers were measured with a Rheometrics mechanical spectrometer in the oscillatory mode over the frequency range 10^{-2}–10^{2} rad/s. Measurements were made with parallel plates (R = 1.25 cm) and the strain amplitude was kept between 3% (high frequency) and 30% (low frequency) in order to stay within the linear viscoelastic regime. Measurements were made between 140 and 250 °C. The dialed temperatures and the thermocouples supplied with the instrument were calibrated against the readings of a thermocouple inserted in the center of a 1.5-mm-thick polystyrene sample. An additional thermocouple was inserted permanently in the environmental chamber to monitor the temperature independently of the instrument electronics. The higher temperatures were necessary to penetrate into the Newtonian region for the highest molecular weight samples. With N_2 purging, no sign of degradation was found over a 3-h period at 220 °C. However, a small correction for degradation (<5%) was made for measurements made over a 1-h period at 250 °C. Mixtures of high molecular weight H-polymer and low molecular weight linear polystyrene (PS25) were also studied. They were slightly less stable than the bulk polymers.

Master curves at 169.5 ± 0.5 °C were constructed from the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, measured at different temperatures. Small corrections were applied to $G'(\omega)$ and $G''(\omega)$ obtained at or above 190 °C. These experimental vertical shifts were somewhat variable but always less than ($\rho_0 T_0/\rho T$), where the zero subscript refers to the reference temperature (169.5 °C). The horizontal shift factor (a_T) required to obtain superposition along the frequency axis for the data at different temperatures can be represented by

$$\log a_T = 770\left(\frac{1}{T - T_0}\right) - 6.20 \qquad (6)$$

where $T_0 = T_g - 55$ °C. This relation is similar to that found previously for linear and star polystyrenes.[18] It was established that the glass transition temperature (T_g) of H4A1A was 1.5 °C lower than the limiting high molecular weight value ($T_{g\infty}$ = 100 °C). The glass transition temperatures of the polymer mixtures were calculated from[35,36]

$$T_g = T_{g\infty} - 1 \times 10^5/\bar{M}_n \qquad (7)$$

where $\bar{M}_n$ is the calculated number-average molecular weight. The isothermal moduli-frequency curves were shifted to convert the data to constant friction coefficient. The shift was calculated with eq 6 and 7.

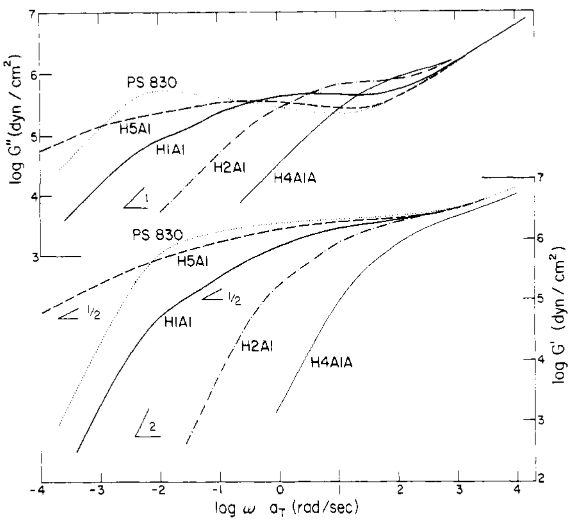

Figure 2. Storage and loss moduli-frequency curves for melts of H-polystyrenes at 169.5 °C. The lines marked PS830 are for a linear polystyrene $M = 8.0 \times 10^5$.

