

Threading of Ring Poly(ethylene oxide) Molecules by Linear Chains in the Melt

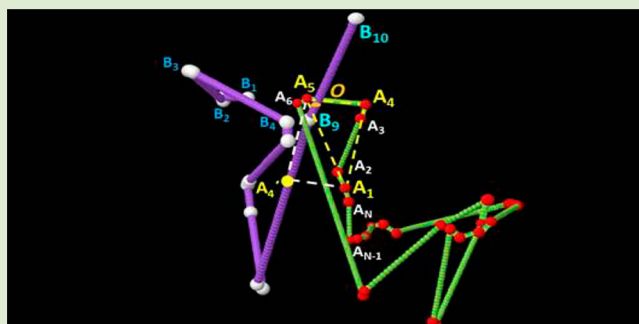
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S Supporting Information

ABSTRACT: We report results from an atomistic molecular dynamics simulation study of ring-linear poly(ethylene oxide) (PEO) melts followed by 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. The simulations have been conducted using ring-linear PEO blends of the same size, over a series of molecular lengths and compositions. For PEO melts characterized by molecular weight (MW) greater than 10044 g/mol, in particular, our computations reveal the occurrence of multiple threading events (penetrations). We further find that the time it takes a linear molecule that threads a cyclic one to fully pass through the latter can be more than 1 order of magnitude larger than the corresponding relaxation time of the ring in its own melt. Our analysis implies that dynamics in ring-linear polymer blends is highly heterogeneous, with many of the threadings being long-lived and with the linear chains (even when present in small amounts) dramatically obstructing the mobility of rings.



Today, there exists convincing experimental and computational evidence that even present in such tiny fractions as 0.1%, linear chain contaminants can have a dramatic influence on the relaxation, dynamics, and rheology of ring polymer melts.^{1–5} As for example has been noted by Kapnistos et al.¹ on the basis of rheological measurements with ring polystyrene samples, linear chains (even when present in such small concentrations as 50× below the overlap concentration) are “bridged” with rings to form a long-lived percolating network throughout the system, thereby totally altering its viscoelastic properties. For example, instead of a power law behavior in the stress relaxation modulus $G(t)$ at intermediate times, an entanglement plateau appears. Halverson et al.³ have discussed the sensitivity of a ring melt to linear contaminants by showing that the viscosity of a melt of bead–spring ring chains containing only 1.5% linear chains is already 1.4× larger than the pure ring melt value.

In this Letter we shed some light on this very important issue by presenting results from a detailed computational study of topological interactions in blends of ring-linear PEO chains with a focus on cyclic threading by linear molecules. Our study entails three main steps. First, detailed molecular dynamics (MD) simulations are performed in the $N_{ch}nPT$ statistical ensemble (N_{ch} denotes the total number of chains, n the number of ethylene oxide monomers per chain, P the pressure, and T the temperature) in a 3d-periodic box for very long times to get a large number of fully equilibrated atomistic configurations at the conditions of interest ($P = 1$ atm and T

= 413 K). Second, the accumulated trajectories are reduced to ensembles of primitive paths (PPs) by applying the so-called CReTA algorithm (Contour Reduction Topological Analysis)⁶ for the static analysis of uncrossability constraints in linear polymer systems. Third, we geometrically analyze the reduced ensemble of PPs to identify threading events between ring and linear molecules and compute their characteristic time scales.

All technical details regarding the preparation of the simulated systems, the force-field employed to carry out the runs, the MD simulations themselves and the reduction of atomistic trajectories to PPs (first and second steps of our methodology) can be found elsewhere.⁷ In this Letter we address the very important issue of ring threading by linear chains (third step). Very briefly, 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 $\text{CH}_3\text{-O}-(\text{CH}_2\text{-CH}_2\text{-O})_n\text{-CH}_3$. The ring component is denoted by R and the linear by L. Three series of systems were studied, corresponding to three different PEO chain lengths n (the same for ring and linear molecules), implying strictly monodisperse melts: $n = 40, 113,$ and 227 monomers per chain. The corresponding MWs (they differ slightly between R molecules and L chains) are 1806, 5022, and 10044 g/mol; we refer to them as PEO-2k, PEO-5k, and PEO-

