

# STRUCTURAL, CONFORMATIONAL, DYNAMIC AND TOPOLOGICAL PROPERTIES OF RING POLY(ETHYLENE OXIDE) MELTS FROM MOLECULAR DYNAMICS SIMULATIONS AND COMPARISON WITH EXPERIMENTAL DATA

Dimitris G. Tsalikis<sup>1</sup>, Thanasis Koukoulas<sup>1</sup>, Vlasis G. Mavrantzas<sup>1,2</sup> and D. Vlassopoulos<sup>3,4</sup>

<sup>1</sup>Department of Chemical Engineering,

University of Patras,

Patras, GR – 26504, Greece

e-mail: tsaliki@chemeng.upatras.gr

<sup>2</sup>Department of Materials,

ETH Zurich,

Zürich, CH-8093, Switzerland

e-mail: vlasis@chemeng.upatras.gr

<sup>4</sup>Department of Material Science and Technology,

University of Crete,

Heraklion, GR – 71003, Greece

<sup>3</sup>IESL-FORTH,

ETH Zurich,

Heraklion, GR – 71010, Greece

e-mail: dvllasso@iesl.forth.gr

**Keywords:** Ring polymers, molecular dynamics, rheology.

**Abstract:** *We present results for the equilibrium conformational and dynamic properties of pure monodisperse ring poly(ethylene oxide) melts and their blends with linear analogues from detailed molecular dynamics simulations. We modified the chain length, corresponding to molecular weights ranging from 5000 to 20000 g/mol, allowing us to study the dependence of these properties on the molecular length. The resulting atomistic trajectories were subject to a topological reduction to ensembles of primitive paths and a detailed geometric analysis using vector calculus, which reveals considerable cyclic threading by the linear chains.*

## 1 INTRODUCTION

Ring polymers are an interesting class of polymers, as they lack free ends and represent the simplest structure in which the mechanism of reptation seems to be inapplicable. To understand, in particular, the rheological behavior of ring polymer closed-loop, one should study the well-understood architectures of linear and branched ones. A major contribution to our knowledge here was made by Pierre-Gilles de Gennes,[1] who introduced the concept of “reptation” and later refined by S. F. Edwards, and M. Doi.[2] The reptation theory was founded in order to interpret the dynamical properties of entangled polymer chains with free ends. The reptation theory expanded later by many researchers to include more complex molecular architectures such as the branched polymers.[3-5] Experimental and theoretical research in the past years enhanced our knowledge about the rheological behavior of linear and branched polymers in high molecular weight in the melt. Still one polymer architecture is not yet fully understood. This is the enigmatic case of ring polymers which chains have no free

ends and cannot “reptate” as the tube model predicts. Much experimental effort has been devoted in order to understand the dynamics and rheological properties of ring melts in the past years.[5-10] Also early experimental results in dilute solutions of long ring molecules and in melts of small molecules viscosity measurements showed a generally agreement with the predictions provided from Rouse[11] and Zimm[12] and theories but there were a certain amount of measurements which gave inconsistent results most likely because the samples were contaminated with linear chains.[8-10] An important finding from Kapnistos et al.[10] is that even a trace amount of linear chains inside a melt are capable of changing the dynamics and viscoelasticity. Newest methods of purifying the samples from linear contamination have been introduced but even these methods do not guarantee the best approach.

Computer simulations on the other hand seem to fit perfectly in this challenging task since they provide a clean solution avoiding side effects as polydispersity, concatenation and self-knotting. Halverson et al.[13,14] using both equilibrium and nonequilibrium molecular dynamics (MD) simulations with a coarse grained bead-spring model studied the structure, dynamics, and rheology of ring-linear polymer blends. Linear contaminants were found to increase the zero-shear viscosity of the ring melt by about 10% around one fifth of the corresponding overlap concentration. Tsolou et al.[15] employed atomistic simulations for linear and ring polyethylene systems with lengths ranging from C24 to C400. They present simulation results for a variety of rheological properties of these systems, and their variation with chain length together with a thorough analysis of Rouse model for the ring polymers. The predictions of Rouse model are also exhibit and compared with the properties extracted from the simulation. In more a recent study[16] full atomistic MD simulations with a short ring poly(ethylene oxide) (PEO) melt were found to yield results fully consistent with a neutron spin echo spectroscopy (NSE), confirming the faster diffusion of the centers-of-mass of these molecules in comparison to the linear polymer. In some sense, the work here extends that of Ref. [16] by addressing PEO ring conformation and dynamics in systems of chain length significantly higher than the entanglement molecular weight ( $N_e \approx 2000$  g/mol)

