Primitive Path Analysis and Stress Distribution in Highly Strained Macromolecules

Hsiao-Ping Hsu* and Kurt Kremer**

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128, Mainz, Germany

Supporting Information

ABSTRACT: Polymer material properties are strongly affected by entanglement effects. For long polymer chains and composite materials, they are expected to be at the origin of many technically important phenomena, such as shear thinning or the Mullins effect, which microscopically can be related to topological constraints between chains. Starting from fully equilibrated highly entangled polymer melts, we investigate the effect of isochoric elongation on the entanglement structure and force distribution of such systems. Theoretically, the related viscoelastic response usually is discussed in terms of the tube model. We relate stress relaxation in the linear and nonlinear viscoelastic regimes to a primitive path analysis (PPA) and show that tension forces both along the original paths and along primitive paths, that is, the backbone of the tube, in the stretching direction correspond to each other. Unlike homogeneous relaxation along the chain contour, the PPA reveals a so far not observed long-lived clustering of topological constraints along the chains in the deformed state.

Mechanical properties of polymer melts and glasses, polymer (nano)particle composites, and elastomers are extremely versatile and the basis for many technological applications. Systems can range from very soft (hydro-)gels to hard and tough glasses. Performance upon mechanical load or during production is intimately linked to the composition of a material and a delicate relation between entanglement density and chain length, filler polymer interaction, distance from the glass temperature, and so on, and the intrinsic relaxation times of the systems. The interplay of rather different time scales, which typically can be located between the Rouse time of an entanglement length \( \tau_e \) and that of the whole chain \( \tau_{eN} \) makes a microscopic explanation of the Payne or the Mullins effects,\(^1\)\(^−\)\(^8\) to name just two, rather difficult. There is a wealth of literature on experimental data and constitutive equations, providing a rather good technical, that is, procedural understanding and guidance, see, for example, ref \(S\). Theoretical work is mainly based on the reptation tube concept,\(^6\)\(^−\)\(^14\) which has been shown to work extremely well in equilibrium and the regime of linear rheology. Based on this, theories for network deformation\(^15\)\(^,\)\(^16\) and the effect of chains sliding along the tube upon strong and fast deformation rates\(^17\) have been developed. A comprehensive tube model based account on polymer melts subject to fast deformation has been given by Graham et al.\(^18\) Despite considerable efforts, many open questions\(^19\)\(^,\)\(^20\) remain, especially in the nonlinear viscoelastic regimes when melts are strongly deformed (e.g., shearing, elongation, etc.). Others employed primitive path network models to account for viscosity changes in entangled polymers upon elongational and shear flow.\(^21\)\(^−\)\(^24\) They can rationalize viscosity changes for strain rates below the inverse Rouse time of the chains, they seem to fail for faster sample deformation. Recently Wang and co-workers\(^25\),\(^26\) questioned the validity of the tube concept for nonlinear rheology of highly entangled polymer melts at all. In general our understanding is least developed in the regime of nonlinear viscoelasticity of highly entangled polymer melts,\(^18\)\(^,\)\(^27\)\(^,\)\(^28\) where the deformation rate is faster than \(\tau_{eN}^{-1}\) and slower than \(\tau_e^{-1}\).

We approach this problem from the computational side. Starting from well equilibrated highly entangled polymer melts of \(17 \leq Z \equiv N/N_e \leq 72\) \((N_e \approx 28, \text{ being the entanglement length and } d_1 \approx \sqrt{N_e} \sigma \approx 5.02 \text{ the tube diameter})\), prepared by a new, efficient hierarchical methodology,\(^29\)\(^−\)\(^31\) we study systems described by the standard bead–spring model with a bond-bending potential\(^32\)\(^−\)\(^32\) with a bending constant of \(k_b = 1.5\) under strong isochoric elongational deformation in the nonlinear rheological regime and their subsequent relaxation. Our central system contains \(n_e = 1000\) chains of length \(N = 2000\). So far, based on the tube model\(^6\)\(^,\)\(^7\)\(^,\)\(^18\)\(^,\)\(^33\) the assumption is that on large length scales the tube deforms affinely, while deviations from this occur on shorter scales of \(O(d_1)\). To test this in detail, we focus on the primitive paths (PPs) of the systems, that is, the backbone of the tube.

