Entanglement Molecular Weight

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In some literature, entanglement molecular weight M_e is discussed as a material property that characterizes magnitudes of entanglement for polymeric liquids. However, M_e was introduced as a model parameter for theories that explain the plateau modulus, and the value is model dependent. A value of M_e may induce misleading analysis if it is presented without noting the underlying theoretical model. Meanwhile, attempts in molecular simulations allow us to extract M_e from a snapshot of entwining molecules via the topological analysis. However, the relation has not been fully clarified yet between the extracted network and the entangled polymer dynamics; the latter is the retarded molecular motion observed for dense polymeric liquids with high molecular weight. Analysis of the reduction of entanglement density under deformations is also a matter of discussion since some molecular theories can reproduce non-linear rheology with stable entanglement density.

Key Words: Viscoelasticity / Polymers / Rheology / Simulation / Plateau modulus

ENTANGLEMENT OF POLYMERS

Entanglement phenomenon represents the retarded molecular motion observed in dense polymeric liquids with high molecular weight¹⁾. For polymer melts with low molecular weight, the diffusion coefficient D and the viscoelastic relaxation time τ depend on the molecular weight M described as $D \sim M^{-1}$ and $\tau \sim M^2$. These behaviours can be explained by the Rouse theory²⁾, in which the effects of surrounding polymers are embedded into the friction constant of the bead-spring chain. As the molecular weight increases, the power-law exponent changes as $D \sim M^{-2.2}$ and $\tau \sim M^{3.5}$, demonstrating a significant slow-down of the molecular motion^{1, 3-5)}. Polymeric systems in such a state are so-called “entangled polymers”, and the correlation between the polymers that induces the retarded molecular motion is referred to as entanglement coupling¹⁾.

The fundamental mechanism of the retardation has not been fully clarified yet. There have been reported no structural transition at the critical molecular weight for entanglement^{1, 3-5)}. Meanwhile, it has been established that uncrossability between chains has been specified to play a significant role. The coarse-grained molecular simulations, in which the uncrossability is guaranteed via the excluded volume,

reproduce the entangled polymer dynamics^{6, 7)}. Attempts have been made from the topology between chains or the magnitude of entwining among the chains⁸⁻¹²⁾.

Meanwhile, some theoretical models have attained remarkable success with hypothetical setup for the polymer motion^{4, 5, 13-15)}. In these models, the polymers move under dynamic constraint, for which a particular characteristic length is assumed. In the temporal network model¹⁶⁾ and the slip-link model¹⁷⁾, the polymer segments are trapped at specific nodes distributed in space with a certain correlation length. In the tube model^{18, 19)}, the polymer dynamics is represented by a single chain motion confined in a tube that has a specific diameter. The rubber-like plateau in the viscoelastic relaxation hints such a characteristic length since the modulus can be interpreted as thermal energy per characteristic volume.

The term “entanglement molecular weight”, usually referred to as M_e , is a chemistry dependent parameter for the theoretical models mentioned above. In what follows, we note that the value of M_e depends on the underlying theoretical model, even if the plateau modulus is experimentally specified²⁰⁾. Besides, we review some attempts in molecular simulations, in which the entanglement network is extracted from intertwining polymers.

M_e FROM G_N

As mentioned above, M_e is experimentally obtained

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from the plateau modulus G_N . The most widely used definition is as follows.

$$M_e = \frac{\rho RT}{G_N} \quad (1)$$

Here, ρ is the polymer density, R the gas constant, and T the temperature. We wish to note that a model-dependent constant A is hidden in equation 1 as

$$M_e = A \frac{\rho RT}{G_N} \quad (2)$$

The expression given in eq. 1 stands for the case of $A = 1$. We shall review the value of A that depends on the molecular model behind. Note that we follow the binary assumption of entanglement to have four diverging strands from one network node, and the effect of functionality is not discussed below.

