Do Deviations from Reptation Scaling of Entangled Polymer Melts Result from Single- or Many-Chain Effects?

Chen-Yang Liu,[1,2] Roland Keunings,[3,*,†] and Christian Bailly[1,*,‡]

[1]Unité de Chimie et de Physique des Hauts Polymères, Université Catholique de Louvain, B-1348 Louvain-La-Neuve, Belgium
[2]Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China
[3]CESAME, Université Catholique de Louvain, B-1348 Louvain-La-Neuve, Belgium

(Received 7 July 2006; published 12 December 2006)

By studying the relaxation of small amounts of short entangled "probe" chains in a high molecular weight matrix, we show that the deviations from reptation scaling of the longest relaxation time are not as much dominated by single-chain effects (usually referred to as contour length fluctuations or CLF) as assumed by current mesoscopic models but also originate to a very significant extent from mutual chain relaxation effects. This result is in fact consistent with literature data on tracer and self-diffusion. Moreover, tube theories also overpredict the influence of CLF on the plateau modulus. Improved theories, simulations, and careful experiments are urgently needed to resolve this important question.

DOI: 10.1103/PhysRevLett.97.246001 PACS numbers: 83.10.Kn, 61.41.+e

The longest melt relaxation time τ_d and the zero-shear viscosity η_0 of entangled linear macromolecules increase with molecular weight (M) as $M^{3.4\pm0.1}$ [1,2]. This reflects the relaxation scaling of topological interactions. The observed dependence is also a simple touchstone to test detailed theories of polymer dynamics [3], in particular, the mesoscopic reptation model first proposed by de Gennes [4] and further developed by Doi and Edwards [5]. In its simplest form, reptation considers a single snakelike linear chain trapped in a network of permanent entanglements. The network "obstacles" hinder lateral excursions of the chain at length scales larger than the network mesh size, and confines its motion within a 1D curvilinear path, called the tube. The longest characteristic time for the probe chain to escape out of the tube is proportional to the cube of the number of entanglements per chain ($Z = M/M_e$, with M_e being the molecular weight between entanglements). Concurrently, the diffusion coefficient (D) is predicted to scale as $Z^{-2.0}$, while the experimental observation is $Z^{-2.3\pm0.1}$ [6]. The exact origin of the deviations from reptation scalings is a long-standing problem in polymer physics.

Graessley [7] conjectured that the nonreptation scaling should be ascribed to the relaxation of some portion of the stress by faster processes competing with reptation, which would asymptotically reduce the viscosity relative to the theoretical prediction. Doi [8] subsequently incorporated a fundamental modification to the tube model by allowing springlike motions of the test chain inside the tube, usually referred to as contour length fluctuations (CLF) [9,10], in order to speed up relaxation and reduce the stress level. The zero-shear viscosity, apparent plateau modulus (G^0_{app}), and terminal relaxation time are hence predicted by Doi to depend on Z as follows:

$$\eta_0^{(F)} = \eta_0^{(NF)}[1 - \mu(1/Z)^{1/2}]^3, \tag{1}$$

$$G_{\mathrm{app}}^{0(F)} = G_{\mathrm{app}}^{0(NF)}[1 - \mu(1/Z)^{1/2}], \tag{2}$$

$$\tau_d^{(F)} = \tau_d^{(NF)}[1 - \mu(1/Z)^{1/2}]^2 \cong \eta_0^{(F)}/G_{\mathrm{app}}^{0(F)}. \tag{3}$$

Superscripts (F) and (NF) stand for "with fluctuations" and "without fluctuations" and μ is a universal numerical prefactor (1.47 or higher). Recent models [10] give very similar dependence on Z despite using different analytical forms for the equations. Accounting for the CLF effect in this way can suitably reproduce the experimental scaling for τ_d or η_0. Indeed, for Z ranging from 10 to 100, Eq. (1) predicts η_0 to scale as $Z^{3.4}$ with a smooth transition to $\eta_0 \propto Z^{3.0}$ beyond $Z = 200$ [10,11]. However, the observed Z dependence of G^0_{app} is much weaker than predicted by Eq. (2), which questions the validity of the explanation based on CLF for viscosity [12].