The simulation box is isochorically elongated along the \(x\)-direction up to a factor \(\lambda \approx 5\) using the ESPResSo++
The normal stress

is the normal stress

deformation. This is the experimentally most relevant strain

for nonlinear viscoelasticity of highly entangled

polymer melts. Beyond some tests, the effectively averaged strain rate is chosen to be \( \dot{\varepsilon}_{e} t_{RN} = 77 \) (\( N = 2000 \)), that is, \( \dot{\varepsilon} \approx 0.015 \tau_{c}^{-1} \). This allows for relaxation of up to approximately 8\( N_{c} \) during deformation. This is the experimentally most relevant strain rate regime for nonlinear viscoelasticity of highly entangled polymer melts.\(^{8,18} \)

Figure 1 illustrates the relaxation after deformation at fixed simulation box geometry for two typical chains. After fast initial

short-range relaxation further relaxation is delayed by entanglement effects. This is the process we analyze in detail.

Strecthing the simulation box results in characteristic normal stress differences (see Figure 2a), related to the stress relaxation modulus \( G(\lambda, t) \), given by\(^{35} \)

\[
G(\lambda, t) = \sigma_{\text{norm}}(\lambda, t) / (\lambda^{2} - 1 / \lambda)
\]

(1)

where \( \sigma_{\text{norm}}(\lambda, t) = \sigma_{xx} - \frac{1}{2}(\sigma_{yy} + \sigma_{zz}) \) is the normal stress difference. Figure 2b shows results for the stress relaxation in differently strained samples. For a small (but fast) deformation the time dependent modulus \( G(\lambda, t) \) relaxes toward the plateau

modulus\(^{6,7} \)

\[
G_{0}^{\text{eff}} = \frac{4}{5} k_{B} T / N_{c}
\]

for \( \tau_{c} \ll t \ll \tau_{d} \), as predicted by reptation theory in excellent quantitative agreement with the prediction of the primitive path analysis (PPA).\(^{10,11,36} \)

For the highly, but slowly, elongated sample, stress relaxation already starts at a value lower than the unperturbed plateau (a signature of the Mullins effect\(^{24,4} \)) and then decays further after about a time corresponding to the inverse strain rate. This large time decay of \( G(t) \) seems independent of the initial strain rate. Systems strained very fast, even compared to \( \tau_{c}^{-1} (\dot{\varepsilon}_{e} = 6.3) \), follow the same softening pattern once the time reaches the inverse strain rate of the slower deformation. This indicates that crucial chain chain interpenetration did not change significantly during the slow stretching process, that is, topological constraints are not released up to some chain end effects. For different chain sizes \( N \) and strain rates, see the SI.

For unperturbed polymer melts, entanglements and the tube backbone can be investigated through PPA\(^{10,11,30} \) and related methods.\(^{36,38-39} \)

Both the original polymer paths (OPs) and their corresponding primitive paths (PPs) behave as ideal chains, the latter only above \( N_{c} \). Though the applicability of PPA to quantify the time-dependent moduli of highly deformed melts is not entirely clear, it provides very valuable information for conformational relaxation. For this we focus on the highly entangled polymer melt of \( n_{c} = 1000 \) chains of size \( N = 2000 \).

For PPA, the chain-ends are fixed in space, all intrachain interactions up to the FENE bonds are switched off, while the interchain excluded volume is kept and the energy of the system is minimized. Finally, chains shrink to a sequence of straight pieces connected at (relatively sharp) kinks.\(^{10,11} \)

The length of the PP, \( L_{PP} = (N - 1) b_{PP} \) being the PP bond length, can be seen as the contour length of the tube. Considering the backbone of the tube, that is, the PP, in a dense mesh of entanglement constraints, it has to follow the local mesh deformation. In case of a perfectly affine deformation, this requires \( b_{PP,\text{str}} = b_{PP}(5 + 2 / \sqrt{5}) / 3 \approx 1.96 b_{PP} \approx 0.61 \sigma \) to accommodate for the increase in \( L_{PP} \) (see the SI), unlike the contour length of the original chain, which stays constant. We also compare two melts subject to very fast elongation (\( \dot{\varepsilon}_{e} = 6.3 \)), one with free chain ends and one where the chain ends are constrained to affinely follow the box deformation. We find \( L_{PP,\text{str}} \approx 0.57 \sigma \) (constrained) and \( 0.57 \sigma \) (free ends, both fast and slow deformation). Thus, the deformation rate, once significantly faster than \( \tau_{RN}^{-1} \), seems to have no significant effect on the tube length. Small deviations from affine deformation prediction do not originate from freely fluctuating ends.