## 2 SIMULATION METHODS

The ring PEO chains considered in our simulations are represented by the formula  $-\text{CH}_2-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_2-$  while the linear analogues by the formula  $\text{CH}_3-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_3$ , with  $n$  in both cases denoting the number of monomers per chain (the same for both species). Four different chain sizes were considered characterized by  $n = 40, 113, 226, 452$  respectively (implying strictly monodisperse melts). The corresponding molecular weights (they differ slightly between ring and linear molecules) were equal to 5018 g/mole, 10044 g/mole and 20088 g/mole and we will refer to them as the PEO-5000, PEO-10000 and PEO-20000 systems, respectively.

We conducted our MD simulations with GROMACS,[17] using the modified TrAPPE united-atom (UA) force-field, proposed by Fischer et al.[18,19] for pure melts. The corresponding potential functions describing bond stretching, bond bending, torsional, Lennard-Jones and electrostatic interactions can be found elsewhere.[20] All runs were conducted in the isothermal-isobaric (NPT) statistical ensemble at temperature  $T = 413$  K and pressure  $P = 1$  atm.

## 3 RESULTS AND DISCUSSION

- A. Structural Properties.** The conformational properties of the simulated ring and linear PEO melts have been analyzed in terms of the mean-square chain radius of gyration  $\langle R_g^2 \rangle$  and the results are shown as a function of chain length  $N$  in Figure 1. A direct comparison shows that, for the same chain length, the average dimension of a ring polymer is always smaller than that of its linear counterpart, clearly pointing to a more compact overall structure of ring molecules compared to their linear analogues. This is best reflected in the values of the characteristic exponents quantifying the power-law dependence of  $\langle R_g^2 \rangle \sim N^\nu$  on chain length  $N$  for ring and linear PEO melt chains. We find that  $\langle R_g^2 \rangle \sim N^\nu$  with for rings  $\nu=0.86$  and with  $\nu=1.0$  (implying that  $\langle R_g^2 \rangle \sim N$ ) for linear melts (which is a direct manifestation of the Gaussian structure of the linear analogues). This behavior is consistent with simulation[13], [15], [21], [22] and experimental works.[23-25]. We have also computed the values of the mean-square chain end-to-end distance  $\langle R_{ee}^2 \rangle$  for the linear PEO melts and we have found that, for all systems, the results obey the random-coil relation, namely that  $\langle R_g^2 \rangle / \langle R_{ee}^2 \rangle$  for, to an excellent approximation.

- B. Dynamical Properties.** The self-diffusion behavior of the PEO rings is examined in Figure 2, which shows a typical plot of the mean-square displacement of the ring center-of-mass

$\phi_{\text{cm}}(t) = \langle (\mathbf{R}_{\text{cm}}(t) - \mathbf{R}_{\text{cm}}(0))^2 \rangle$  for the three different chain lengths (5k, 10k, 20k) as a function of time  $t$ . In the small-time regime, a non-Fickian, subdiffusive behavior is observed, where  $\phi_{\text{cm}}(t) \sim t^b$  with  $b=0.75$ , as has already been observed in other simulations, both with atomistic[17] and with coarse-grained models.[3] In the long-time regime, however, a linear dependence of  $\phi_{\text{cm}}(t)$  on  $t$  is indeed seen, and this permits the calculation of the self-diffusion coefficient  $D$  through the Einstein relation by the slope of the long