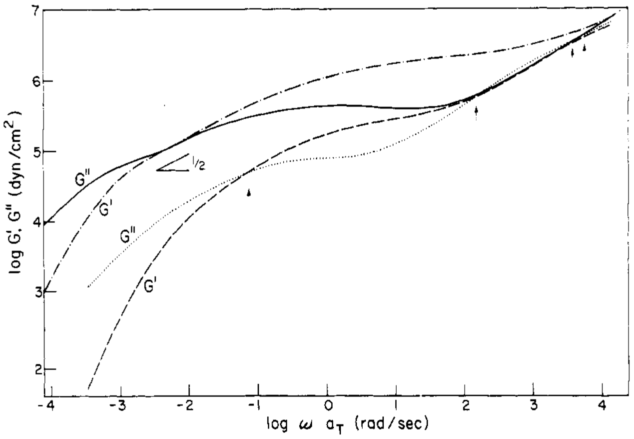

Figure 3. Dynamic moduli-frequency curves for melts of H-polystyrenes: top, H3A1; bottom, H5A1 + PS25 (0.375).

Results

The viscosities of the 0.255 g/mL solutions of the H-polymers in *n*-butylbenzene are given in Table I and plotted logarithmically against $[\eta]_\Theta^2$ in Figure 1. The experimental points lie on the master curve established previously for linear and star polystyrenes.[34]

In Figures 2 and 3 typical storage (G') and loss (G'') moduli-frequency (ω) curves for the melts of H-polymers are shown. These master curves, at T_g + 69.5 °C, are qualitatively very different from those for narrow molecular weight distribution linear polymers, especially when the molecular weight of the H-polymer is large. The $G''(\omega)$ curves depend linearly on ω in the low-frequency (terminal) range. The Newtonian viscosity η_0 is calculated from

$$\eta_0 = \lim_{\omega \to 0} [G''(\omega)/\omega] \qquad (8)$$

The values of η_0 are summarized in Table II. For H5A1 ($\bar{M}_w = 1.04 \times 10^6$) η_0 could not be determined experimentally because the terminal zone could not be reached before severe polymer degradation occurred. An estimate of η_0 is based on a comparison of the $G''(\omega)$ curve of H5A1 with that of H3A1A.

In the plateau region the $G''(\omega)$ curve of H-polymers rises slowly with increasing ω and a small maximum is reached. This is particularly clear for the higher molecular weight samples. The area under the plateau loss moduli

Table II
Melt Properties of H-Polymers at 169.5 °C Corrected to Constant Friction Factor

sample[a]	$\eta_0 \times 10^{-6}$, P	$J_e^0 \times 10^6$, cm^2/dyn	$G_N^\circ \times 10^{-6}$, dyn/cm^2	Γ[b]	ω_0, s^{-1}	$\eta_0 J_e^0 \omega_0$
H4A1A	0.036	1.36	1.6	1.15	1.26×10^1	0.63
H2A1	0.51	2.3	2.1	1.23	4.9×10^{-1}	0.57
H1A1	17.0	8.3	1.9	3.5	5.25×10^{-3}	0.74
H3A1A	130.0	12.9	2.0	8.1	4.07×10^{-4}	0.68
H5A1	(6000)		1.9[c]	~77.0		
H5A1 + PS25 (0.625)	88.0	30.0	0.88	5.4	2.75×10^{-4}	0.73
H5A1 + PS25 (0.375)	4.4	38.0	0.23	1.4	3.7×10^{-3}	0.62
H6A1 + PS25 (0.375)	76.2	77.0	0.25	4.4	1.26×10^{-4}	0.74

[a] Values in parentheses indicate the weight fraction of H-polymer in the mixture. [b] Calculated eq 12 and $\log (\eta_0)_{calcd} = 9.00 + 3.4 (\log [\eta]_\Theta^2 + \log [\bar{M}_w/(M_w)_{bulk}])$, where $[\eta]_\Theta$ is the Θ-temperature intrinsic viscosity, $\bar{M}_w$ the weight-average molecular weight of the mixture, and $(M_w)_{bulk}$ the molecular weight of the H-polymer. [c] Low-frequency tail not taken into account.