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10k, respectively. To capture the dependence of threading on blend composition, for each one of these systems, several mixtures were studied corresponding to different values of the mass fraction w_L of the linear component L, from very small to very high. We also mention that, in order to render the CReTA algorithm⁶ applicable to ring molecules that possess no chain ends, we have considered each ring to be topologically equivalent to two linear subchains having exactly the same molecular length (half of the total ring) and sharing the same end points. In our work, these two subchains are topologically considered as two different (independent) chains in the course of CReTA, subject, however, to the constraint that their two ends should always coincide.⁷ At the end of CReTA, an atomistic configuration of a ring-linear PEO blend has been reduced to a configuration of PPs, namely, a network of successive straight strands with a kink in-between (see Figure 1 in the Supporting Information (SI)). For ring molecules, these PPs are closed loops, and for linear chains they are open loops.

By default, CReTA identifies all possible interchain topological constraints (kinks) in the system arising due to chain uncrossability (except self- or intrachain entanglements), irrespective of their origin (another ring or another linear chain). Thus, it provides no information about linear-ring interactions corresponding to threading events, that is, situations where a linear chain penetrates (threads) a ring molecule. Such threading events have been speculated in the literature¹ to significantly affect ring dynamics, even at low fractions of the linear content. This is because kinks (ring-linear topological constraints) as calculated directly from CReTA without any further analysis and threading events (ring-linear penetrations) as calculated from the present geometric analysis represent topological interactions with a different strength. Kinks that do not correspond to threading events will overall be characterized by short survival times (they will be short-lived constraints). In contrast, our geometric analysis in this Letter shows that most threading events are characterized by very long survival times which, in some cases, can be up to 1 order of magnitude higher than the characteristic ring orientational relaxation time in the pure ring melt. By pinning down several ring segments for long times, these linear-ring threadings can dramatically slow down the diffusive motion and relaxation of ring polymers.

Unfortunately, there exists no methodology today to identify and quantify linear-ring threading events. We address this issue in this Letter using ring triangulation and vector calculus as follows: At the level of the PP, a ring molecule is a closed chain of $N-1$ straight segments with successive segments sharing exactly one point while nonsuccessive ones having no intersection (see also, Figure 2 in the SI). A cyclic molecule (green chain in Figure 1) can therefore be regarded as a three-dimensional (3d) object having the shape of an irregular, solid polygon. Every such polygon spans a surface in 3d space which we approximate in this Letter by the sum of surfaces of all successive triangular edges making up the polygon. Linear molecules, on the other hand, can be represented (at the level of the PP consideration) as open sequences of successive straight segments defining what we call an entanglement strand. For example, in Figure 1, the linear molecule (in purple) is topologically represented by the sequence of the following $M-1$ segments: $B_1B_2, B_2B_3, \dots, B_{M-1}B_M$, where M denotes the number of kinks detected in the course of the contour reduction process. We determine then whether or not a cyclic molecule is threaded by a linear chain by geometrically checking if the

