Packing Length Influence in Linear Polymer Melts on the Entanglement, Critical, and Reptation Molecular Weights

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ABSTRACT: We have shown in previous studies that the entanglement molecular weight for a polymer melt, \( M_e \), is related by a power law to \( p \), the packing length of the polymer species. We now find that power laws also describe the molecular weights characterizing the melt viscosity, \( M_c \), marking the onset of entanglement effects and \( M_r \), the crossover to the reptation form. The packing length exponents for \( M_e \), \( M_c \), and \( M_r \) differ significantly, however. The long-held notion that the ratio \( M_r/M_e \) has the same value for all species is therefore incorrect. Further, the observed and predicted values of \( M_c \) for two species, 1,4-polybutadiene and polyisobutylene, have been found to agree, within the uncertainties, with the projected values. Finally, the variations with packing length are such that all three characteristic molecular weights would appear to converge on the same value near \( p = 9 \AA \). As yet, no species with such a large packing length has been completely studied rheologically. But the range is not outlandish and is clearly reachable by appropriate synthetic methods.

Introduction

It is well-known that the melt viscosity for linear polymers of many species varies with molecular weight in essentially the same manner. Thus, after a chain end correction, the viscosity goes from direct proportionality for short chains to a much stronger dependence for long chains, with a smooth crossover at a molecular weight \( M_c \) whose value is characteristic of the polymer species:

\[
\eta_0(M,T) = K(T)M \quad M < M_c \quad (1a)
\]
\[
\eta_0(M,T) = K(T)M^{3.4} \quad M > M_c \quad (1b)
\]

Variations in \( M_c \) with polymer species parallel the variations in entanglement molecular weight (\( M_e \)) as calculated from the plateau modulus of the species in the melt state:

\[
M_e = \frac{\rho RT}{G_0^o} \quad (2)
\]

in which \( R \) is the universal gas constant (\( R = 8.314 \text{ K}^{-1} \text{mol}^{-1} \text{K} \)), \( T \) is the temperature, and \( \rho \) is the polymer melt density. We return to the traditional definition of \( M_e \) for this paper, omitting the Doi–Edwards prefactor of \( \eta_0 \) used in our previous papers.6–8 This was done in order to retain the original relationship of \( M_c \) with \( M_e \). The inference was drawn that these molecular weights are related quite generally by the approximate equality \( M_c = 2M_e \). This relation was based on data for several species where both \( M_e \) values were available. In this report we show that this perceived universal kinship of \( M_e \) and \( M_c \) is incorrect.

Recent work8 has shown that the species dependence of entanglement molecular weight can be expressed by what appears to be a universal power law (for flexible linear Gaussian chains) in the packing length of the species:

\[
M_e = \frac{\rho RT}{G_0^o} = n_i^2N_a\rho p^3 \quad (3)
\]

where \( N_a \) is the Avogadro number. The coefficient \( n_i \) of eq 3 is taken as insensitive to temperature8,9 and equal to 21.3 ± 7.5%. It is dimensionless and denotes the number of entanglement strands present per cube of the tube diameter.9 The packing length10 is

\[
p = M_e[(R_0^2)/N_a\rho] = M\nu[M_b(R_0^2)] \quad (4)
\]

where \( \nu \) denotes the average volume of a chain per bond, \( M \) the chain molecular weight, \( M_b \) the average molecular weight per bond, and \( (R_0^2) \) is the root-mean-square end-to-end distance of the polymer chain. A more detailed description of \( p \) and its physical interpretation is available in Appendix I of ref 8.

Data Sources

We were able to identify 10 polymer species with well-established values of \( M_c \) and \( (R_0^2)/M \) in the melt state; the data are given in Table 1. Theta condition dilute solution data11,12 were used as the unperturbed chain dimension source for PVA, PMMA, and SBR. Some values of \( M_e \) were taken directly from the 1968 Berry–Fox review13 while the others are more recent. The \( M_c \) values for the PC, PVC, and 1,4-PI entries of Table 2 were obtained by extrapolation to the melt state from solution-based data assuming an inverse dependence on concentration.3 Those results are accompanied by the
Results and Discussion

The boldfaced type denotes melt-based chain dimensions via SANS while the regular type denotes theta condition measurements. The abbreviations of the species names used in the tables and text are given in Table 3.