The relation between modulus and molecular weight of the network strand has been well-investigated for rubber elasticity^{21, 22)}. Indeed, the notation of eq. 1 was introduced according to the analogy to the affine network theory²³⁾, in which the strand molecular weight M_C is used instead of M_e . This theory assumes that the network deforms affinely, and the node position does not fluctuate at all, as schematically described in Fig. 1(a). For entangled polymers, Ferry¹⁾ utilized $A = 1$ in his book to tabulate the value of M_e determined from the data for G_N .

Although the affine assumption is convenient, the idea is somewhat incompatible to the use of entropic spring for each network strand. Namely, the entropic spring comes from thermal fluctuations of the Kuhn segments. If such fluctuations are allowed, the position of network nodes must fluctuate at least in the same order of magnitudes with the segments, as depicted in Fig. 1(b). The phantom network theory^{24, 25)} takes account of such fluctuations, and the theory gives $A = 1/2$. Although this value of A has not frequently been employed for entangled polymers, it is consistent with the value of M_e determined by the primitive path analysis, as mentioned later.

For the entanglement network, the fluctuation along the chain contour comes into play. In the tube model proposed by Doi and Edwards³⁾, the tube deforms affinely, whereas the segments are allowed to slip inside the tube, as shown in Fig. 1 (c). This slippage gives $A = 4/5$, and Fetters²⁶⁾ tabulated the value of M_e according to this A value.

The realistic situation would be with both of the fluctuations explained above. Namely, fluctuations are considered for the position of the network nodes and the number of

segments on each network strand, as shown in Fig. 1 (d). For the slip-tube model proposed by Rubinstein and Panyukov²²⁾, the value of A for such a case is $A = 4/7$. This value is close to the empirical parameter for the multi-chain slip-link model determined as $A = 2/3$ by Masubuchi *et al.*^{27, 28)}.

There is another class of molecular models, so-called slip-spring models²⁹⁻³²⁾. In this framework, the entanglement is replaced by a spring that connects two chains, as seen in Fig. 1 (e). This modelling of entanglement induces additional

Fig. 1 Schematic representation of theoretical models for the elasticity of a polymer network. Fig (a) depicts the affine network model, in which the network deforms affinely without fluctuations. In the phantom network model shown in Fig (b), the network nodes are allowed to fluctuate around its equilibrium position, as indicated by red curved arrows. The tube model can be replaced by the slip-link network seen in Fig (c), where the network nodes do not fluctuate in space, whereas the chain slides along its contour through the network nodes, as shown by blue arrows. Fig (d) represents the multi-chain slip-link model that takes account of the fluctuations for the node position and the chain sliding. The multi-chain slip-spring model adds the other fluctuations to the slip-link model by the virtual springs that connect two chains, as shown in Fig (e).

Table I A values in eq. 2 for various network models.

Model	Fluctuations	A value
Affine network ²³⁾	N/A	1
Phantom network ^{24, 25)}	Brownian motion of nodes	1/2
Tube model ³⁾ (Slip-link network)	Chain sliding	4/5
Slip-tube model ²²⁾ (Multi-chain slip-link network)	Brownian motion of nodes and chain sliding	4/7 2/3*
Multi-chain slip-spring model ³⁴⁾	Brownian motion of nodes, chain sliding, and node flexibility	~1/4

*Empirically obtained^{27, 28)}

 Table II M_e values of polymers used for some models.

Model	PS	PI	PB	Bead-spring model*
Affine network ¹⁾	18100	—	2500	—
Tube ³⁶⁻³⁸⁾	14470	4820	1930	72
Multi-chain slip-link ^{28, 34)}	11000	3500	1600	40
Multi-chain slip-spring ^{34, 35, 39)}	4400	1400	—	28

*For the standard model proposed by Kremer and Grest⁴⁰⁾.

fluctuations to the abovementioned models, in which the bundled chains share the position of entanglement. Uneyama³³⁾ has recently derived $A \sim 0.24$, which is close to the values empirically employed for the multi-chain slip-spring simulations.

The A values mentioned above are summarized in Table I. Because G_N and ρ are defined experimentally, the value of A affects the estimation of M_e . Table II shows the M_e values. Apart from the data taken from Ferry's book¹⁾, the values are used for the fitting of theoretical results of $G'G''$ data to experiments. Although not in a fully quantitative agreement, the M_e values are consistent with A values in Table I. For instance, if we compare the value of M_e for polystyrene estimated from the tube theory ($A = 4/5$) and the slip-spring model ($A \sim 0.24$), the value for the latter is 30 % of the former.