was used to calculate G_N°, the plateau modulus, according to[1]

$$G_N^\circ = \frac{2}{\pi} \int_{-\infty}^{+\infty} [G''(\omega) - G_s''(\omega)] \, d \ln \omega \qquad (9)$$

where $G_s''(\omega)$ is the contribution of the transition zone to $G''(\omega)$.[18] Values of G_N° are given in Table II. They are essentially identical with those of entangled linear and regular star polystyrenes.[18]

The $G'(\omega)$ curves of the H-polymers have a low-frequency terminal zone in which a ω^2 dependence is observed. This is used to calculate J_e^0 according to

$$J_e^0 = \frac{1}{\eta_0^2} \lim_{\omega \to 0} \frac{G'(\omega)}{\omega^2} \qquad (10)$$

Values of J_e^0 are given in Table II. The J_e^0 values for the high molecular weight H-polymers are not very accurate because they are based on the low-frequency, high-temperature measurements of $G'(\omega)$. The relative behavior of $G''(\omega)$ and $G'(\omega)$ for an H-polymer is shown in Figure 3. The moduli–frequency curves of H5A1 diluted with a low-M linear polymer (PS25, M = 22 000) are also shown in Figure 3. The low-frequency range of the diluted H-polymer is qualitatively similar to that for the pure H-polymer melts, although the moduli are smaller. On the high-frequency side of the plateau region, the moduli of the H-polymer mixtures increase to the ordinary values for polystyrene. The moduli curves of these mixtures have four frequencies at which $G''(\omega) = G'(\omega)$. This is also found in mixtures of high molecular weight linear polymers with PS25. The η_0, G_N°, and J_e^0 data for the mixtures with PS25 are given in Table II.

Discussion

The molecular weight dependence of the melt viscosity of the H-polymers is compared with that for linear polystyrenes in Figure 4. The linear polymer results are well represented by eq 1. The data agree numerically with previous results.[18] In contrast, the zero-shear melt viscosities of the H-polymers lie on a continuous curve which is below that for linear polymers at low M but rises steeply above the line for linear polymers at high M. In order to compare η_0 of the H-polymers correctly with those of linear polymers, the size reduction of the branched polymers has to be taken into account. Comparison at equal size as measured by the unperturbed mean-square radius of gyration $\langle s^2 \rangle_0$ suggests that eq 1 be replaced by[3]

$$\eta_0 = \text{constant}(\langle s^2 \rangle_0)^a = \text{constant}'([\eta]_\Theta^2)^a \qquad (11)$$

The second part of eq 11 follows from $\langle s^2 \rangle_0 \propto \langle M \rangle$ and $[\eta]_\Theta \propto \langle M \rangle^{1/2}$. The exponent a is either unity or 3.4. Evidence that the Θ-solvent intrinsic viscosity is indeed a good parameter to describe the effect of the smaller size of H-polymers on their η_0 is shown in Figure 1 for the case of the 0.255 g/mL solutions. Similar good agreement was observed previously for solutions of star and comb polymers.[28,34]

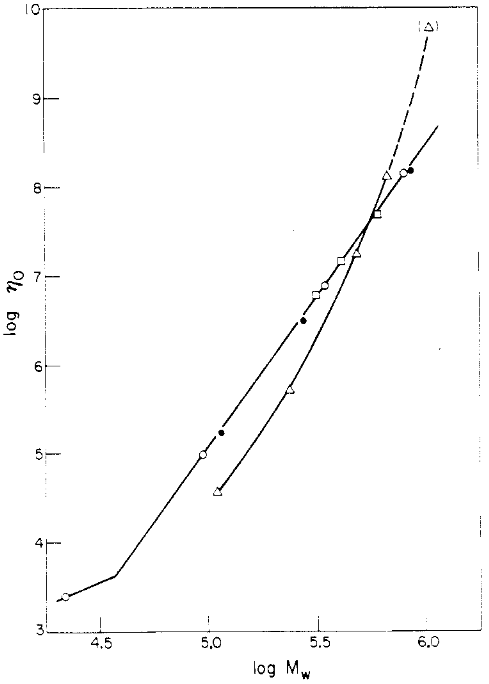

Figure 4. Zero-shear melt viscosity at 169.5 °C vs. molecular weight: open circles, linear polymers; closed circles, linear polymers (ref 18); squares, linear polymers diluted with PS25; triangles, H-polymers.