Somewhat incomplete melt-based data for four species that have unusually large packing lengths. The abbreviations of the species names used in the tables and text are given in Table 3.

Table 1. Molecular Characteristics and Melt-Based Rheological Molecular Weights

<table>
<thead>
<tr>
<th>polymer</th>
<th>T (K)</th>
<th>ρ (g cm⁻³)</th>
<th>m₀</th>
<th>⟨R⟩₀/M (Å)</th>
<th>p (Å)</th>
<th>Mₑ × 10⁻³</th>
<th>Mₑ × 10⁻⁵</th>
<th>Mₑ × 10⁻⁴</th>
<th>refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>298</td>
<td>1.20</td>
<td>42.5</td>
<td>0.890</td>
<td>1.55</td>
<td>1.6/1.2²</td>
<td>6.0/3.9⁶</td>
<td>3, 11, 12, 32</td>
<td></td>
</tr>
<tr>
<td>POE</td>
<td>303</td>
<td>1.39</td>
<td>31.25</td>
<td>0.750</td>
<td>1.59</td>
<td>1.5</td>
<td>3.9/4.8⁶</td>
<td>3, 11, 33, 34</td>
<td></td>
</tr>
<tr>
<td>1,4-PI</td>
<td>298</td>
<td>0.900</td>
<td>17.5</td>
<td>0.596</td>
<td>3.10</td>
<td>6/7.3⁵</td>
<td>14/15³</td>
<td>6, 8, 11, 12</td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td>433</td>
<td>0.920</td>
<td>55</td>
<td>0.323</td>
<td>5.59</td>
<td>49/44⁶</td>
<td>69³</td>
<td>6, 8, 11, 12</td>
<td></td>
</tr>
<tr>
<td>PCHE</td>
<td>393</td>
<td>1.00</td>
<td>206</td>
<td>0.167</td>
<td>9.94</td>
<td>268/270⁷</td>
<td>255⁷</td>
<td>38, 39</td>
<td></td>
</tr>
<tr>
<td>PBPPHM</td>
<td>393</td>
<td>1.17</td>
<td>234</td>
<td>0.154</td>
<td>10.8</td>
<td>355/340⁸</td>
<td>310⁹</td>
<td>38, 39</td>
<td></td>
</tr>
<tr>
<td>PMMA−CH₃</td>
<td>363</td>
<td>1.17</td>
<td>198</td>
<td>0.123</td>
<td>11.5</td>
<td>485⁸</td>
<td>485⁸</td>
<td>36, 37</td>
<td></td>
</tr>
</tbody>
</table>

The values in italicized melt-based data for four species that have unusually large packing lengths. The abbreviations of the species names used in the tables and text are given in Table 3.

The boldfaced type denotes melt-based chain dimensions via SANS while the regular type denotes theta condition measurements. The values in italicized melt-based data for four species that have unusually large packing lengths. The abbreviations of the species names used in the tables and text are given in Table 3.

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Results and Discussion

Critical Molecular Weight. Fox and Allen² proposed a relationship between Mₑ and ⟨R⟩₀/M which, in the terminology used here, can be expressed as follows:

\[ Mₑ = 6 \times Nₚ N_p \]  

where ⟨R⟩₀ is the mean-square unperturbed radius of gyration and the quantity 6XₚNₚ is proposed to be universal with X_c = 45.7 ± 9.2. Accordingly, the data for the various species ¹¹–¹³ in Table 1 should give a straight line through the origin when plotted as Nₑ = Mₑ/m₀ vs p. This relationship, shown in Figure 1, exhibits a rather poor fit to the data and yields a correlation coefficient R of only 0.853. A log−log plot of Mₑ/m₀ vs p, testing the possibility of a power law with an exponent other than unity, gives no improvement in the fit.
Figure 2. Plot of $M_e^{-1}$ vs packing length for melt-based $M_e$ values. The dashed line ($M_e^{-1}$) is based upon eq 3.

Figure 3. Plot of $M_e^{-1}$ vs packing length for PC, PVC, 1,4-PI (open squares; data from concentrated solutions), and PMA–CH$_3$ (filled square; estimate for the melt state). The line is based upon eq 8.