One may argue that the small M_e values in some models are inconsistent with the transition between unentangled and entangled behaviours seen for the molecular weight dependence of the diffusion and the relaxation time. Ferry¹⁾ summarized that the critical molecular weight for the transition, M_c , is $M_c \sim 2M_e$. However, this relation was obtained for $A = 1$, and it depends on the A value. In the other extreme, for the slip-spring simulations, $M_c \sim 8M_e$ is observed^{34, 35)}. This result can be rationalized by the fact that the fluctuations weaken the constraint of entanglement to the chain dynamics.

We note that the value of A is independent of the polymer density. For each model, with the number density of the network strand ν , the unit of modulus can be defined as $G_0 = \nu k_B T$, in a sense that the modulus is the density of

thermal energy. According to this expression, one may argue that the value of A is a matter of conversion for the unit of length and the node number in the unit volume. However, we emphasize that A is not related to the conversion of density. Indeed, G_0 does not corresponds to the plateau modulus G_N , and the parameter A compensates the difference as $G_N = AG_0$. For instance, for the multi-chain models, the conversion of density is excluded³⁴⁾ in the values of A shown in Table II.

In the discussion above, the plateau modulus G_N is regarded as a well-defined experimental quantity. However, the values of G_N reported in the literature are in a spread. For instance, Liu *et al.*⁴¹⁾ mentioned that the literature value of G_N for polyethylene ranges from 1.1 MPa to 2.6 MPa. The reason for this scattering is i) the difference of the estimation method, ii) the molecular weight dependence of G_N , and iii) the effect of the molecular weight distribution.

The most reliable and widely used method is the so-called integration method, in which G_N is obtained as the integration of G'' over the terminal relaxation peak¹⁾. The advantage of this method is that the obtained G_N is insensitive to the molecular weight distribution if the terminal relaxation is sufficiently separated from the Rouse modes. There are a few other methods that are practically convenient. Namely, G_N is determined from G' at the frequency where G'' shows the minimum¹⁾, the maximum⁴²⁾, or the cross-over¹¹⁾ with G' . For scarcely entangled systems, some of these methods are inapplicable because G'' does not exhibit clear bottom nor peak. Besides, G_N from these methods is strongly affected by the molecular weight distribution. Meanwhile, for

well-entangled and monodisperse systems, the G_N values obtained from the various methods agree with each other within ca. 10 % error⁴¹⁾.

The tabulated values of G_N in the literature can be regarded as the value at the long-chain limit. Meanwhile, G_N depends on the molecular weight because of the structural and kinetic reasons. Flory⁴³⁾ has argued that a fraction of cross-linkers is formed inter-molecularly, and it does not contribute to the modulus. Based on this idea, the following equation for the affine network theory can be derived.

$$G_N = G_N^\infty \left(1 - \frac{2M_e^{AN}}{M} \right) \quad (3)$$

Here, G_N^∞ is the value of G_N at the long chain limit, and M_e^{AN} is the value of M_e based on the affine network theory ($A = 1$). Meanwhile, for the tube model, Doi⁴⁴⁾ proposed the following relation based on the contour-length fluctuation theory.

$$G_N = G_N^\infty \left[1 - C \left(\frac{M_e^T}{M} \right)^{1/2} \right] \quad (4)$$

Here, M_e^T is M_e from the tube theory ($A = 4/5$), and C is a constant. Masubuchi *et al.*^{27, 28)} have proposed another equation for the multi-chain slip-link model considering the cycle rank of the network.

$$G_N = G_N^\infty \left(1 - \frac{3M_e^{MS}}{M} \right) \quad (5)$$

Here, M_e^{MS} is M_e for the multi-chain slip-link model ($A = 2/3$). Nevertheless, the molecular weight dependence of G_N has not been established experimentally. Figure 2 shows an example of the comparison between experimental data and the theory by Masubuchi *et al.*^{27, 28)}, demonstrating the scattering of the

experimental values⁴⁵⁻⁴⁷⁾ in low M regime. Besides, this plot implies that the convergence of G_N to G_N^∞ is seen in highly entangled systems, in which $M \gtrsim 100M_e^{MS} \sim 50M_e^{AN}$. This condition for M is similar to that mentioned by Liu *et al.* for the evaluation of G_N by the integration method. However, their condition comes from a different aspect, in which the Rouse and the terminal relaxations must be well-separated.

