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Chain Entanglement in Polymer Melts and Solutions

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Introduction

We consider the problem of entanglement in polymer melts and solutions with no excluded-volume interactions (Θ solvent). A number of simple ideas on this subject, cast in the form of scaling theories, have recently been proposed in the literature. At first glance these ideas are seemingly unrelated. First we show the relation between the various scaling pictures of polymer entanglement. In so doing, we will develop a clearer picture of the underlying physics associated with each idea. We will show that the differences between the scaling ideas arise because there are two independent length scales in the problem, which means that scaling must rely on a conjecture about the nature of entanglement. We then examine experimental data on polymer melts and solutions to test these ideas.

Scaling Theory

A rather general framework for thinking about the problem of entanglement was introduced by Graessley and Edwards.[1] They started with the idea that the plateau modulus G_0 should be determined solely from the density of chain contour length (νL, where ν is the number density of chains and L is the contour length of a chain) and the Kuhn length of a chain, l. A simple dimensional argument leads to the main result of their paper:

$$G_0 l^3/kT \sim (\nu L l^2)^{\alpha} \qquad (1)$$

The exponent α was not calculated explicitly by Graessley and Edwards but determined from experiment to be in the range $2 \le \alpha \le 2.3$. We can cast eq 1 in terms of measured quantities, as the number density of chains $\nu = cm_0/M$ (c is the number density of the main-chain bonds, m_0 is the average molecular weight per main-chain bond, and M is the polymer molecular weight) and the contour length $L = Ml_0/m_0$ (l_0 is the average length of a main-chain bond) lead to the following expression for the density of chain contour length:

$$\nu L = (cm_0/M)(Ml_0/m_0) = cl_0 \qquad (2)$$

Using Flory's characteristic ratio[2] $C_\infty = l/l_0$, we arrive at

$$G_0/kT \sim C_\infty^{2\alpha-3} l_0^{3(\alpha-1)} c^{\alpha} \qquad (3)$$

This leads to the tube diameter (the length scale of entanglement) a having the concentration dependence $a \sim c^{(1-\alpha)/2}$. As we shall see, several other scaling ideas about entanglement lead to predictions which are in the form of eq 3, with specific values of the exponent α.

Kavassalis and Noolandi[3-5] and Lin[6] have suggested that entanglements are determined from a fixed number of strands in an entanglement volume a^3. We define N_e to be the number of Kuhn segments in an entanglement strand, and $N_e°$ to be the number of main-chain bonds per entanglement strand. The number of entanglement strands per unit volume is just $c/N_e°$, and the number of strands per volume a^3 is

$$N_{\text{strand}} \cong a^3 c/N_e° \sim C_\infty^{3/2} l_0^3 (N_e°)^{1/2} c \qquad (4)$$

since $a = (C_\infty N_e°)^{1/2} l_0$. References 3–6 assume

$$N_{\text{strand}} = \text{constant} \qquad (5)$$

which effectively requires

$$N_e° \sim 1/(C_\infty^3 l_0^6 c^2) \qquad (6)$$

The plateau modulus is therefore

$$G_0/kT \cong c/N_e° \sim C_\infty^3 l_0^6 c^3 \qquad (7)$$

which is a special case of the general Graessley–Edwards result (eq 3) with $\alpha = 3$. Note also that eq 7 is of the same form as the one proposed by Ronca[7] and implies that $a \sim c^{-1}$, a result originally due to Doi.[8]

An alternative scaling based on a fixed number of binary contacts making an entanglement strand has been discussed extensively[9-12] (see also ref 1). $N_{\text{strand}}N_e$ is the total number of Kuhn segments in the volume a^3. The probability of finding a single Kuhn segment is therefore $N_{\text{strand}}N_e l^3/a^3$. The number of binary contacts between Kuhn segments along a strand is then

$$(N_{\text{strand}} N_e l^3/a^3) N_e = \text{constant} \qquad (8)$$

Since we only treat the case with no excluded volume, $N_e = (a/l)^2$ and

$$N_{\text{strand}} N_e^{1/2} = \text{constant} \qquad (9)$$

Combining with eq 4 for N_{strand}, using $N_e° = C_\infty N_e$, this implies

$$N_e° \sim 1/(C_\infty l_0^3 c) \qquad (10)$$

and the plateau modulus

$$G_0/kT \cong c/N_e° \sim C_\infty l_0^3 c^2 \qquad (11)$$

which is a special case of the Graessley–Edwards result (eq 3) with $\alpha = 2$.

