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_c/M_e has the same value for all species is therefore incorrect. Further, the observed and predicted values of M_r 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 $p = 9$ Å. 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:[1−3]

$$\eta_0(M,T) = K(T)M \qquad M < M_c \tag{1a}$$

$$\eta_0(M,T) = K(T)M^{3.4} \qquad M > M_c \tag{1b}$$

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:[4]

$$M_e = \frac{\rho RT}{G_N^o} \tag{2}$$

in which R is the universal gas constant ($R = 8.314$ K^{-1}), T is the temperature, and ρ is the polymer melt density. We return to the traditional[3,4] definition of M_e for this paper, omitting the Doi−Edwards[5] prefactor of $^4/_5$ used in our previous papers.[6−8] This was done in order to retain the original[3,4] relationship of M_e with M_c. 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 values were available. In this report we show that this perceived universal kinship of M_c and M_e is incorrect.

Recent work[8] 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:

$$M_e = \rho RT/G_N^o = n_t^{\,2} N_a \rho p^3 \tag{3}$$

where N_a is the Avogadro number. The coefficient n_t of eq 3 is taken as insensitive to temperature[8,9] 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 length[10] is

$$p = M/[\langle R^2\rangle_0 N_a \rho] = MV_b/[m_b\langle R^2\rangle_0] \tag{4}$$

where V_b denotes the average volume of a chain per bond, M the chain molecular weight, m_b the average molecular weight per bond, and $\langle R^2\rangle_0$ 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 $\langle R_g^2\rangle_0/M$ in the melt state; the data are given in Table 1. Theta condition dilute solution data[11,12] were used as the unperturbed chain dimension source for PVA, PαMS, and SBR. Some values of M_c were taken directly from the 1968 Berry−Fox review[3] 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

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Table 1. Molecular Characteristics and Melt-Based Rheological Molecular Weights[a]

polymer	T (K)	ρ (g cm^{-3})	m_b	$\langle R^2\rangle_0/M$ (Å^2)	p (Å)	$M_e \times 10^{-3}$	$M_c \times 10^{-3}$	$M_r \times 10^{-3}$	refs
PE	443^b	0.768^c	14	**1.21**^{c}	1.79^c	1.15^c	3.48	*680*^{d}:***710***	3, 6, 13, 14
POE	353	1.081	14.7	**0.805**	1.91	2.00	5.87	*920*:***940***	3, 6, 15
1,4-PBd	298	0.895	14	**0.876**	2.12	2.00	6.38	~630^e/*610*:***710***	6, 16−18
PEP	373	0.812	18.5	**0.851**	2.40	3.10	8.10	*590*:***580***	6, 19
SBR	298	0.930	22.2	0.708	2.52	2.96	8.21	*460*:***630***	4, 12
1,2-PBd	300	0.889	27	**0.720**	2.59	3.85	8.20	*540*:***590***	6, 20, 21
1,4-PI	243	0.950	17.5	**0.583**	3.00	6.40	10.0	*510*:***550***	6, 22, 23
PVA	428	1.08	43	0.490	3.14	9.10	24.5	*600*:***600***	3, 6, 8, 11, 24
PαMS	459	1.04	59	0.460	3.47	13.3	28.0	*600*:***530***	3, 11, 25
PIB	490	0.817	28	**0.570**	3.57	10.5	17.0	~430^f/*420*:***410***	6, 26−30
PMMA	490	1.09	50	**0.425**	3.58	13.6	29.5	*540*:***540***	3, 6, 8, 31
PS	490	0.959	52	**0.434**	3.99	18.1	31.2	*470*:***430***	3, 6, 31
PDMS	298	0.970	37	**0.422**	4.06	12.0	24.5	*290*:***430***	3, 4, 6

[a] The boldfaced type denotes melt-based chain dimensions via SANS while the regular type denotes theta condition measurements. [b] M_c = measurement temperature. [c] The ρ, p, $\langle R^2\rangle_0/M$, and M_e values are those at the measurement temperature of M_c. Where applicable, the ρ values are taken from ref 11, p 81. [d] Via eq 13. Italicized values of M_r were calculated using measured M_e. The values in italicized boldfaced type used calculated M_e. The two entries in standard type are experimental. [e] Based on $M_r/M_e \cong 316$; ref 41. [f] Based on $M_r/M_e \cong 41$; ref 30.