In real polymer melts, the chains surrounding the test chain are mobile as well, and therefore entanglements are not always permanent on the time scale of the reptation process. This has led to a second modification of the original theory, i.e., constraint release (CR) or tube motions. This is a "many-chains" effect as opposed to fluctuations, which is a "single-chain" effect. Including CR effects dramatically improves predictions about the width of the relaxation spectrum [13–18]. Because CR is a "many-body problem," its full description of is out of reach and various approximations have been proposed. Dynamic tube dilution [16] and double reptation [18] are simple to implement but drastically oversimplify the dynamics of motions of surrounding chains. Another approach is based on the description of the tube as a Rouse chain, first proposed by Klein [13], Daoud and de Gennes [14], and Graessley [15], and fully developed by Rubinstein and Colby [17]. The influence of CR on deviations from reptation scaling of the terminal relaxation time or viscosity is unsettled both experimentally and theoretically. Graessley's model predicts a rapidly vanishing Z^{-2} influence on τ_d, while the more involved Rouse chain approaches as well as tube dilation or (generalized) double reptation predict a M-independent acceleration factor around 2.5, and hence no significant effect on M scaling. However, none of these models takes into account the specific influence of chain ends on the entanglement network. An alternative picture has been proposed by Kavassalis and Noolandi [19] who describe entanglements as collective topological constraints. The model predicts a specific transition from the entangled to the unentangled state as the chain length is shortened. Consequently, the viscosity and plateau modulus should deviate from the pure reptation scaling through the small M dependence of the molecular weight between entanglements.

In this Letter, we investigate whether deviations from reptation scaling for the viscosity and terminal relaxation time of entangled polymers primarily arise from single-chain effects, i.e., CLF, or many-chain effects, i.e., CR.

We have recently undertaken a systematic analysis of the relaxation dynamics of a small fraction (10%) of short entangled probe chains of 1,4-polybutadiene (PBD), 1,4-polyisoprene (PI), and polystyrene (PS) in a high-M matrix. We refer to this approach as "probe rheology" [20]. In this way, we create a model environment of "quasipermanent entanglements" for the probe chains, where tube motions are suppressed at the time scale of the probe chains reptation, while CLF remain unaffected. Comparing the relaxation dynamics of the probe in two environments, either as a homopolymer melt or when diluted in a high-M matrix, reveals contributions from tube motions to the terminal relaxation. Combining this information with literature results on tracer and self-chain diffusion coefficients ($D_{\rm tr}$ and D_s), as well as the Z dependence of $G^0_{\rm app}$, should help clarify the physical origin of the nonreptation scalings.

By comparison with the relaxation of a self-melt, the relaxation of a probe in a high-M matrix presents several important features, which are independent of polymer species [20]. First, due to the absence of tube motions, the probe chains terminal peak is narrower, with a $G''(\omega) \sim \omega^{-1/2}$ high frequency slope [20,21], in agreement with the prediction of the original reptation theory [5]. Moreover, the angular frequency position of the G'' peak, $\omega_{\max_{G''}}$, shifts to lower values. This means that the longest relaxation time τ_d of the probe chains is increased, as compared to a melt of pure probe chains, since the $\omega_{\max_{G''}}$ is connected to τ_d by the following simple relation [7,20–23]:

$$\tau_d = 1/\omega_{\max_{G''}}. \qquad (4)$$

The retardation factors $\tau_{d_{\rm probe}}/\tau_{d_{\rm self\text{-}melt}}$ for three polymers are plotted as a function of the probe entanglement number Z in Fig. 1, which also includes the rare data extracted from the literature [24,25]. We find that the retardation behavior exhibits two regions depending on Z. For well-entangled chains with $Z > 100$, the retardation factor is independent of Z and has a value of about 2.5. This agrees with the tube dilation picture [16] or the Rubinstein-Colby [17] and Likhtman-McLeish [10] CR models. At lower Z, the magnitude of the retardation factor is larger than 2.5 and increases with decreasing Z as $Z^{-0.3}$, which points to an