A third scaling idea for entanglements has been proposed by Colby and Rubinstein.[13] In this case entanglements were conjectured to be determined by a constant number of binary contacts per volume a^3. This is determined by multiplying the probability of finding a Kuhn segment $N_{\text{strand}}N_e l^3/a^3$ with the total number of Kuhn segments in the entanglement volume a^3 which is $N_{\text{strand}}N_e$, so

$$(N_{\text{strand}} N_e l^3/a^3) N_{\text{strand}} N_e = \text{constant} \qquad (12)$$

which we can rewrite as

$$N_{\text{strand}}^2 N_e^{1/2} = \text{constant} \qquad (13)$$

Combining eq 4 for N_{strand} with $N_e° = C_\infty N_e$, we get

$$N_e° \sim 1/(C_\infty^{5/3} l_0^4 c^{4/3}) \qquad (14)$$

and the plateau modulus

$$G_0/kT \cong c/N_e° \sim C_\infty^{5/3} l_0^4 c^{7/3} \qquad (15)$$

which is a special case of eq 3 with $\alpha = 7/3$.

All three scaling ideas about entanglements are, therefore, specific cases of the Graessley–Edwards form (eqs 1 and 3). Why is it that scaling fails to provide a clear answer? As discussed by Helfand,[14] the reason is that there are two independent length scales in the problem (the Kuhn length l and the average distance between

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Table I
Statistical Analysis of Literature Data on Concentration Dependence of Plateau Modulus in Θ Solvents

polymer	solvent	DF[a]	α[b]	ref
polystyrene ($M = 6.77 \times 10^6$)	cyclohexane, $T = 35$ °C	7	2.41 ± 0.25	17
polystyrene ($M = 2.06 \times 10^7$)	cyclohexane, $T = 35$ °C	7	2.43 ± 0.16	17
polystyrene ($4.48 \times 10^6 < M$ $< 2.06 \times 10^7$)	dioctyl phthalate, $T = 30$ °C	12[c]	2.37 ± 0.13	18
polystyrene ($M = 3.8 \times 10^6$)	polystyrene ($M = 1.03 \times 10^4$)	4	2.20 ± 0.11	19
polybutadiene ($M = 9.25 \times 10^5$)	dioctyl phthalate, $T = 25$ °C	5	2.33 ± 0.06	20

[a] Degrees of freedom (number of data points minus 2). [b] α values with 95% confidence intervals. [c] Three samples at low concentration and low molecular weight were excluded because they deviate from the power law (too close to the overlap concentration).

contour lines $(\nu L)^{-1/2}$ in eq 1). This means that some conjecture about entanglements is required for scaling to provide an answer. Three conjectures were discussed above, but others are of course possible. In fact, recent results of Edwards and co-workers[15,16] indicate that scaling may not be applicable to the problem of chain entanglement. However, experimental data suggest that scaling is at least approximately obeyed. In the remainder of the paper, we will treat the exponent α as an adjustable parameter of the general Graessley–Edwards scaling theory and turn to experimental data to evaluate α.

Comparison with Experiments

One direct method of evaluating the exponent α is to determine the variation of plateau modulus with concentration in a Θ solvent. We determine α from five such data sets in the literature, and the results are summarized in Table I. Clearly there are no apparent differences between results from various polymer/Θ solvent systems, as the 95% confidence intervals from all five determinations overlap extensively. We compute a mean value of α (weighted by the reciprocal of the standard deviation) and a pooled precision estimate for Θ solvent data to be $\alpha = 2.33 \pm 0.13$ (95%), which is in excellent agreement with $\alpha = 7/3$.

Another way to evaluate α is to correlate entanglement spacings of different polymers in their melt state with the molecular parameters C_∞, l_0, m_0, and ρ (concentration $c = \rho/m_0$ where ρ is the polymer density and m_0 is the average molecular weight per main-chain bond), as done in ref 5. The generalized Graessley–Edwards relation leads us to expect that the following combination of molecular parameters (called K_α) should be a universal constant for the properly chosen exponent α:

$$K_\alpha \equiv C_\infty^{3-2\alpha} l_0^{3(1-\alpha)} (\rho/m_0)^{1-\alpha} / N_e^\circ \qquad (16)$$

The necessary data have been gathered for 13 polymers in ref 5. We plot the standard deviation in K_α for these 13 polymers as a function of α in Figure 1 (solid curve). The standard deviation has a minimum value of roughly 19% of the mean at $\alpha = 2.8$. Statistical analysis indicates $\alpha = 2.80 \pm 0.44$ from this data set with a 95% confidence interval. Unfortunately, due to the large errors associated with measuring quantities such as plateau modulus (yielding N_e°) and chain dimensions (yielding C_∞), and densities in some cases only reported to one significant figure, this data set cannot define α with much precision.