M_e FROM MOLECULAR SIMULATIONS

Although the value of M_e is hardly obtained experimentally, it could be measured in molecular simulations. The widely-used method is relying on the mean-square-displacement, in which a few inflection points are predicted before exhibiting the normal diffusion according to the tube theory^{3, 40)}. One of such inflections gives the squared tube diameter that corresponds to the chain dimension of a segment with the molecular weight of M_e . However, the value thus obtained is smaller than that estimated from the modulus (with $A = 4/5$)⁴⁹⁾.

There are a few attempts, in which the entanglement network is extracted among the entwining chains in the simulation box. The pioneering work is the so-called primitive path analysis (PPA) proposed by Everaers *et al.*⁵⁰⁾. For a well-equilibrated snapshot of the molecular simulation, they fixed all the chain ends in space, and tightened the chains up by reducing the temperature and removing the intrachain excluded volume. Then they obtained the network of taut chains tangled with the other chains. Assuming that the fastened chains thus obtained corresponds to the primitive chain considered in the tube model, they calculated the chain statistics to estimate the average molecular weight of the tube segment. They reported that the obtained value is consistent with M_e for $A = 4/5$. They have elaborately reported that the PPA-based M_e follows the packing length theory for various polymers⁵¹⁾. Although this method prepares the statistics of taut chains as a whole, the network topology is hardly analyzed. In other words, one cannot specify individual entanglement points. For this issue, the other methods have been proposed to extract entanglements from the minimization of contour length⁵²⁻⁵⁴⁾. Interestingly, the value of M_e obtained from this method is consistent with $A = 1/2$. Everaers⁵⁵⁾ explained this difference by the thermal fluctuations around the entanglement, as an analogy to the rubber theories mentioned in the previous section. Namely, the M_e obtained from PPA is the value for the energetically minimized network without fluctuations. In contrast, the value obtained from the topological analysis is for a snapshot of the fluctuating network. This idea

Fig. 2 Molecular weight dependence of G_N . Red curve shows the theoretical prediction of eq. 5. Black symbols are experimental data from literature⁴⁵⁻⁴⁷⁾. Red circle is the result from the multi-chain slip-link simulation⁴⁸⁾.

could be rationalized by the results from the iso-configurational analysis⁵⁶⁾, where M_e is defined from the magnitudes of fluctuations, and the obtained value is consistent with $A = 1/2$.

An intriguing outcome from the topological analysis is the distribution of M_e . Based on the classical theories^{57, 58)}, in which the binary entanglement occurs along the chain randomly, the single-exponential function has been proposed. However, the distribution obtained from the topological analysis⁵³⁾ has a peak, as shown in Fig. 3. A similar distribution has been reported from the multi-chain slip-link simulation⁵⁹⁾. Tzoumanekas and Theodorou⁵³⁾ proposed the following functional form for this distribution by considering blocking events, which prevents clustering of entanglements along the chain.

$$P(n) = \frac{1}{\langle n \rangle} \frac{1}{\alpha - \beta} \left[\exp\left(-\frac{n/\langle n \rangle}{\alpha}\right) - \exp\left(-\frac{n/\langle n \rangle}{\beta}\right) \right] \quad (6)$$

Here, n is the number of monomers between two adjacent network nodes, and $\langle n \rangle$ is the average. α and β are numerical parameters empirically determined by fitting. Uneyama⁶⁰⁾ has derived the distribution function from the free energy of the slip-link network with assuming a repulsive interaction between network nodes. The approximated formula in the long chain limit is reported as follows.