Inspection of Table 1 shows that the $M_e$/$M_o$ ratio is species dependent and that there is a trend toward smaller ratios with increasing packing length. Hence, a $p^3$ dependence of $M_o$, paralleling the behavior of $M_e$ according to eq 3, seems ruled out. We found, however, that a quite reasonable fit could be achieved with a log–log plot of $M_e^{-1}$ vs $p$. This is shown in Figure 2, and the expression takes the following form:

$$M_e = C N_o p^x$$  

(6)

We find $C = 1918$ (using the units listed in Table 1), $x = 2.35 \pm 0.15$, and $R = 0.942$. Thus, $M_e$ has a weaker dependence on $p$ than $M_o$ shown by the dashed line in Figure 2, which is based upon eq 3. Unlike the dimensionless coefficient in eq 3, the coefficient $C$ has dimensions, an observation that we return to below. As shown in Figure 3, the best-fit straight line in Figure 2 is also consistent with the solution-derived results$^{32-39}$ (Table 2) of PC, PVC, and 1,4-PI. Equation 6 is consonant as well with the $M_e$ estimate from melt-based data$^{36,37}$ for PMA–CH$_3$ (Table 2 and Figure 3). The latter was not included in Figure 2, however, since only one value of viscosity beyond $M_e$ was available.$^{37}$

Equations 3 and 6 can be combined to yield the following expression for the relationship between $M_e$ and $M_o$:

$$M_e = M_o^{1.34}$$  

(7)

in which $p^x = 9.2$ Å. Note that $M_e$ overtakes $M_o$ at $p = p^x$. $M_o$ can then be expressed in terms of $M_e$ by combining eqs 3 and 7:

$$M_o = n_0^2 N_o p^{3x} \frac{[p]^{10.65}}{[p]} = M_e^{[p]^{10.65}}$$  

(8)

With $M_e$ expressed in this way, the result seems very strange indeed since it requires that $M_e$ overtakes $M_o$ (see Figure 2) as the packing length approaches some $p^x$ value in the $9$–$10$ Å range. This is larger than the packing length of any species that has been studied in rheological detail. However, the last three species$^{36-39}$ listed in Table 2 have $n$ values that exceed $p^x$ so exploring the implications of eq 8 is certainly feasible.

**Pure Reptation Threshold.** While the number of polymers with known values of $M_e$ in the melt state is smaller than that$^{6-9}$ for $M_o$, those listed in Table 1 still cover an extensive range. The range is even larger if we also include those species in Table 2 for which the existing $M_e$ data are at least consistent with eq 8. If eq 8 does indeed apply to all flexible chain species, there are then important consequences for our view of polymer melt dynamics. It would mean, for example, that the nature of the entanglements in a melt cannot be characterized by a single parameter such as $M_e$. Stated another way, the result implies that there is an increase in what may be called the “entanglement efficiency” as $p$ increases. PE, POE, and 1,4-PBd (Table 1) seemingly require $\sim 3$ entanglement events per chain for entry into the regime where $\eta_o \propto M^{3.4}$ while PS needs only $\sim 1.7$ entanglements. Hence, the degree of entanglement as specified by $M_e$ is not sufficient to fully characterize the entanglement effects.

There is another aspect of viscosity behavior, coming from molecular theory in this case, that also supports the implications of eq 8. The Doi–Edwards theory,$^5$ based on the reptation process alone, requires the viscosity in the entanglement regime be proportional to $M^3$, rather than $M^{3.4}$ as observed experimentally. Two other relaxation processes are also important in the dynamics of entangled liquids: tube length fluctuations$^{40,41}$ and constraint release$^{42}$ Moreover, recent work$^{41}$ has shown that the apparent higher power can now be explained, without introducing new parameters, by the gradual reduction in the fluctuation contribution as chain length increases. Accordingly, beyond some second characteristic molecular weight, $M$, the experimental viscosity reverts to the expected $M^3$ dependence and is based on a combination of reptation and constraint release$^{42}$ An example of this is shown in Figure 1 of ref 41.