Table 2. Molecular Characteristics and Melt-Based Rheological Molecular Weights[a]

polymer	T (K)	ρ (g cm^{-3})	m_b	$\langle R^2\rangle_0/M$ (Å^2)	p^c (Å)	$M_e \times 10^{-3}$	$M_c \times 10^{-3}$	refs
PC	298^b	1.20	42.5	0.890	1.55	1.6/*1.2*^{d}	6.0^e/*3.9*^{f}	3, 6, 11, 32
PVC	303	1.39	31.25	0.750	1.59	1.5	6.3^e/*4.8*	3, 11, 33, 34
1,4-PI	298	0.900	17.5	**0.596**	3.10	6.8/*7.3*	14^e/*15*	6, 35
PCHE	433	0.920	55	**0.323**	5.59	49/*44*	*68*	6, 8
PAPHM	393	1.0	206	**0.167**	9.94	268/*270*	*255*	38, 39
PBPPHM	393	1.0	234	**0.154**	10.8	355/*340*	*310*	38, 39
PMA−CH$_3$	363	1.17	198	**0.123**	11.5	*485*	~500^g/*420*	36, 37

[a] The boldfaced type denotes melt-based chain dimensions via SANS while the regular type denotes theta condition measurements. [b] M_e or M_c measurement temperature. [c] Packing length values at the measurement temperature of M_c. [d] Italicized values calculated from eq 3. [e] From concentrated solution measurements. [f] Italicized values calculated via eq 8; measured M_e values used when possible. [g] Estimated value for the melt state.

Table 3. Identification of Polymer Acronyms

PE	polyethylene
POE	poly(oxyethylene)
1,4-PBd	1,4-polybutadiene (~8% vinyl; ~50% cis and ~42% trans)
PEP	essentially an alternating copolymer of ethylene and propylene (hydrogenated 1,4-polyisoprene)
SBR	solution prepared copolymer (anionic polymerization) styrene−butadiene (~34% vinyl; ~19% cis and ~47% trans) 25 wt % styrene
1,2-PBd	atactic 1,2-polybutadiene (~98% vinyl content)
1,4-PI	1,4-polyisoprene (~8% 3,4; ~70% cis and ~20% trans)
PVA	atactic poly(vinyl acetate)
PαMS	atactic poly(α-methyl styrene)
PIB	polyisobutylene
PMMA	atactic poly(methyl methacrylate)
PS	atactic polystyrene
PDMS	poly(dimethylsiloxane)
PC	polycarbonate
PVC	poly(vinyl chloride)
PCHE	atactic poly(cyclohexylethylene); via the hyrogenation of polystyrene
PAPHM	atactic poly[6-{4(methoxycarbonyl)phenoxy}-hexyl methacrylate]
PBPPHM	atactic poly[6-{4(butoxycarbonyl)phenoxy}-hexyl methacrylate]
PMA−CH$_3$	atactic poly[6-{4(tolylcarbonyl)phenoxy}-hexyl methacrylate]

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.

Results and Discussion

Critical Molecular Weight. Fox and Allen[2] proposed a relationship between M_c and $\langle R_g^2\rangle_0/M$ which, in the terminology used here, can be expressed as follows:

$$M_c = 6X_cN_am_bp \tag{5}$$

where $\langle R_g^2\rangle_0$ is the mean-square unperturbed radius of gyration and the quantity $6X_cN_a$ is proposed to be universal with $X_c = 45.7 \pm 9.2$. Accordingly, the data for the various species[11−31] in Table 1 should give a straight line through the origin when plotted as $N_c = M_c/m_b$ 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 M_c/m_b vs p, testing the possibility of a power law with an exponent other than unity, gives no improvement in the fit.

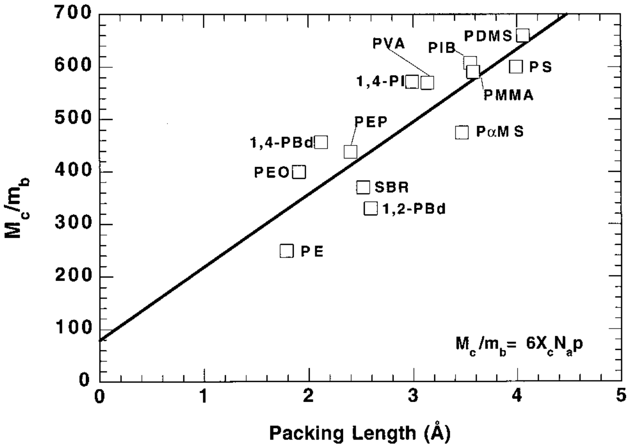

Figure 1. Plot of melt state M_c/m_b (N_c) vs packing length for the polymers in Table 1.

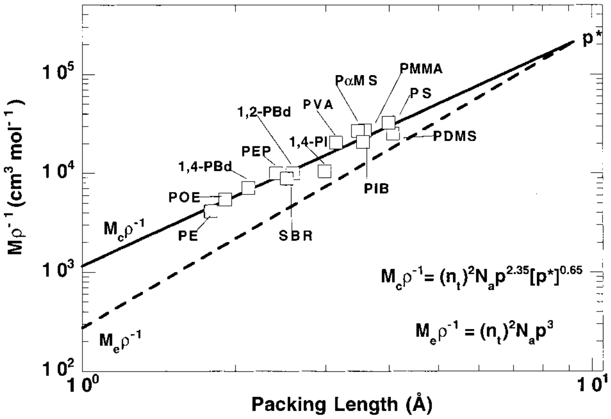

Figure 2. Plot of $M_c\rho^{-1}$ vs packing length for melt-based M_c values. The dashed line ($M_e\rho^{-1}$) is based upon eq 3.