$$P(n) = \frac{25}{6} \left(\frac{10n^3}{\pi \langle n \rangle^5} \right)^{1/2} \exp\left(-\frac{5n}{2\langle n \rangle}\right) \quad (7)$$

Greco⁶¹⁾ proposed a different functional form from the thermodynamics, yet the agreement with the data is compatible with eq. 6. As a consequence of M_e distribution, the network strand length and the number of entanglements on each chain also have distributions. Nevertheless, the effect of distributions on rheology and polymer dynamics has not been clarified yet. For instance, melt rheology can be reasonably reproduced by the molecular theories, both with and without the distribution of entanglement network.

Another interesting direction is the analysis of topological network under deformations. Baig *et al.*⁶²⁾ elaborated to observe the modified topological network under steady shear for the full-atomistic simulation of polyethylene. They reported that the number of network nodes decreases with an increase of shear rate. A similar reduction of network nodes has been observed for some coarse-grained models⁶³⁻⁶⁵⁾. These results are in harmony with some theories, in which the entanglement density is assumed to decrease under fast deformations. The representative one is the tube theory proposed by Doi-Edwards⁶⁶⁾, who derived the damping function under large step deformations from the loss of entanglement

Fig. 3 Distribution of monomer number on the network strand. Unfilled symbols show the distribution for the topological network extracted from the snapshot of atomistic molecular simulations for various polymers⁵³⁾. Cross indicates the result from the multi-chain slip-link simulation⁵⁹⁾. Black and red curves show eqs. 6 and 7. For eq. 6, $\alpha = 0.77$ and $\beta = 0.26$.

induced by the chain contraction. The so-called Q tensor expresses the non-linearity based on the loss of entanglement. Due to the remarkable success of the Doi-Edwards theory and the extended model⁶⁷⁾, the loss of entanglement is frequently discussed for non-linear rheology of entangled polymers. For instance, in the interrupted shear experiments⁶⁸⁻⁷³⁾, the reduced stress overshoot observed in the second start-up flow is analyzed in terms of the recovery of entanglement during the interval between consecutive flows. In the superposed shear experiments⁷⁴⁻⁷⁷⁾, in which oscillatory deformations are additionally applied to steady shear, a softening in the oscillatory response is related to the amount of disentanglement. Towards industrial direction, in some numerical simulations where the microscopic models are combined with macroscopic calculations, the spatial distribution of entanglement density has been reported in macroscopic flow channels^{78, 79)}.

However, it must be noted that most of the rheological properties can be explained even if the entanglement density is unchanged. Marrucci *et al.*⁸⁰⁾ have shown that the damping function derived from the force balance around entanglement (with a constant entanglement density) is very close to the Doi-Edwards prediction. The constitutive equation based on the theory by Marrucci *et al.*⁸¹⁾ reasonably reproduces a variety of non-linear viscoelastic phenomena. The other model developed by Graham *et al.*^{82, 83)} is also capable of semi-quantitative prediction with a constant entanglement density. These results imply that the modification of the entanglement network might be an artefact, and there would be other different explanations for the experimental data.

CONCLUDING REMARKS

In this short review, we note that entanglement molecular weight is a parameter for a specific theoretical model, and not a material property intrinsically defined. Misleading analysis and discussion might be conducted if the value of M_e is given without the model description and the method of determination. For example, the M_e values for $A = 1$ and $A = 4/5$ must be discriminated. The characteristic time of the coarse-grained models, such as the entanglement time τ_e in the tube model, must be consistently defined with M_e , as mentioned by Larson *et al.*²⁰⁾ Besides, the evaluation method of G_N should be indicated. Concerning molecular simulations, the topological analysis is widely used, and empirical consistency for the obtained value of M_e has been accumulated with the value from the other methods. However, we note that the relation between the obtained topology from frozen snapshots and the retarded polymer dynamics has not been revealed yet. Flow-induced modification of the topological network attracts attention, and the idea may stimulate developments in the polymer industry. Nevertheless, note that the related experimental observations for rheological response could be reproduced with the models that do not take account of the change of entanglement density.

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