Figure 1. Snapshots of conformational relaxation of two typical polymer chains of sizes \( N = 500 \) and 2000 after deformation vs time \( t \) in units of \( \tau_{c} \approx 22.66 \).\(^{31} \)

The initial state after deformation (\( t / \tau_{c} = 0 \)) is shown in light gray.

Figure 2. Diagonal terms of the normal stress tensor \( \sigma_{ii}(t) \) (a) and rescaled stress relaxation modulus \( G(\lambda, t) / G_{0}^{\text{eff}} \) (b) plotted as a function of the rescaled relaxation time \( t / \tau_{c} \) after uniaxial elongation. The corresponding stretch ratio \( \lambda \) and the strain rate \( \dot{\varepsilon} \) are shown as indicated.
To investigate the subsequent relaxation we concentrate on the PPs. Kinks in the PPs result from (at least) two chains linked with each other. We call them "entanglement points" (EPs), being aware of the fact that this is not a precise characterization of entanglements since it only captures a subset of the overall topological constraints. Figure 3a,b shows a typical example before and after deformation. It is important to stress that results qualitatively look the same for all chains, see also the SI, and that averages are always taken over the whole system. To identify EPs, we have chosen the sequence of absolute values of bond angles \( \theta_{j+5} \) between bonds \( b_j \) and \( b_{j+5} \) along the chain (see the SI). Figure 3 shows the primitive paths and \( \theta_{j+5} \) for the very same chain before (parts a and c) and after elongation (parts b and d). Before elongation we observe a high density of kinks equally distributed along the chain. Immediately after elongation, the number of kinks reduces, sharper kinks occur, and the distribution along the contour of the chains becomes inhomogeneous.

By construction, PPs provide detailed insight into the forces along the primitive path. The intramolecular tension forces of the corresponding PPs along the stretching direction are given by

\[
F^{(PP)}_{i\parallel} = F^{(PP)}_{j} \cdot \lambda
\]

for \( j = 2, 3, ..., N \), where only \( F^{(PP)}_{FENE} \) is to be considered. Figure 3c,d shows \( F^{(PP)}_{\parallel} \) on top of the bond angles along the chain. As expected for a chain in an equilibrium melt, many sign switches due to the \( O(N = 2000/N_e \approx 72) \) entanglement points (Figure 3c) are observed. The correlation between bond angle and sign switch is even more pronounced for the stretched sample (Figure 3d), however, with a striking difference. The projected force stays constant for extended stretches (about 10\( N_e \) and more!) along the chain, that is, EPs do not affinely follow the rather slow deformation of the sample, while the overall shape of the chains does.

To extend on this, we use the PPA to shed light onto the subsequent relaxation process and its relation to the strain softening in Figure 2. Keeping the elongated simulation box fixed, we allow for chain relaxation to up to \( 2649 \tau_e \approx 0.52 \tau_R \) of equilibrium chains. Note that the density of topological constraints upon affine deformation measured along the chain contour, up to fluctuating end effects, remains constant. Based on the tube picture, the force pattern is expected to slowly relax from a scheme shown in Figure 3d back to the one similar to Figure 3c, that is, the chains first relax along the backbone of the tube, without affecting the overall tube conformation significantly.

Figure 3. Snapshot of PP of one particular chain of size \( N = 2000 \) in a melt before (a) and immediately after (b) elongation by a factor of \( \lambda = 5 \). (c, d) Estimates of the bond angle \( \theta_{j+5} \) plotted against \( j \) with \( j = 2, 3, ..., N - 5 \) along the PP (red dashed curve) of the same chain as in (a) and (b), respectively. In (c) and (d), the actual projection of the tension force \( F^{(PP)}_{\parallel} [\varepsilon/\sigma] \) with \( j = 2, 3, ..., N \) along the PP is shown by a bold black curve for comparison.