When the melt viscosities of H-polymers are compared with those of linear polymers on the basis of size, agreement is only good at low M. This is shown in Figure 5. The high molecular weight H-polymers have η_0 larger than predicted by eq 11. The observed enhancement of viscosity Γ is given by

$$\Gamma = (\eta_0)/(\eta_0)_{calcd} \qquad (12)$$

where for the melts $(\eta_0)_{calcd} = 1 \times 10^9([\eta]_\Theta^2)^{3.4}$. Values of Γ are given in Table II. Similar enhancement of viscosity is observed in melts of stars[13,16-20] and in combs.[25,28] As suggested by eq 3, log Γ is plotted against the number of entanglements per branch in Figure 6. For the H-polymers $M_{br} = M/5$ and $M_e = M_c/2$ = 18 000 for polystyrene. The line for the four-arm stars is taken from Figure 7 of ref 18. The line for three-arm stars is calculated from a comparison of Γ in three-arm and four-arm polybutadienes[2,16,17] and polyethylenes.[19] From Figure 6 it can be seen that the onset of enhancement of η_0 for H-polymers begins when each branch is involved in about 2 entan-

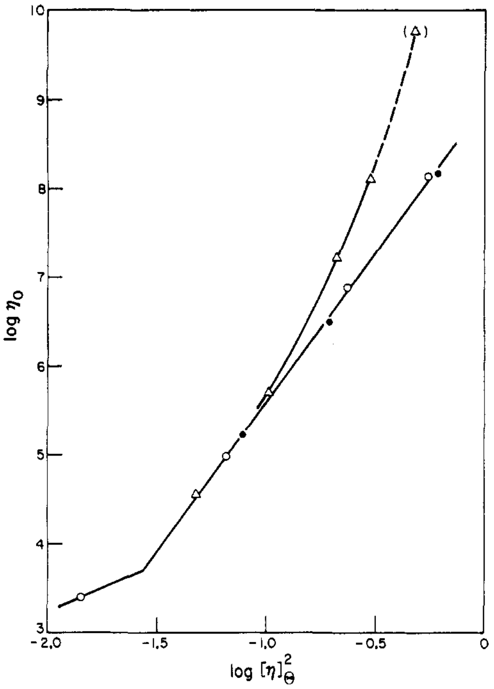

Figure 5. Zero-shear viscosity vs. the square of the Θ-temperature intrinsic viscosity. Symbols as in Figure 4.

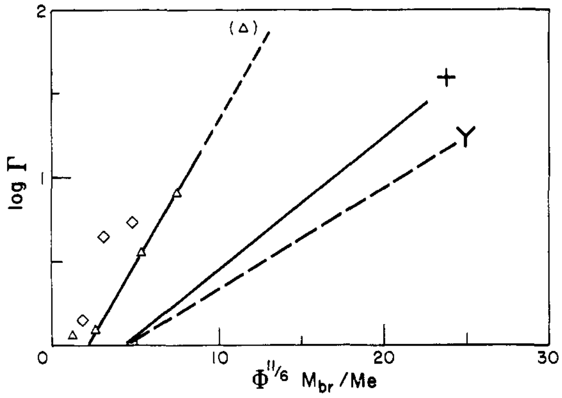

Figure 6. Enhancement of zero-shear viscosity Γ vs. number of entanglements per branch: triangles, H-polymers; diamond, H-polymers diluted with PS25. Lines are for regular stars indicated by their symbols.

glements rather than 4 or 5 as in the star polymers. Furthermore, log Γ increases with the number of entanglements per branch roughly twice as fast in the case of H-polymers as for a four-arm star and 2.8 times faster than for a three-arm star.