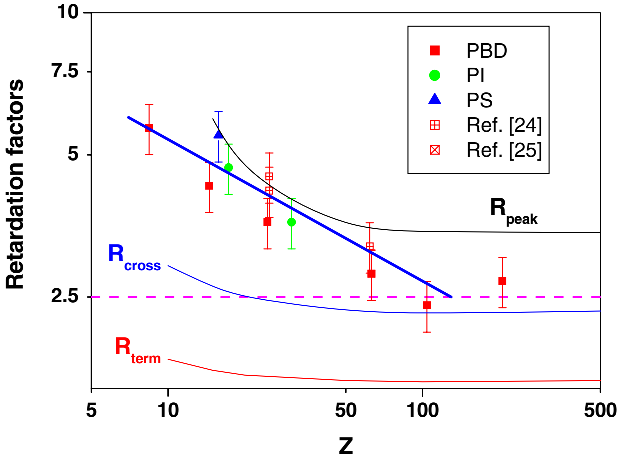

FIG. 1 (color online). Experimental (points) and predicted (thin lines) [10] retardation factors for the longest relaxation time as a function of the entanglement number Z. Experimental data should mainly be compared with $R_{\rm peak}$. Refer to [10] for the definitions of $R_{\rm cross}$ and $R_{\rm term}$. Horizontal dashed line: constant retardation factor of about 2.5 predicted by the dynamic tube dilution model [16] for the well-entangled case. Thick solid line: -0.3 slope.

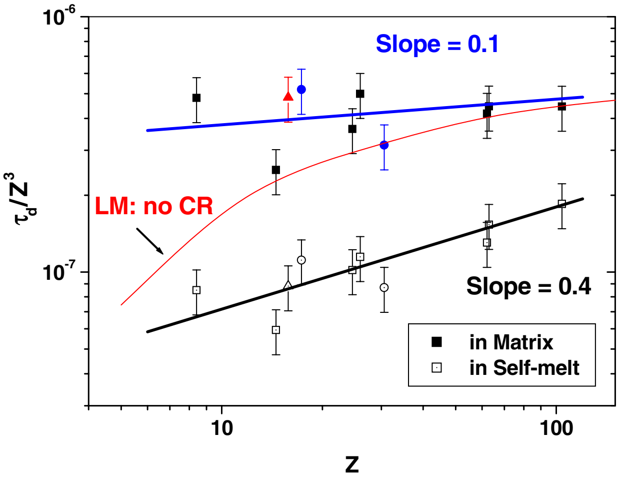

FIG. 2 (color online). Longest relaxation time τ_d for the probe chains in two entangled environments, plotted as τ_d/Z^3 vs Z to highlight deviations from the reptation scaling. The PI (circles) and PS (triangles) data were superimposed on the PBD (squares) data by a vertical shift. The thin line represents the prediction by the Likhtman-McLeish (LM) theory [10] in the absence of CR.

acceleration of tube motion and/or a gradual transition from the entangled to the unentangled state [19].

The Z dependence of the retardation factor reflects a different scaling for τ_d in self-melt or high-M matrix environments as the exponent goes from 3.4 to 3.4–0.3 = 3.1. The accuracy on the exponent is of the order of 0.1 since a $Z^{-0.4}$ or $Z^{-0.2}$ power law in Fig. 1 would not correctly represent the data. The scaling change is clearly revealed by plotting τ_d/Z^3 vs Z, as shown in Fig. 2. In this format, any deviation from the predicted Z^3 is clearly visible. The observed scaling exponent for probe in matrix systems is significantly reduced vs self-melts and compatible with $0.1 = 3.1$–3.0 (again within an accuracy of 0.1). Since, from the standpoint of the probe chains, the motions of surrounding chains are suppressed in a high-M matrix, whereas CLF remain unaffected, the contribution of tube motions on the τ_d scaling is clearly isolated. Our results hence indicate that the motions of surrounding chains have a significant influence on the 3.4 exponent for τ_d and η_0. Conversely, were the fluctuations of the probe chain the dominant factor for the deviating scaling, as proposed by Doi [8], the same 3.4 scaling should be observed in *both* entangled environments. Figures 1 and 2 also include predictions by advanced tube models [10] for the retardation factor and τ_d/Z^3 in the absence of CR. The overall Z dependence is still not correctly predicted by theory.