time behavior of the chain center of mass. The dependence of the extracted self-diffusion coefficients on chain length  $N$  is shown in Figure 3, together with experimental data.<sup>30</sup> The first point to notice about the data presented in Figure 3 is the very good agreement between simulation and experimental values for the self-diffusion coefficient  $D$ : For all PEO melts, the experimentally measured values are very close to the simulation results. The second point is the agreement of both the simulation data and the experimental measurements about the dependence of  $D$  on  $N$ . Both sets suggest that ring dynamics in PEO melts with molecular weight  $M_w$  is described quite accurately by a power law of the form  $D \propto N^{-1}$  for rings. This result is in agreement with simulation studies<sup>[26]</sup> and the theoretical predictions of Rubinstein et al.<sup>[27]</sup>

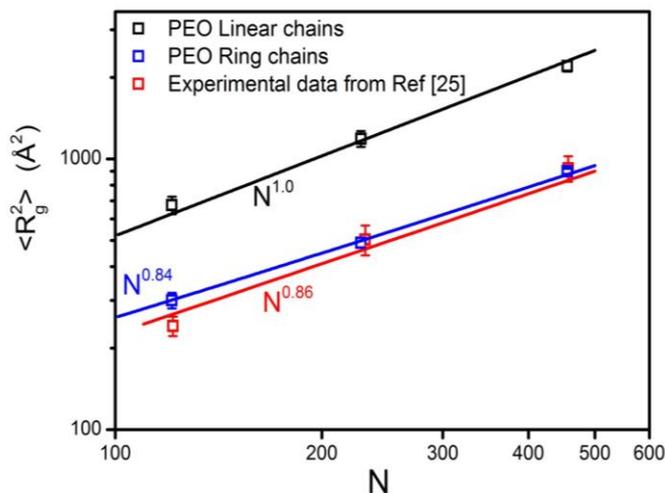


Figure 1. Dependence of the mean-square chain radius-of-gyration  $\langle R_g^2 \rangle$  on chain length  $N$  as obtained from the present MD simulations for ring ( $\square$ ) and linear ( $\square$ ) PEO melts, together with experimental data ( $\square$ ) for the rings from SANS measurements. The scaling of  $\langle R_g^2 \rangle$  with  $N$  for the two types of melts (ring versus linear) is also indicated.

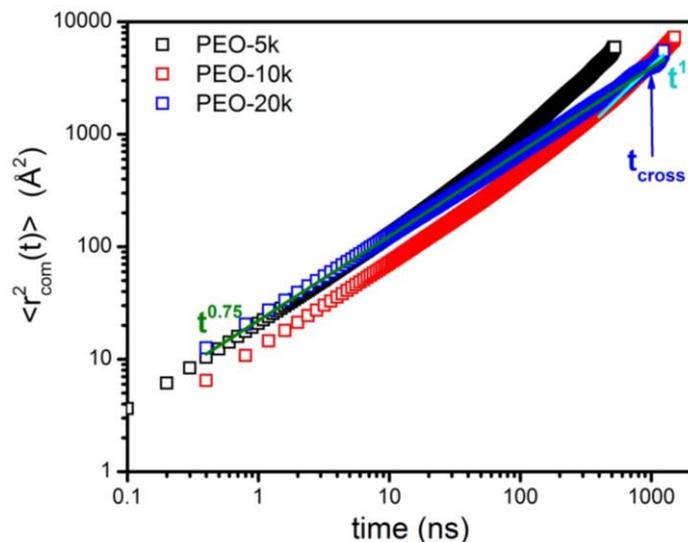


Figure 2. MD simulation predictions for the mean-square displacement of the chain center-of-mass  $\langle r_{\text{com}}^2(t) \rangle$  as a function of time  $t$  in a log-log plot, for all (ring and linear) PEO chain lengths studied in the present work (5k, 10k, 20k). Also shown in the figure is the scaling of  $\langle r_{\text{com}}^2(t) \rangle$  with  $t$  in the sub-diffusive and Fickian regimes. The self-diffusion coefficient is extracted from the Einstein regime in the long time regime (slope equal to 1).