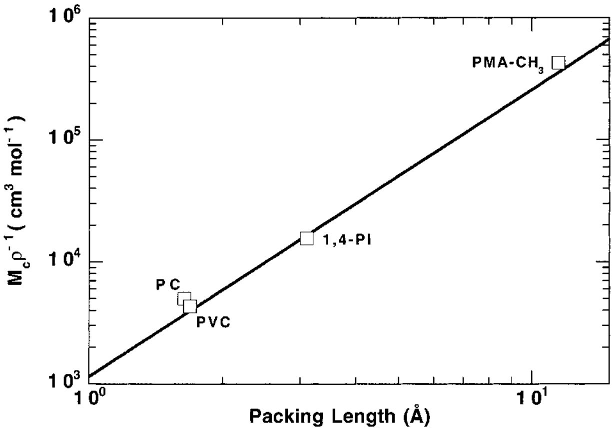

Figure 3. Plot of $M_c\rho^{-1}$ vs packing length for PC, PVC, 1,4-PI (open squares; data from concentrated solutions), and PMA−CH$_3$ (filled square; estimate for the melt state). The line is based upon eq 8.

Inspection of Table 1 shows that the M_c/M_e ratio is species dependent and that there is a trend toward smaller ratios with increasing packing length. Hence, a ρp^3 dependence of M_c, 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 $M_c\rho^{-1}$ vs p. This is shown in Figure 2, and the expression takes the following form:

$$M_c = CN_a\rho p^x \tag{6}$$

We find $C = 1918$ (using the units listed in Table 1), $x = 2.35 \pm 0.15$, and $R = 0.942$. Thus, M_c has a weaker dependence on p than M_e 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[32−35] (Table 2) of PC, PVC, and 1,4-PI. Equation 6 is consonant as well with the M_c 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_c was available.[37]

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

$$\frac{M_c}{M_e} = 4.24p^{-0.65} = \left[\frac{p^*}{p}\right]^{0.65} \tag{7}$$

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

$$M_c = n_t^2 N_a \rho p^{3.0}\left[\frac{p^*}{p}\right]^{0.65} = M_e\left[\frac{p^*}{p}\right]^{0.65} \tag{8}$$

With M_c expressed in this way, the result seems very strange indeed since it requires that M_e overtakes M_c (see Figure 2) as the packing length approaches some p^* 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 p values that exceed p^* so exploring the implications of eq 8 is certainly feasible.

Pure Reptation Threshold. While the number of polymers with known values of M_c in the melt state is smaller than that[6−8] for M_e, 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_c 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 ∼3 entanglement events per chain for entry into the regime where $\eta_0 \propto M^{3.4}$ while PS needs only ∼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, which we will call the reptation molecular weight, M_r, 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_r can be obtained as follows. The observed viscosity behavior above M_c can be written as

$$\eta_0(M) = \left[\frac{M}{M_c}\right]^{3.4}\eta_0(M_c) \tag{9}$$

and the prediction for pure reptation is[42,43]

$$\eta_0(M) = Q\frac{M^3}{M_e^{\,2}M_c}\eta_0(M_c) \tag{10}$$

Table 4. Packing-Length-Based Equations

$G_N^o = k_bT/n_t^2p^3$	$n_t = [M_e\langle R^2\rangle_0/M]^{1/2}p^{-1}$
$M_e = n_t^2N_a\rho p^3$	entanglement length $= pn_t$
$M_r = M_e[p^*/p]^{3.9}$	$\langle R^2\rangle_0/M = n_t^{2/3}M_e^{-1/3}(\rho N_a)^{-2/3}$
$M_c = M_e[p^*/p]^{0.65}$	

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 $Q = 1.13$

$$\frac{M_r}{M_e} = \left[1.13\left(\frac{M_c}{M_e}\right)^{2.4}\right]^{1/0.4} = 1.36\left[\frac{M_c}{M_e}\right]^{6.0} \qquad (11)$$

or, on making use of eq 8

$$M_r = M_e\left[\frac{1.08p^*}{p}\right]^{3.9} \qquad (12)$$

Thus, eqs 3, 8, and 12 are governed by the same dimensionless coefficient, n_t^2.