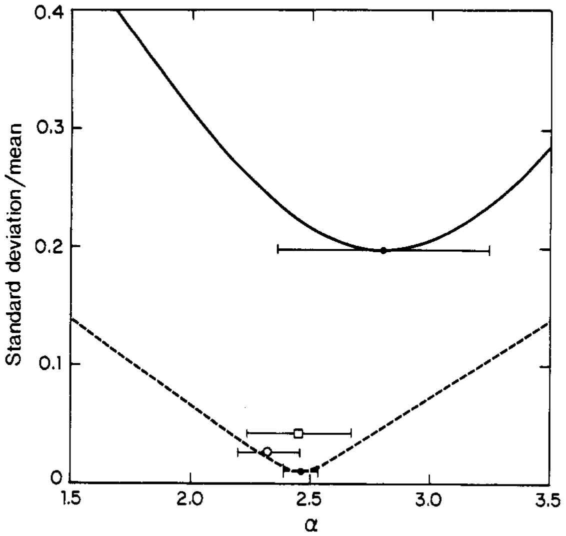

Figure 1. α dependence of relative error in K_α (eq 16) for the 13-polymer melt data set of ref 5 (—) and K_α' (eq 17) for the PEP melt data set of ref 21 (Table II) (- -). The pooled estimate of α from Θ solvent data (Table I) is ○ and from all three data sets is □. Error bars represent 95% confidence intervals. The theoretical predictions are $\alpha = 2$, $7/3$, and 3.

Table II
Temperature Dependence of Parameters Controlling Plateau Modulus (for Poly(ethylenepropylene) Data from Reference 21)

T, K	ρ,[a] g/cm^3	C_∞	$G_0(T)/G_0(448\text{ K})$
373	0.8096	6.54	1.0800
423	0.7818	6.21	1.0123
457	0.7635	6.09	0.9930
492	0.7451	5.98	0.9520
523	0.7292	5.89	0.9490
548	0.7166	5.84	0.9345
573	0.7042	5.80	0.933
590	0.6959	5.77	0.932

[a] Density data calculated from the thermal expansion coefficient reported in ref 21.

A preferable technique for assessing α from melt samples is to study the temperature dependence of the plateau modulus, chain dimensions, and density for a single high molecular weight polymer. The advantage to this is that while absolute measurement of the plateau modulus and chain dimensions will still vary by the usual ca. ±5%, primarily due to sample loading in the case of mechanical measurements and intensity calibrations in the case of scattering, the changes of these experimental quantities with temperature can be measured quite precisely because the primary sources of error are not varied. Such measurements have recently been reported by Butera et al.[21] on alternating poly(ethylenepropylene) (PEP) over a 217 K temperature range. Since only a single polymer is used, quantities such as bond lengths and masses are incorporated into the effective constant, leading to the following combination of measurable (temperature-dependent) quantities being constant:

$$K_\alpha' \equiv (G_0/T) C_\infty^{3-2\alpha} \rho^{-\alpha} \qquad (17)$$

The temperature dependences of the plateau modulus, characteristic ratio, and density of PEP from ref 21 are listed in Table II. The standard deviations in K_α' for these data are plotted as a function of α in Figure 1 (dashed curve). A minimum is observed with a standard deviation of 1% of the mean at $\alpha = 2.46$. As seen in Figure 1, this minimum is more than an order of magnitude smaller than the minimum for the data set for ref 5 (solid curve). Statistical analysis (with a 95% confidence interval) on the PEP data set indicates $\alpha = 2.46 \pm 0.07$.

Conclusions

Three scaling ideas about entanglement in polymer solutions have been shown to be special cases of the Graessley–Edwards scaling framework, with particular values of the exponent α (=2, $^7/_3$, and 3) arising from different conjectures about the nature of entanglement. Data on the concentration dependence of the plateau modulus in Θ solvent indicate that $\alpha = 2.33 \pm 0.13$. Data compiled in ref 5 on various polymer melts indicate $\alpha = 2.80 \pm 0.44$. Data on the temperature dependence of the plateau modulus, chain dimensions, and density for poly(ethylenepropylene) alternating copolymer from ref 21 indicate that $\alpha = 2.46 \pm 0.07$. There is no apparent difference between solution and melt determinations of α, as the 95% confidence intervals of the three data sets overlap. We compute a mean value of α for all three data sets (solution and melt), weighted by the reciprocal of their standard deviations, and pool the precision estimate to conclude that the experimental value of α is 2.45 ± 0.22 (95%). This value is clearly is best agreement with the prediction of ref 13 ($\alpha = {}^7/_3$).

We presume that the larger standard deviation from the 13-polymer data set of ref 5 is due to random errors in measuring the density, plateau modulus, and chain dimensions. However, the possibility of nonuniversal behavior (different polymers leading to different best values of α) cannot be ruled out. For this reason, data similar to the PEP data of ref 21 are truly needed for other polymers. It appears that the temperature dependence data on melts can be determined with sufficient precision to address this question of universality. Data on the temperature dependence of the density, plateau modulus, and chain dimensions for polymers other than PEP should be treated as independent data sets to determine whether their confidence intervals for α overlap.

Note Added in Proof: A recent compilation of melt data[22] for ten polymers indicates $\alpha = 2.67$, consistent with results discussed here.

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