**C. Topological Analysis.** The resulting atomistic trajectories were subject to a detailed topological analysis using vector calculus<sup>26</sup> which revealed significant threading of a ring molecule by

neighboring rings. In fact, in many cases, these threading events were of multiple origins, meaning that more than one ring simultaneously passed through a reference ring. A typical snapshot indicating multi-threading events between ring chains is presented in Figure 4

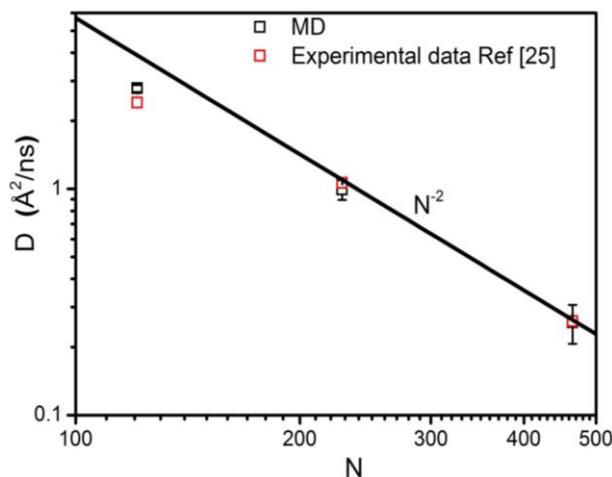


Figure 3. Predicted ( $\square$ ) and experimental ( $\square$ ) self-diffusion coefficients versus chain length  $N$  in a log-log plot, for the simulated ring and linear PEO melts. The scaling of  $D$  with  $N$  is also shown.

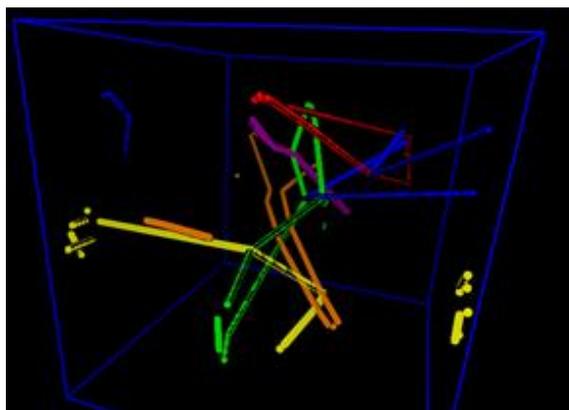


Figure 4. Typical snapshot from the topological analysis with the PEO-10k melt indicating an occasion of a multi-threading event: here, a reference ring molecule (green chain) is simultaneously penetrated by two neighboring rings (orange and purple chain) and at the same time it penetrates into two other ring molecules (yellow and blue chains).

Our topological analysis was further employed to blends of ring chains with their linear analogues (modifying the linear contamination  $w_L$  from 0 up to 0.75) to investigate the molecular mechanisms associated with the slow dynamics in the blends. From a dynamical point of view, of paramount importance is information not only about the number and distribution of threading points but also about their characteristic (persistence) time scales. In the absence of linear chains, the longest relaxation time  $\tau_R$  in a cyclic PEO melt is determined either by the time associated with center-of-mass diffusion or by the time it takes the unit vector directed along a ring diameter vector to decorrelate. In a ring-linear melt, however, where strong topological interactions prevail, the longest characteristic time will be determined by those threading events that have the longest persistence time. To quantify these, we monitored the displacement of all ring-linear intersection points along the contour of the linear chain involved in the threading, from birth to death. The results (in units of  $\tau_R$ ) for the PEO-10k blends are reported in Figure 4 and reveal a surprisingly broad distribution, especially as the contamination in linear chain increases. For example, when  $w_L = 0.25$  (25% of the total chains are linear), Figure 5 suggests threadings that remain active for as long as  $5\times$  the relaxation time  $\tau_R$  of pure rings. But when  $w_L = 0.50$ , we observe threadings that remain active for times up to  $15\times$  the pure ring relaxation time

$\tau_R$ . We further examined how the presence of even a tiny amount (2%) of linear chains affects the topological interactions between ring molecules. In Figure 6 we can see that the distribution of survival times for ring-ring entanglements significantly increases. The existence of a significant number of threading events with exceptionally long lifetimes has dramatic consequences for the dynamics of ring molecules in the blend.