An additional point to make is that for η_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

$$M_r \cong M_e\left[\frac{p^*}{p}\right]^{3.9} \qquad (13)$$

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_c 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_c/M_e. Thus, for $M_c/M_e = 3$ we obtain $M_r/M_e = 724$ while for $M_c/M_e = 2$ we have $M_r/M_e = 64$. Indeed the value of M_r decreases so quickly with increasing p ($M_r \propto p^*/p$ 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 $M^{3.4}$ behavior beyond about $M_r/M_e \approx 200$ 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_c line the viscosity behaves in a Rouse-like mode. Above the M_r line the viscosity is controlled essentially by reptation. Between the M_c and M_r lines the fluctuation effects[40–43] come into play.

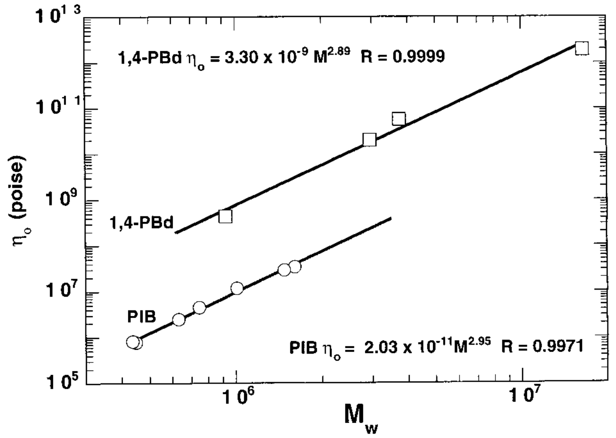

Figure 4. A log–log plot of zero-shear η_0 vs M_w for 1,4-polybutadiene at 298 K (ref 17) and polyisobutylene at 448 K (ref 30).

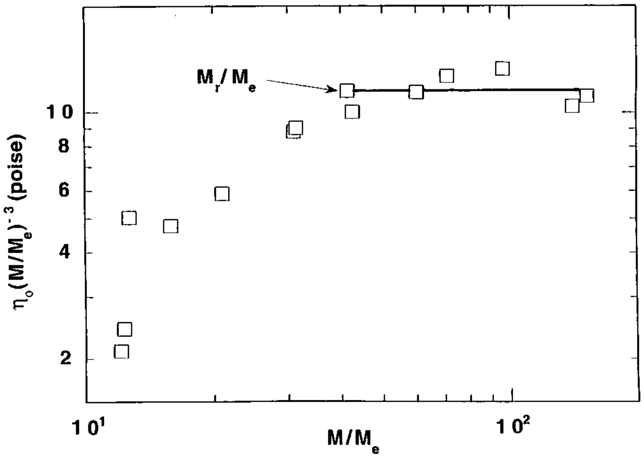

Figure 5. Plot of $\eta_0(M/M_e)^{-3}$ vs M/M_e for polyisobutylene at 448 K. The M_r/M_e insert denotes the position of the estimated value of 41. The line is drawn with the gradient of zero. Identical results are obtained from the 423 and 473 K data sets of ref 30.

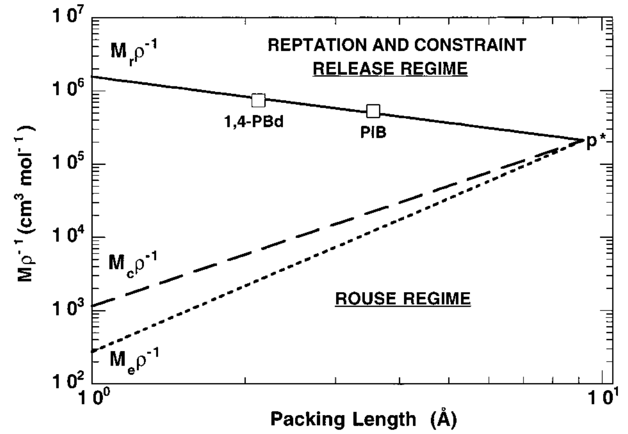

Figure 6. Plots of $M_e\rho^{-1}$, $M_c\rho^{-1}$, and $M_r\rho^{-1}$ as a function of packing length. The lines are calculated via eqs 3, 8, and 13. The symbols denote the experimental $M_r\rho^{-1}$ values for 1,4-PBd and PIB.

Figure 6 suggests two additional questions regarding polymer rheology. First, what happens when $p > p^*$? 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 $p > p^*$. They do however show that it is possible to have polymers where $p > p^*$. A prime example would be an amorphous poly(α-olefin) with a long *n*-alkyl side chain such as poly(octadecene) where $p \approx 11$ Å 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 ($p = 5.59$ Å), with projected values of $M_c \approx 6.8 \times 10^4$ and $M_r \approx 3.4 \times 10^5$. PS ($p = 3.99$ Å and the projected $M_r \approx 4.7 \times 10^5$) and PDMS ($p = 4.06$ Å 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_r/M_c 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.

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