The enhancement of the viscosity of stars is due to the suppression of reptation by the long side chains.[5,13] The longest time relaxation process becomes then a kind of breathing of the tethered arms which depends exponentially on M_{br}/M_e but is essentially independent of the number of arms.[9] In three-arm stars reptation is probably not completely suppressed as indicated by the slightly lower Γ values than for stars with more arms. The branches of the H-polymers will breath as the arms of stars but this process will not relax the central part that is fixed between the two branch points. This part of the molecule can only relax by reptation of the whole molecule and this requires that two opposite branches of the H-polymer acquire simultaneously a favorable configuration for reptation. The probability of this happening will be the square of the probability for one branch to acquire such configuration. The latter is given by the inverse of the relaxation times of four-arm stars. It follows then, as is experimentally observed, that the slope of log Γ vs. M_{br}/M_e for H-polymers is twice that for a four-arm star. It would be interesting to study the effect of the length of the central subchain of H-polymer on the slope in the log Γ against M_{br}/M_e plot.

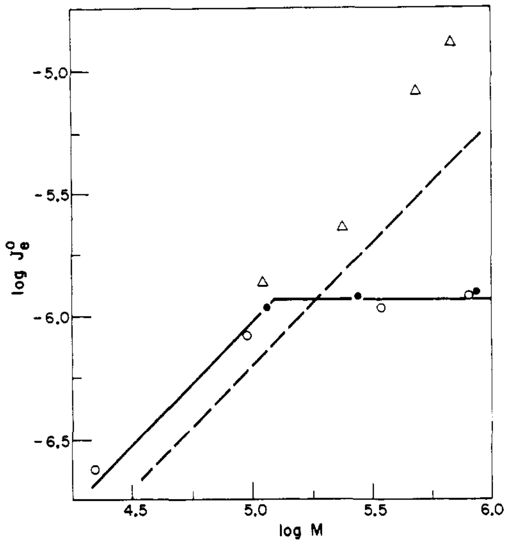

Figure 7. Zero-shear recoverable compliance vs. molecular weight. Symbols as in Figure 4. The solid line represents eq 2 for linear polymers. The broken line represents the Rouse–Ham prediction for H-polymers, eq 13 with $g_2 = 0.677$.

It was found previously that comb polystyrenes with 30 branches per backbone have enhanced melt viscosities although the number of entanglements per branch is small (<5).[25,28] The present results suggest that this may be due to the type of enhancement found in H-polymers. It is difficult to conceive of 30 branches simultaneously allowing for reptation of the whole molecule however. The high segment density in the combs may lead to considerable intramolecular cooperation. It may be significant that the combs with the larger spacing between the branch points exhibit the larger Γ.[28]

The molecular weight dependence of the zero-shear recoverable compliance for H-polymers is compared with that of linear polymers in Figure 7. J_e^0 of H-polymers increases with increasing M. This is also observed for stars.[18,19] In stars, J_e^0 follows the Rouse–Ham model as given by eq 4. For the H-polymers studied, $g_2 = 0.677$.[37] Although the linear dependence of J_e^0 on M holds approximately, eq 4 is not obeyed quantitatively by the H-polymer melts. The values of J_e^0 are such that eq 4 describes them correctly when $g_2 \approx 1$ or slightly larger. Values of J_e^0 for the mixtures of H-polymers with PS25 are too few and inconclusive on whether J_e^0 depends on c^{-1} as required by eq 4 and found in stars.[19,21]

For combs it is observed that $J_{eR} = J_e^0(c_{bb}RT/M_{bb})$, where c_{bb} and M_{bb} are the concentration and molecular weight of the backbone, is a single function of $c_{bb}M_{bb}$:

$$J_{eR} = 0.4\left(\frac{c_{bb}M_{bb}}{\rho M_c'}\right)^b \qquad (13)$$

where $b = 0$ or -1 when $c_{bb}M_{bb}$ is less than or greater than $(\rho M_c')$, respectively. For the smallest two H-polymers, $J_{eR} = 0.4$ as expected when $c_{bb}M_{bb} < \rho M_c'$. For the other samples and their mixtures with PS25, $J_{eR} = 0.60$.