A formula for estimating $M_e$ can be obtained as follows. The observed viscosity behavior above $M_e$ can be written as

$$\eta_o(M) = \left[M_e^{-1.34}\right] \eta_o(M_e)$$  

(9)

and the prediction for pure reptation is$^{42,43}$

$$\eta_o(M) = \left[\frac{M_e^3}{M} \eta_o(M_e)\right]$$  

(10)
where \( M_e \) is defined in eq 3, and \( Q \) is equal to 15/4. By one estimate,\(^{43} \) constraint release reduces \( Q \) to a value of about 0.3(15/4) = 1.13. The viscosities denoted by eqs 9 and 10 become equal at \( M = M_r \). By setting the viscosities from eqs 9 and 10 equal, we find that for \( Q = 1.13 \)

\[
\frac{M_r}{M_e} = 1.13 \left( \frac{M_c}{M_e} \right)^{1.36} = 1.36 \left( \frac{M_c}{M_e} \right)^{1.08p^{1.39}} \tag{11}
\]

or, on making use of eq 8

\[
M_r = M_q \left( \frac{p^{1.08p^{1.39}}}{1} \right) \tag{12}
\]

Thus, eqs 3, 8, and 12 are governed by the same dimensionless coefficient, \( \eta_0 \).

An additional point to make is that for \( \eta_0 \) in the molecular weight regime of \( M^3 \), the constraint release correction lessens. From eqs 3, 8, and 12 (and within the uncertainties of the data) it seems that \( M_e, M_c, \) and \( M_r \) converge toward the same value when the packing length for the species approaches 9–10 Å. Thus

\[
M_r \approx M_q \left( \frac{p^{1.08p^{1.39}}}{1} \right) \tag{13}
\]

Table 4 summarizes these packing-length-based equations.

The values of \( M_r \) estimated for the various species via eq 13 are given in Table 2. They are very large when compared with \( M_e \) since the represented species are well below the 9–10 Å range for \( p \). The values of \( M_r \) are thus projected to be a very strong function of \( M_r/M_e \). Thus, for \( M_r/M_e = 3 \) we obtain \( M_r/M_e = 724 \) while for \( M_r/M_e = 2 \) we have \( M_r/M_e = 64 \). Indeed the value of \( M_r \) decreases so quickly with increasing \( p \) (\( M_r \propto p^{1.08p^{1.39}} \)) from eq 13 that the onset of the \( M^3 \) viscosity dependence should be more accessible in polymers with large packing lengths even though their entanglement molecular weights are large. This is in contrast to earlier suggestions\(^{5,16,43} \) that \( \eta_0 \propto M^3 \) would always be very difficult to observe since \( M_r \) was taken to be several decades, or more, larger than \( M_c \).

Nonetheless, the transition to \( \eta_0 \propto M^3 \) has been seen clearly for two species. Figure 4 displays the molecular weight range for 1,4-polybutadiene\(^{17} \) and polyisobutylene\(^{30} \) where the reptation gradient of 3 is found. Colby et al.\(^{17} \) reported significant departures from \( M^3 \) behavior above \( M_r/M_e \approx 200 \) corresponding to \( M_r \approx 4 \times 10^5 \) for 1,4-PBd. Milner and McLeish\(^{41} \) estimate the somewhat larger value of \( M_r/M_e \approx 316 \) for 1,4-PBd which yields \( M_r \approx 6.3 \times 10^5 \). We have reexamined previously published\(^{30} \) data on PIB over the temperature range 423–473 K. Experimentally, we find \( M_r \approx 4.3 \times 10^5 \), which is 41 times \( M_e \). This is illustrated in Figure 5 where we plot \( \eta_0(M/M_e)^3 \) vs \( M/M_e \) at 448 K. The experimental values of \( M_r \) for both polymers thus agree reasonably well with the predictions in Table 1.

One revealing way to consider the notions presented herein is to compare \( M_e, M_c, \) and \( M_r \) vs packing length as shown in Figure 6. The molecular weight packing length plane is divided into regions of distinct rheological behavior. Below the \( M_e \) line the viscosity behaves in a Rouse-like mode. Above the \( M_c \) line the viscosity is controlled essentially by reptation. Between the \( M_e \) and \( M_r \) lines the fluctuation effects\(^{40–43} \) come into play.