The importance of CR effects is further highlighted when comparing literature data for self-chain and tracer diffusion coefficients D_s and D_{tr}. Since tracer diffusion results from the diffusion of a probe chain in a high-M matrix, the two environments for D_{tr} and D_s are exactly the same as those in our rheological tests. Lodge [6] has collected extensive literature data on self-diffusion of entangled hydrogenated PBD [26–30], and Wang [31] has further taken into account additional tracer diffusion data [28,32]. Interestingly, the two authors have reached very different conclusions from almost the same set of self-diffusion data (Fig. 3). By analogy with the τ_d analysis in Fig. 2, the D-Z relation is well revealed by plotting $D/M^{-2.0}$ vs Z. A slope of -0.5 for $D_s/Z^{-2.0}$ at low Z and a crossover to pure reptation scaling at $Z \sim 30$ are inferred by Wang for self-diffusion (see Fig. 1 in [31]). However, a slope of -0.35 and a crossover at $Z \sim 100$ are just as reasonable, according to Lodge's analysis (see Fig. 2 in [6]). Lodge argues that the self-diffusion scaling is about -2.3 and CLF explain the deviations from pure reptation scaling of both η_0 and D_s as proposed by Milner and McLeish [9]:

$$D_s^{(F)} = D_s^{(NF)}[1 - 2\mu(1/Z)^{1/2}]^{-1}, \qquad (5)$$

where Eq. (5) is consistent with Doi's Eqs. (1)–(3) from the CLF standpoint. In this way, the Z dependence of diffusion and viscosity can be reconciled for entangled polymers as the product $\eta_0 D_s \sim Z$. On the contrary, Wang argues that the nonreptation scaling for self-diffusion is a result of CR effects [13–15] because of the observed $Z^{-2.0}$ scaling for tracer diffusion.

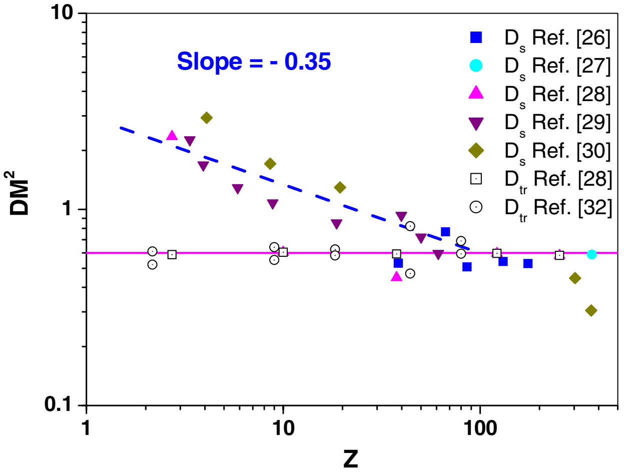

FIG. 3 (color online). Self-chain and tracer diffusion coefficients D_s and D_{tr} [26–30,32] plotted as (D_s or D_{tr}) $M^{2.0}$ vs Z to highlight deviations from the reptation scaling. The dashed line is the -0.35 slope considered by Lodge [6].