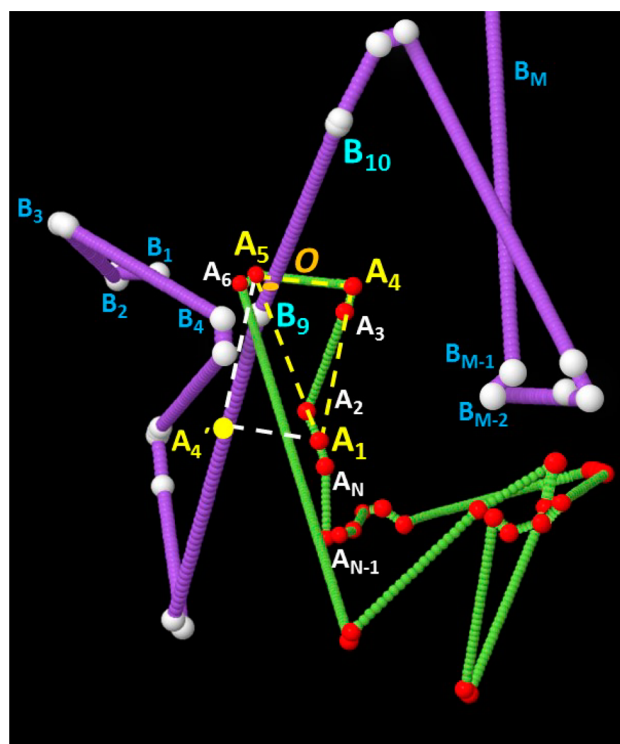


Figure 1. Representative snapshot from the geometric analysis of the PEO-10k blend, demonstrating the threading of a cyclic PEO molecule (sequence of green strands) from a linear one (sequence of purple strands). Red and white colors are used to indicate the beads of the corresponding ring and linear chain primitive paths, respectively.

sequence of straight segments $B_1B_2, B_2B_3, \dots, B_{M-1}B_M$ along the linear chain intersects the corresponding sequence of planar triangles (e.g., the series $A_1A_2A_3, A_2A_3A_4, \dots, A_{N-2}A_{N-1}A_N$ in Figure 1) spanning the surface of the 3d ring molecule.

This is a mathematically well-posed problem which can be addressed by vector calculus as follows: First (see Figure 1), we compute the point O where the straight line that passes through points B_9 and B_{10} intersects the plane spanned by vectors along A_1A_4 and A_4A_5 . And then we have to decide if the point O lies inside the triangle $A_1A_4A_5$. Given that point O lies on the same plane as points (A_1, A_4, A_5) , a very simple way is to check first if it lies inside the parallel-piped $A_1A_4A_5A'_4$ or not. If it lies outside it, then segment B_9B_{10} does not intersect the triangle $A_1A_4A_5$. If it lies inside the parallel-piped $A_1A_4A_5A'_4$ we further check if it lies on the left or right side of the segment A_1A_5 by comparing the angles A_4A_5O and $A_4A_5A'_4$. By repeating the calculations for all segments B_1B_2, B_2B_3, \dots making up linear chain molecule B_1B_M and for all triangles making up the surface of ring molecule $A_1A_2 \dots A_{N-1}A_N$ we can compute the number of intersections of the linear molecule with the surface spanned by the cyclic molecule (at the level of PPs) and thus decide if the cyclic molecule is threaded or not. Details of the mathematical formulation of the problem (in the form of 3d vector equations) and its geometric solution are provided in the SI file. We further clarify that in this Letter we focus only on threading events associated with linear-ring penetrations. Ring–ring intersections⁸ will be addressed by our method in a future study.

Our approach allows one not only to identify the number and distribution of threadings in the blend but also to compute their exact location along the contour of the linear chain. For

example, we can detect if the point where the linear molecule threads the cyclic is located near its ends or deeper along its contour or somewhere else along the chain. Through this we can further calculate the persistence time of the ring-linear constraint (i.e., the time the threading is active) and even more importantly if the linear molecule completely passes through the ring. We can also unambiguously identify and quantify the occurrence of multiple threading events: a ring molecule that is simultaneously threaded by more than one linear chains (we call this type-1 multiple threading) or a linear molecule that simultaneously threads more than one ring chains (we call this type-2 multiple threading).

Numerical results for the relationship between the percentage X of ring molecules that are threaded by linear chains and contamination of the melt in linear chains quantified through w_L are shown in Figure 2. For all simulated systems, the data indicate an increasing dependence of X on w_L .