Figure 4. (a) Comparison of \( F^{(PP)}_{\parallel} = F^{(PP)}_{FENE} [\varepsilon/\sigma] \) exerted on the \( j \)th bond to \( \theta_{j+5} \) along the PP. (b) Comparison of \( F^{(PP)}_{FENE} [\varepsilon/\sigma] \) to the three contributions along the OP, \( F^{(OP)}_{FENE} \), \( F^{(OP)}_{LJ} \) and \( F^{(OP)}_{BEND} \). Data are for the same selected chain as shown in Figure 3, but after relaxing the stretched systems for \( t/\tau_e = 2649 \).
This, however, is not at all the case. Instead of the expected gradual yield stress of the EP distribution the observed inhomogeneity of EPs amplifies (see Figure 4 for the same chain as shown in Figure 3). The lengths of the regions without force sign change grow, indicating a stabilization of the current situation with a significant clustering of kinks along the PP. The very same holds for the projected forces along the OP as well (see Figure 4b). PPA provides a good representation of the structure of elongated chains in a melt and of the stretching forces along their backbones. The linear relationship between these two quantities and results for other related cases can be found in the SI. This suggests that large, less entangled regions of the chains stabilize regions of high density of EPs, similar as knotted polymers, where entropic forces tend to pull knots tight.40

There are several competing mechanisms affecting the relaxation process. Under the simplifying assumption of affine deformation, the tube would be extended along the x axis and compressed along the y and z axes. Besides the increase of the PP bond length b_{PP}, this simultaneously leads to an increase in the average Kuhn length of the PP to \( l_{K,\text{str}} = l_K (\lambda^2 + (2/\lambda))/(\lambda + (2/\sqrt{\lambda})) \approx 4.3 l_K \) (see the SI). Although topological constraints along the chain remain, the local rearrangement along the tube allows relaxation below distances of \( O(100) \) monomers along the chains, as internal distance analysis reveals and in agreement with the deformation rate. Thus, one could expect initial density fluctuations of EPs along the chain on that scale. This would be roughly in accord with the work of Rubinstein et al.15,16 At this stretching ratio, one would expect additional chain contour length stored in the tube segment parallel to the x axis to be around 2.3, close to \( \sqrt{\lambda} \). Although developed for networks, we expect this concept to hold for long chains and intermediate times as well. This would “dilute” EPs by a factor of \( \sqrt{\lambda} \) in stretches parallel to the elongation. Here, however, we find a stronger effect, which even increases with relaxation.

Entanglement effects should become relevant at \( t \approx \tau_{\text{rel}} \) and monomers are restricted to move along the contour of an imaginary tube of diameter \( d_t \). In view of this, it is interesting to estimate the number of monomers \( N_{\text{tube}} \) located inside the tube of original diameter itself. For details of the way of estimating \( N_{\text{tube}} \) see the SI. The probability distributions \( P(N_{\text{tube}}/N) \) in a melt before and at several selected times after deformation are shown in Figure 5a.

\[ P(N_{\text{tube}}/N) \text{ nicely fitted by a shifted Gaussian distribution in terms of the mean value } \langle N_{\text{tube}} \rangle / N \text{ over all chains, and the standard deviation } \sigma(N_{\text{tube}}/N) \approx 0.065, \text{ both in equilibrium and nonequilibrium.} \]

Upon deformation, \( N_{\text{tube}} / N \) first strongly increases (almost twice the value of the unperturbed system) and then decreases and eventually, it even drops down below the equilibrium value for \( t/\tau_{\text{rel}} > 0.25 \) and reaches, as visible for \( N = 2000 \), a minimum, see Figure 5b. The relaxation back to the unperturbed tube occupancy at least takes several Rouse times of the chains (data for \( N = 1000 \)). This agrees with the formation and growth of topologically highly congested areas along the chains. Regions with less confined conformational fluctuations, that is, low density of EPs, seem to stabilize regions with a higher density of EPs, leading to an overall delayed relaxation along the contour. The corresponding distribution of lengths of primitive path segments raises questions about the rheological inhomogeneity of these deformed melts and needs a more thorough investigation. Of course, for equilibrium polymer melts, \( \langle N_{\text{tube}} \rangle / N \approx 0.35(2) \) is independent of time, see Figure 5b.

In summary, we applied PPA10,11,30 to strongly deformed polymer systems. Pronounced deviations of stress relaxation and entanglement point distribution compared to unperturbed melts in the linear viscoelastic regime are observed. PP segment lengths, forces along the stretching direction as well as the average number of monomers inside the tube indicate significantly delayed equilibration processes, which are not described by current theoretical concepts.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.7b00808.

The simulation model, deformation mechanism, size and strain rate-dependent stress relaxation modulus, comparison/correlation between the tension force and the curvature along the PP, affine deformation of PPs, and way of counting monomers inside a tube-like regime (PDF).

**AUTHOR INFORMATION**

Corresponding Authors

*E-mail: hsu@mpip-mainz.mpg.de.
*E-mail: kremer@mpip-mainz.mpg.de.