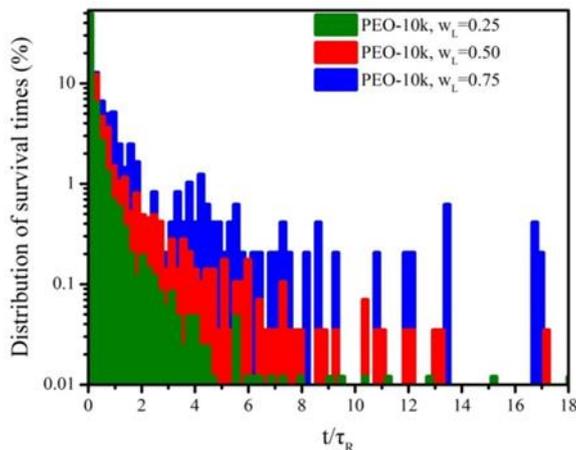


Figure 5. Distribution of the lifetimes of ring-linear threading events (penetrations) in the PEO-10k blend, as a function of  $w_L$ .

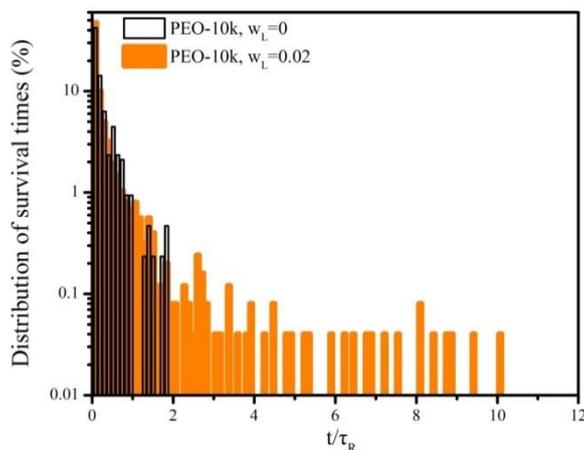


Figure 6. Distribution of the lifetimes of ring-ring threading events (penetrations) in the PEO-10k blend, for pure ring melts and for blends contaminated 2% in linear chains.

#### 4 CONCLUSIONS

We have embarked on a new project aiming at a thorough analysis of the structural, dynamical, and viscoelastic properties of entangled melts of PEO rings through large-scale atomistic MD simulations for systems ranging in MW from 5,000 g/mol up to 20,000 g/mol. Consistent with previous works, our results for the radius of gyration have demonstrated the more compact structure of ring chains in their molten state compared to linear melts of the same chemical composition and length. Additional simulation predictions for the dynamical properties analyzed here in terms of the chain center-of-mass self-diffusion coefficient  $D$  reveal that rings chains are more mobile than linear chains in their own melt. We also studied inter-ring threading and its effect on the dynamics of the melt and in their blends with linear analogues. We find that the presence of linear chains (even in small amounts) can dramatically influence the underlying topological structure of the blend, since it gives rise to strong and long-lived topological interactions (which though leave the conformational properties of the melt practically unaffected). Overall, threading of ring chains by linear molecules causes a dramatic reduction in the diffusivity and orientational relaxation of rings rendering the system's overall dynamics highly heterogeneous.

#### ACKNOWLEDGEMENTS

We acknowledge the LIMMAT foundation via the Project MUSICOMPS for funding this research study. We

are grateful to PRACE for the allocation of significant CPU time through their SEGED machine in NIIF, Hungary.