**Table 4. Packing-Length-Based Equations**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_e^0 )</td>
<td>( k_B T/m_e^2 )</td>
</tr>
<tr>
<td>( \lambda_e )</td>
<td>( n_c = (R/\pi M_e)^{1/2} )</td>
</tr>
<tr>
<td>( M_e )</td>
<td>( n_e = n_c M_e^{1/2} )</td>
</tr>
<tr>
<td>( M_c )</td>
<td>( M_c = M_e )</td>
</tr>
<tr>
<td>( M_r )</td>
<td>( M_r = \frac{1}{1.08p^{1.39}} )</td>
</tr>
</tbody>
</table>

**Figure 4.** A log–log plot of zero-shear \( \eta_0 \) vs \( M_r \) for 1,4-polybutadiene at 298 K (ref 17) and polyisobutylene at 448 K (ref 30).

**Figure 5.** Plot of \( \eta_0(M/M_e)^3 \) vs \( M/M_e \) for polyisobutylene at 448 K. The line is drawn with the gradient of zero. Identical results are obtained from the 423 and 473 K data sets of ref 30.

**Figure 6.** Plots of \( M_r^{-1}, M_c^{-1}, \) and \( M_e^{-1} \) as a function of packing length. The lines are calculated via eqs 3, 8, and 13. The symbols denote the experimental \( M_r^{-1} \) values for 1,4-PBd and PIB.
Figure 6 suggests two additional questions regarding polymer rheology. First, what happens when $p > p^\ast$? It is clear that there is no physical sense if $M_e$ were significantly greater than $M_c$ or $M_r$ for some polymer species. This would imply that the chains move by reptation while in the state where entanglements are absent. However, there are no data to judge the relation of $M_e$ to $M_c$ or $M_r$ for the three examples in Table 2 with $p > p^\ast$. They do however show that it is possible to have polymers where $p > p^\ast$. A prime example would be an amorphous poly(n-octadecene) with a long n-alkyl sidechain such as poly(octadecene) where $p \approx 11 \AA$ is plausible.8

The second query concerns the increase in gap (Figure 6) between $M_e$ and $M_r$ as $p$ decreases. This is the regime where chain motion is most strongly influenced by tube length fluctuations. Since $p$ is related to chain “thickness”, it may make sense that the thinner the chain is the more able it is to execute the movements to its backbone that lead to fluctuations concurrently with the reptative motion along the tube. These speculations certainly need to be examined theoretically. But it will also be useful to study more examples of low-$p$ polymers including those with aromatic rings in the backbone to increase chain stiffness (lower $p$). One such polymer with a $p \approx 1.0$ has been reported.44

Another useful candidate to further test these notions is PCHE, Table 2 ($p = 5.59 \AA$), with projected values of $M_c \approx 6.8 \times 10^4$ and $M_r \approx 3.4 \times 10^5$. PS ($p = 3.99 \AA$ and the projected $M_c \approx 4.7 \times 10^3$ and PDMS ($p = 4.06 \AA$ and $M_r \approx 2.9 \times 10^5$) may also be useful here.45

Conclusions

The reported results demonstrate again the critical importance of the packing length in melt rheological behavior. We have shown that $M_c$ scales with packing length in a different fashion than $M_e$ such that $M_c/M_e$ is not a constant but depends on $p$ as given in eq 8. This also implies that $M_c/M_r$ depends on the packing length and, in fact, decreases with increasing $p$. Experimental data for 1,4-PBD and PIB seemingly support this behavior. The results further suggest that $M_e$, $M_c$, and $M_r$ become equal to one another for packing lengths in the 9–10 Å range. We suggest certain areas for future work, particularly on high- and low-$p$ polymers which could help test these relationships more extensively.

Acknowledgment. We express our gratitude to Prof. R. Colby and Mrs. A. Princen for their exemplary work regarding the 1,4-PBD (ref 17) and PIB (ref 30) melt viscosity measurements.

References and Notes


(20) Roovers, J.; Toporowski, P. M. Rubber Chem. Technol. 1990, 63, 734.
(35) Fetters, L. J. Res. Natl. Bur. Stand. 1965, 69A, 33. The concentrated solution-based $M_c$ value of $1.4 \times 10^4$ reported in this reference is seemingly more accurate than the melt-based counterpart (10^4); see Figures 2 and 3.

An evaluation of the PS data for $\eta_0 \approx M_c^{3/4}$ failed to yield a sufficient number of constant temperature high molecular weight ($> 4 \times 10^4$) data sets needed to evaluate the transition of $\eta_0$ to $\alpha = 3$. MA9906200