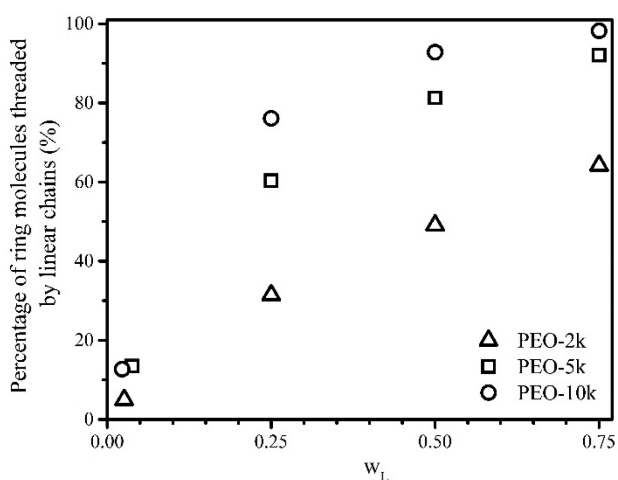


Figure 2. Percentage of ring PEO molecules threaded by linear chains as a function of w_L in the three PEO blends.

The occurrence of multiple threading events is analyzed in Figure 3: Part (a) of the figure shows the fraction of threaded ring molecules in the simulated PEO blends versus the number of linear chains that simultaneously thread them (type-1 threadings). Part (b) of the figure shows the fraction of linear chains that thread ring molecules as a function of the number of ring molecules that are simultaneously being threaded by them (type-2 threadings). Focusing first on Figure 3a, we observe that type-1 threadings become more and more pronounced (in the sense that the data extend to larger and larger values of threading linear chains along the horizontal axis) as the molecular mass of PEO increases. We also see that (for a given MW) the maximum number of linear chains that can simultaneously thread a ring molecule increases significantly with increasing w_L , but this seems to saturate in the PEO-10k melt. For example, the probability to observe a ring that is threaded by 5 linear chains in the blends with $w_L = 0.5$ increases from $\sim 0.15\%$ in PEO-2k to $\sim 4.5\%$ in PEO-5k to $\sim 10\%$ in PEO-10k. As a result, the probability that a ring chain is threaded by exactly one linear chain in the highest MW samples is very small (e.g., in the PEO-10k blend with $w_L = 0.75$, this probability is smaller than 10%), because the large majority of ring molecules in these blends are threaded by more than one chain. In contrast, the corresponding probability in the lower MW blends is higher since multiple threadings in these systems

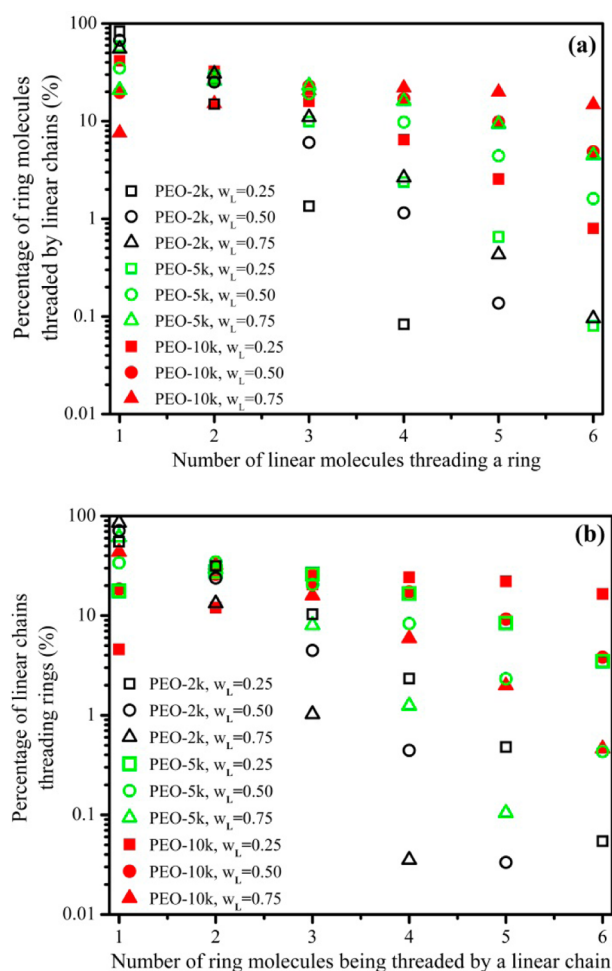


Figure 3. Distribution of type-1 (a) and type-2 (b) multiple threading events and dependence on chain length and linear content.

are less frequent (e.g., in the PEO-2k blend with $w_L = 0.25$ this is $\sim 84\%$). As far as type-2 threadings are concerned (see Figure 3b), we observe that these become more and more pronounced either with increasing chain length or with decreasing w_L . We also observe that, as the chain length increases, the probability for type-2 threadings becomes more uniform, in the sense that a linear chain can equally well thread simultaneously a small number but also a large number of rings. For example, in the PEO-10k blend, a linear chain can thread equally probably 2, 3, 4, 5, or 6 ring molecules.