The increase of τ_d and the decrease of D for probe chains in a high-M matrix can result only from the suppression of mutual chain relaxation effects, while fluctuations remain intact. Since significantly lower scaling exponents than expected are observed for probe systems [28,31–33], the influence of surrounding chains motion has to be higher than usually accepted and the influence of fluctuations less [8–10]. However, considering that the deviations from ideal reptation exponents (about 0.3–0.4) and the Z crossover positions (about 100) are similar for both rheology and diffusion, it is possible to preserve the $\eta_0 D_s \sim Z$ scaling proposed by Lodge [6,29].

In addition, a self-consistent explanation of the 3.4 scaling for η_0 dominated by CLF should automatically lead to a strong Z dependence of the apparent plateau modulus G^0_{app} according to Eq. (2) and advanced models [10]. Recently, we have reanalyzed available experimental plateau modulus data for PBD [12,20], as shown in Fig. 4. The observed Z dependence is weaker than the prediction of recent tube models even if CR effects are artificially removed [10]. It is worth noting that the experimental dependence rather follows the prediction of the Kavassalis-Noolandi picture [19] of collective entanglements. Results of neutron spin-echo experiments [34] and slip-link simulations [35] are also consistent with a Z dependence of G^0_{app} weaker than predicted. This contradiction between relaxation stress [Eq. (2)] and relaxation time [Eq. (1)] reveals an overestimation of CLF effects [8–10]. As a result, the latter cannot generate a full 0.4 additional exponent for η_0 over a wide range of M [12].

In conclusion, our probe rheology experiments reveal a strong M dependence of mutual chain relaxation effects, which is entirely consistent with the literature on tracer

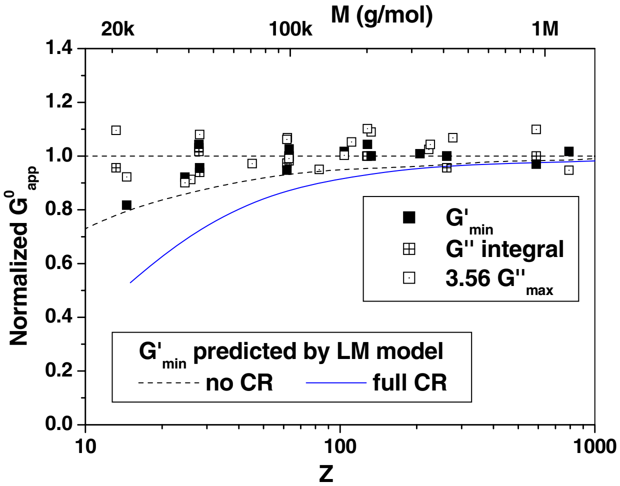

FIG. 4 (color online). G^0_{app} vs Z or M: G^0_{app} normalized by $G^0_N = 1.15$ MPa. Data obtained from [20] and references in [12]. Solid and dashed lines represent the normalized predicted G'_{min} by the Likhtman-McLeish model [10] with and without CR.

diffusion but at variance with current tube models. As a consequence, the deviations from reptation scalings for terminal relaxation time, viscosity, and diffusion appear to originate from many-chains effects at least as much as from single-chain effects. The exact ratio between the two influences is still uncertain because it depends on fractional exponents at the limit of experimental errors. An equal split is consistent with plateau modulus data but seems to underestimate the influence of surrounding chains on the terminal relaxation time. These findings are at odds with the conventional view and hence disturbing, considering that there has been a strong consensus about the viscosity scaling in favor of CLF- and CLF-based models working well in many cases. We are not able at the moment to propose an alternative or improved molecular theory to explain the observed results but we hope this Letter will encourage new theoretical simulations and experimental work (especially combining multiple techniques) to help resolve the uncovered issues.

This work has been supported by the ARC grant of the "Communauté française de Belgique" (C.-Y. L.). We are grateful to Professor W. W. Graessley for his valuable comments.