Deviations from Newtonian behavior occur at lower frequencies for H-polymers than for linear polymers with the same η_0. Values of ω_0, the frequency at which the complex viscosity $\eta^*(\omega) = 0.8\eta_0$, are collected in Table II. Although values of ω_0 vary over 5 orders, the product

Macromolecules 1984, 17, 1200–1208

$\eta_0 J_e^0\omega_0 = 0.6 \pm 0.2$ for all samples. The same value for $\eta_0 J_e^0\omega_0$ was also observed for linear, star, and comb polymers.[18,28]

The moduli–frequency curves of the H-polymer melts are quite different from those of entangled narrow molecular weight linear polymers as shown in Figures 2 and 3. In fact, they resemble the curves for star and comb polystyrene melts.[18,28] This is also true of the corresponding relaxation spectra.[1] The $G''(\omega)$ curves of linear polymer melts are characterized by a single sharp maximum at the low-frequency end of the plateau region and a minimum at the higher frequencies of the plateau (see Figure 2). At the low end of the plateau region, branched polymers, including the H-polymers, have both G' and $G'' \propto \omega^{1/2}$ (Figures 2 and 3), suggesting that the longest relaxation processes are quite Rouse-like. At higher frequencies in the plateau region, $G''(\omega)$ shows a broad maximum that is most pronounced in the branched polymers with the largest enhancement of viscosity. It appears that the frequency of $[G''(\omega)]_{\max}$, $\omega_{\max}$, is a function of the molecular weight of the branch (arm) only and independent of the particular architecture of the branched polymer. This was already suggested by comparison of $\omega_{\max}$ in the two series of combs (τ_{br} in Figure 13 of ref 28).[28] Branched polymer melts have a set of short-time relaxation processes that involve branches or arms and that are independent of the long-time processes that dominate the zero-shear viscosity. The present Doi[14] and Graessley[9] theories for star melts do not explicitly foresee a maximum in $G''(\omega)$.

Acknowledgment. The author is indebted to Drs. D. Pearson and W. W. Graessley of Exxon Research and Engineering Co. for fruitful discussions.

Registry No. Polystyrene (homopolymer), 9003-53-6.