A general rule of thumb implied by experimental findings is that a linear chain cannot thread more rings than its number of entanglements Z . To check this we calculated the average number of ring molecules threaded by a linear PEO chain (the entanglement molecular weight of linear PEO is $\sim 2k$). We found that this number is ~ 1.0 in the PEO-2k blends ($Z \sim 1$), ~ 2.2 in the PEO-5k blends ($Z \sim 2.5$), and ~ 4.6 in the PEO-10k blends ($Z \sim 5$). Our results therefore support the empirical rule of thumb.

Snapshots from our simulations showing situations of type-1 and type-2 multiple threading are shown in Figure 4 of the SI.

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 τ_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 O in Figure 1 along the contour of the linear chain involved in the threading, from birth to death. The results (in units of τ_R) for the PEO-10k blends are reported in Figure 4 and reveal a surprisingly

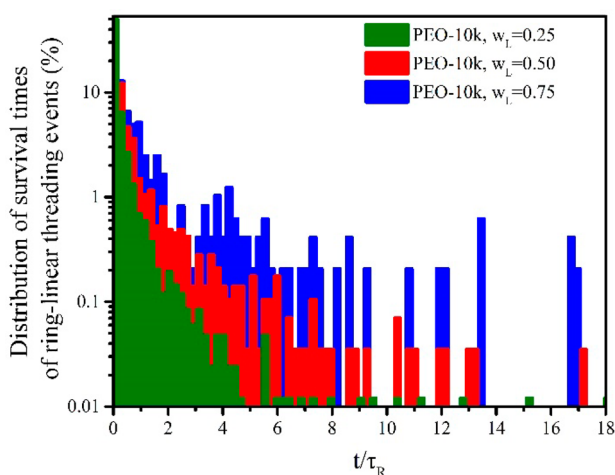


Figure 4. Distribution of the lifetimes of ring-linear threading events (penetrations) in the PEO-10k blend, as a function of w_L .

broad distribution, especially as the contamination in linear chain increases. For example, when $w_L = 0.25$, Figure 4 suggests threadings that remain active for as long as $5\times$ the relaxation time τ_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 τ_R .

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. This was confirmed by carrying out three more calculations: First, we computed the time needed for the orientational relaxation of the most threaded ring molecules in the PEO-10k blend. Second, we calculated the mean-square displacement of the chain center-of-mass of these strongly threaded rings. We found (results not shown here) that both of these relaxation processes (orientational and translational) are dramatically reduced compared to the average ring dynamics in the blend. Threading is so strong that the dynamics of certain rings is decelerated to such a degree that these appear as frozen on the time scale that their average population has relaxed, demonstrating the strong heterogeneous character of dynamics in ring-linear blends. Third, we calculated the percentage of threading events characterized by survival times longer than τ_R as a function of w_L . In all three PEO blends, this percentage was found to be important, even for the lowest possible linear content ($\sim 2\%$) that could be simulated. For example, for the PEO-10k melt with a 2% linear content (for which Figure 2 shows that $\sim 10\%$ of its ring molecules are threaded by linear chains), this percentage was computed to be $\sim 6\%$. Our atomistic simulation study, therefore, indicates that one needs to go to a very high purity of ring melts (above at least 98%) for these most

persistent penetrations to “go away” in the context of a rheological measurement.

In conclusion, we have carried out a detailed study of topological interactions in ring-linear PEO blends by reducing atomistic configurations accumulated in the course of detailed MD simulations to ensembles of PPs and subjecting them to a detailed geometric analysis to identify penetrations of ring molecules by linear molecules. 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.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional analytical details and computational results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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