ORCID

Kurt Kremer: 0000-0003-1842-9369

Notes

The authors declare no competing financial interest.
\section{ACKNOWLEDGMENTS}

We are grateful to M. Doi, G. S. Grest, D. Vlassopoulos, T. Ohkuma and K. Ch. Daoulas for stimulating and helpful discussions, and A. C. Fogarty and B. Dünweg for a critical reading of the manuscript. This work has been supported by European Research Council under the European Union’s Seventh Framework Programme (FP7/2007-2013)/ERC Grant Agreement No. 340906-MOLPROCOMP. We also gratefully acknowledge the computing time granted by the John von Neumann Institute for Computing (NIC) and provided on the supercomputer JUROPA at Julich Supercomputing Centre (JSC), and the Max Planck Computing and Data Facility (MPCDF).

\section{REFERENCES}

(1) Payne, A. The dynamic properties of carbon black-loaded natural rubber vulcanizates Part I. J. Appl. Polym. Sci. 1962, 6, 57.

(2) Mullins, L. Softening of rubber by deformation. Rubber Chem. Technol. 1969, 42, 339.

(3) Hentschke, R. The Payne effect revisited. eXpress Polym. Lett. 2017, 11, 278−292.

(4) Dian, J.; Fayolle, B.; Gilormini, P. A review on the Mullins effect. Eur. Polym. J. 2009, 45, 601.

(5) Graessley, W. W. Polymeric Liquids and Networks: Structure and Properties; Garland Science: London and New York, 2008.

(6) de Gennes, P. G. Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, NY, 1979.

(7) Doi, M.; Edwards, S. The Theory of Polymer Dynamics; Oxford University Press: New York, 1986.

(8) McLeish, T. C. B. Tube theory of entangled polymer dynamics. Adv. Polym. Sci. 2002, 159, 1379−1527.

(9) McLeish, T. C. B. Present puzzles of entangled polymers. Rheology Reviews 2003, 197−233.

(10) Everaers, R.; Sukumaran, S. K.; Grest, G. S.; Svaneborg, C.; Sivasubramanian, A.; Kremer, K. Rheology and microscopic topology of entangled polymeric liquids. Science 2004, 303, 823.

(11) Sukumaran, S. K.; Grest, G. S.; Kremer, K.; Everaers, R. Identifying the primitive path mesh in entangled polymer liquids. J. Polym. Sci., Part B: Polym. Phys. 2005, 43, 917.

(12)Padding, J. T.; Briels, W. J. Systematic coarse-graining of the dynamics of entangled polymer melts: the road from chemistry to rheology. J. Phys.: Condens. Matter 2011, 23, 233101.

(13) Qin, J.; Milner, S. T.; Stephanou, P. S. Stephanou Effects of tube persistene length on dynamics of mildly entangled polymers. J. Rheol. 2012, 56, 707−723.

(14) Larson, R. G.; Wang, Z. In The Oxford Handbook of Soft Condensed Matter; Terentjev, E. M., Weitz, D. A., Eds.; Oxford University Press: Oxford, 2015; Chapter 6, pp 233−269.

(15) Rubinstein, M.; Panyukov, S. Nonaffine deformation and elasticity of polymer networks. Macromolecules 1997, 30, 8036−8044.

(16) Rubinstein, M.; Panyukov, S. Elasticity of polymer networks. Macromolecules 2002, 35, 6670−6686.

(17) Cates, M. E.; McLeish, T. C. B.; Marrucci, G. The rheology of entangled polymers at very High shear rates. EPL 1993, 21, 451.

(18) Graham, R. S.; Likhtman, A. E.; McLeish, T. C. B.; Milner, S. T. Microscopic theory of linear, entangled polymer chains under rapid deformation including chain stretch and convective constraint release. J. Rheol. 2003, 47, 1171−1200.

(19) Likhtman, A. E.; Sukumaran, S. K.; Ramirez, J. Linear viscoelasticity from molecular dynamics simulation of entangled polymers. Macromolecules 2007, 40, 6745−6757.

(20) Likhtman, A. E. Whitther tube theory: From believing to measuring. J. Non-Newtonian Fluid Mech. 2009, 157, 158−161.

(21) Nielsen, J. K.; Hassager, O.; Rasmussen, H. K.; McKinley, G. H. Observing the chain stretch transition in a highly entangled polyisoprene melt using transient extensional rheometry. J. Rheol. 2009, 53, 1327.