## REFERENCES

- [1] P. G. De Gennes, *J. Chem. Phys.* 55, 572 (1971).
- [2] M. Doi, S. F. Edwards, *The Theory of Polymer Dynamics*. (Clarendon Press, 1986).
- [3] M. Rubinstein, R. Colby, *Polymer Physics*. (Oxford Univ. Press, 2003).
- [4] P. G. De Gennes, *J. Phys. France* 36, 1199 (1975).
- [5] M. Doi and N. B. Kuzuu, *J. Pol. Sci.* 18, 775 (1980).
- [6] J. Roovers, *Macromolecules* 18, 1359 (1985).
- [7] Y.Y. Chien and W.T. Winter, 18, 1357 (1985).
- [8] P. J. Mills, J. W. Mayer, E. J. Kramer, G. Hadziioannou, P. Lutz, C. Strazielle, P. Rempp and A. J. Kovacs, *Macromolecules* 20, 513 (1987).
- [9] J. Roovers, *Macromolecules* 21, 1517–1521 (1988).
- [10] M. Kapnistos, M. Lang, D. Vlassopoulos, W. Pyckhout-Hintzen, D. Richter, D. Cho, T. Chang, and M. Rubinstein, *Nature Mater.* 7, 997 (2008). [11] P. E. Rouse, *J. Chem. Phys.* 21, 1272 (1953)
- [12] B. H. Zimm, *J. Chem. Phys.* 24, 269 (1956).
- [13] J. D. Halverson, W. B. Lee, G. S. Grest, A. Y. Grosberg, and K. Kremer, *J. Chem. Phys.* 134, 204905 (2011).
- [14] J. D. Halverson, G. S. Grest, A. Y. Grosberg, and K. Kremer, *Phys. Rev. Lett.* 108, 038301 (2012).
- [15] G. Tsolou, N. Stratikis, C. Baig, P. S. Stephanou, and V. G. Mavrantzas, *Macromolecules* 43, 106952 (2010).
- [16] A. R. Brás, R. Pasquino, T. Koukoulas, G. Tsolou, O. Holderer, A. Radulescu, J. Allgaier, V. G. Mavrantzas, W. Pyckhout-Hintzen, A. Wischniewski, D. Vlassopoulos, and D. Richter, *Soft Matter* 7, 11169 (2011). [17] D. Van Der Spoel, et al. *J. Comp. Chem.* 26, 1701–18 (2005).
- [18] J. Fischer, D. Paschek, A. Geiger and G. Sadowski, *J. Phys. Chem. B* 112, 2388 (2008).
- [19] J. Fischer, D. Paschek, A. Geiger and G. Sadowski, *J. Phys. Chem. B* 112 (2008).
- [20] D. G. Tsalikis, T. Koukoulas and V. G. Mavrantzas, *React. Funct. Polym.* 80, 61 (2014).
- [21] R. Ozisiki, E. D. von Meerwall and W. L. Mattice, *Polymer* 43, 629 (2002).
- [22] E. von Meerwall, R. Ozisik, W. L. Mattice and P. M. Pfister, *J. Chem. Phys.* 118, 3867 (2003).
- [23] V. Arrighi, S. Gagliardi, A. C. Dagger, J. A. Semlyen, J. S. Higgins, and M. J. Shenton, *Macromolecules* 37, 8057 (2004).
- [24] A. Takano, Y. Kushida, Y. Ohta, K. Masuoka, and Y. Matsushita, *Polymer* 50, 1300 (2009).
- [25] S. Gooßen, A. R. Brás, M. Krutyeva, M. Sharp, P. Falus, A. Feoktystov, U. Gasser, W. Pyckhout-Hintzen, A. Wischniewski and D. Richter, *Phys. Rev. Lett.* 113, 168302 (2014).
- [26] K. Hur, R. G. Winkler, and D. Y. Yoon, *Macromolecules* 39, 3975 (2006).
- [27] S. P. Obukhov, M. Rubinstein, and T. Duke, *Phys. Rev. Lett.* 73, 1263 (1994).
- [28] D. G. Tsalikis and V. G. Mavrantzas, *ACS Macro Lett.* 3, 763 (2014).