---

*Corresponding author.
†Electronic address: roland.keunings@inma.ucl.ac.be
‡Electronic address: christian.bailly@uclouvain.be

[1] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980).
[2] W. W. Graessley, Adv. Polym. Sci. **16**, 1 (1974).
[3] F. Bueche, *Physical Properties of Polymers* (Wiley, New York, 1962); W. W. Graessley, J. Chem. Phys. **47**, 1942 (1967); A. S. Lodge, Rheol. Acta **7**, 379 (1968); M. Fuchs and K. S. Schweizer, Macromolecules **30**, 5133 (1997).
[4] P. G. de Gennes, J. Chem. Phys. **55**, 572 (1971); P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
[5] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
[6] T. P. Lodge, Phys. Rev. Lett. **83**, 3218 (1999).
[7] W. W. Graessley, J. Polym. Sci., Polym. Phys. Ed. **18**, 27 (1980).
[8] M. Doi, J. Polym. Sci., Polym. Lett. Ed. **19**, 265 (1981); J. Polym. Sci., Polym. Phys. Ed. **21**, 667 (1983).
[9] S. T. Milner and T. C. B. McLeish, Phys. Rev. Lett. **81**, 725 (1998); A. L. Frischknecht and S. T. Milner, Macromolecules **33**, 5273 (2000).
[10] A. E. Likhtman and T. C. B. McLeish, Macromolecules **35**, 6332 (2002).
[11] R. G. Larson *et al.*, J. Rheol. (N.Y.) **47**, 809 (2003).
[12] C. Y. Liu, J. S. He, R. Keunings, and C. Bailly, Macromolecules **39**, 3093 (2006).
[13] J. Klein, Macromolecules **11**, 852 (1978).
[14] M. Daoud and P. G. de Gennes, J. Polym. Sci., Polym. Phys. Ed. **17**, 1971 (1979).
[15] W. W. Graessley, Adv. Polym. Sci. **47**, 67 (1982).
[16] G. Marrucci, J. Polym. Sci., Polym. Phys. Ed. **23**, 159 (1985).
[17] M. Rubinstein and R. H. Colby, J. Chem. Phys. **89**, 5291 (1988).
[18] J. des Cloizeaux, Macromolecules **23**, 4678 (1990).
[19] T. A. Kavassalis and J. Noolandi, Phys. Rev. Lett. **59**, 2674 (1987); Macromolecules **21**, 2869 (1988); **22**, 2709 (1989).
[20] C. Y. Liu, A. F. Halasa, R. Keunings, and C. Bailly, Macromolecules **39**, 7415 (2006).
[21] S. Ndoni, A. Vorup, and O. Kramer, Macromolecules **31**, 3353 (1998).
[22] J. Roovers, Polymer **30**, 2174 (1989).
[23] K. Urayama, K. Yokoyama, and S. Kohjiya, Macromolecules **34**, 4513 (2001).
[24] M. J. Struglinski and W. W. Graessley, Macromolecules **18**, 2630 (1985).
[25] S. F. Wang *et al.*, Macromolecules **36**, 5355 (2003).
[26] C. R. Bartels, B. Crist, and W. W. Graessley, Macromolecules **17**, 2702 (1984).
[27] B. Crist *et al.*, Macromolecules **22**, 2857 (1989).
[28] J. von Seggern, S. Klotz, and H. J. Cantow, Macromolecules **24**, 3300 (1991).
[29] D. S. Pearson *et al.*, Macromolecules **27**, 711 (1994).
[30] H. Tao, T. P. Lodge, and E. D. von Meerwall, Macromolecules **33**, 1747 (2000).
[31] S. Q. Wang, J. Polym. Sci., Part B: Polym. Phys. **41**, 1589 (2003).
[32] J. Klein, D. Fletcher, and L. J. Fetters, Nature (London) **304**, 526 (1983).
[33] P. F. Green *et al.*, Phys. Rev. Lett. **53**, 2145 (1984); P. F. Green and E. J. Kramer, Macromolecules **19**, 1108 (1986).
[34] A. Wischnewski, Phys. Rev. Lett. **88**, 058301 (2002).
[35] Y. Masubuchi *et al.*, J. Chem. Phys. **119**, 6925 (2003).