References and Notes

(1) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(2) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(3) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(4) Rouse, P. E., Jr. *J. Chem. Phys.* **1953**, *21*, 1272.
(5) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(6) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans.* **1978**, *74*, 1789, 1802, 1818.
(7) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 27.
(8) Doi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 265.
(9) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(10) Donth, E. *Polym. Bull.* **1982**, *7*, 417.
(11) Wendel, H.; Noolandi, J. *Macromolecules* **1982**, *15*, 1318.
(12) de Gennes, P.-G. *J. Phys. (Paris)* **1975**, *36*, 1199.
(13) Graessley, W. W., Masuda, T.; Roovers, J.; Hadjichristidis, N. *Macromolecules* **1976**, *9*, 127.
(14) Doi, M.; Kuzuu, N. Y. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 775.
(15) Graessley, W. W. *Acc. Chem. Res.* **1977**, *10*, 332.
(16) Kraus, G.; Gruver, J. T. *J. Polym. Sci., Part A* **1965**, *3*, 105.
(17) Rochefort, W. E.; Smith, G. G.; Rachapudy, H.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1197.
(18) Graessley, W. W.; Roovers, J. *Macromolecules* **1979**, *12*, 959.
(19) Raju, V. R.; Menezes, E. V.; Marin, G.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1981**, *14*, 1668.
(20) Raju, V. R. Ph.D. Thesis, Northwestern University, Evanston, IL, 1980.
(21) Roovers, J. *Polymer* **1981**, *22*, 1603.
(22) Ham, J. S. *J. Chem. Phys.* **1957**, *26*, 625.
(23) Fujimoto, T.; Narukawa, H.; Nagasawa, M. *Macromolecules* **1970**, *3*, 57.
(24) Fujimoto, T.; Kajiura, H.; Hirose, M.; Nagasawa, M. *Polym. J.* **1972**, *3*, 181.
(25) Pannell, J. *Polymer* **1972**, *13*, 1.
(26) Isono, Y.; Fujimoto, T.; Kajiura, H.; Nagasawa, M. *Polym. J.* **1980**, *12*, 369.
(27) Isono, Y.; Fujimoto, T.; Inagaki, H.; Shishido, M.; Nagasawa, M. *Polym. J.* **1980**, *12*, 131.
(28) Roovers, J.; Graessley, W. W. *Macromolecules* **1981**, *14*, 766.
(29) Masuda, T.; Nakagawa, Y.; Ohta, Y.; Onogi, S. *Polym. J.* **1972**, *3*, 92; *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1982**, *23*, 40.
(30) Valles, E. M.; Macosko, C. W. *Macromolecules* **1979**, *12*, 521.
(31) Graessley, W. W.; Prentice, T. S. *J. Polym. Sci., Part A-2* **1968**, *6*, 1887.
(32) Roovers, J.; Toporowski, P. M. *Macromolecules* **1981**, *14*, 1174.
(33) Graessley, W. W.; Hazelton, R. L.; Linderman, L. R. *Trans. Soc. Rheol.* **1967**, *11*, 267.
(34) Utracki, L. A.; Roovers, J. *Macromolecules* **1973**, *6*, 366.
(35) Krause, S.; Iskandar, M.; Iqbal, M. *Macromolecules* **1982**, *15*, 107.
(36) Roovers, J.; Toporowski, P. M. *J. Appl. Polym. Sci.* **1974**, *18*, 1685.
(37) Pearson, D. S.; Raju, V. R. *Macromolecules* **1982**, *15*, 294.

Thermoreversible Gelation of Poly(4-methyl-1-pentene) in Cyclopentane and Cyclohexane

Gérard Charlet,* Hong Phuong-Nguyen, and Geneviève Delmas

Chemistry Department, Université du Québec à Montréal, C.P. 8888, Succ. A, Montréal, Québec H3C 3P8, Canada. *Received July 7, 1983*

ABSTRACT: The conditions for the occurrence of thermoreversible gelation of poly(4-methyl-1-pentene) (P4MP1) in cyclopentane and cyclohexane are investigated. The results depend on the history of the polymer sample and are described for a highly isotactic material, either in its nascent state (sample N) or after slow recrystallization from the melt (sample M). At the dissolution temperature of the chain-folded crystals, T_D, where sample M forms a solution, sample N experiences gelation at polymer volume fraction higher than 0.03. However, the M solutions turn to clear gels if left standing at an observation temperature higher than the chain-folding crystallization temperature. P4MP1 gels exhibit a high thermal stability since the gel–solution transition (or solation), T_S, is observed well above the solvent boiling point. The results are consistent with the existence in N but not in M of network junctions which can be destroyed and formed again in solution of any polymer sample after a suitable solvent and thermal history. Since neither a sizeable X-ray crystallinity of the gels between T_D and T_S nor any heat effect at T_S can be detected, the origin of the junctions in P4MP1 gels is discussed in terms of associations of polymer helical sequences, probably stabilized by a favorable interaction between the helices and the small-size cycloalkane solvent.

The P4MP1 gels, formed without either supercooling or stirring, belong to a new class of gels, different from those of other polyolefins, such as isotactic polystyrene or polyethylene.

In nonpolar polymer systems, the occurrence of thermoreversible gelation is associated with a certain co-

0024-9297/84/2217-1200$01.50/0