Conformational dynamics and topological/geometric analysis of polymer ring melts through atomistic molecular-dynamics simulations and comparison with experimental data

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INTRODUCTION

- Due to the lack of chain ends, ring polymers present some unique structural, topological and rheological properties which are different from those of their linear counterparts:
  - $R_g \sim N^{\nu}$ with $1/3 < \nu < ½$.[1]
  - High MW rings diffuse faster.[2]
  - Rings exhibit lower zero-shear rate viscosity η_0.[3]
  - The shear relaxation modulus $G(t)$ of entangled ring polymers does not exhibit the stress plateau.[4]
- Experimental measurements[4] have shown that the rheological response of a polystyrene ring melt contaminated with linear chains differs significantly from that of the corresponding pure ring system.

OBJECTIVE-STRATEGY

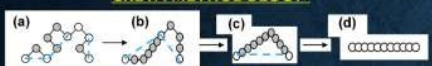
- Our simulation strategy entails three main steps:
  - Detailed, atomistic MD simulations of model, ring poly(ethylene oxide) melts in the NPT (P=1atm and T=413K)) ensemble in a 3d-periodic box for very long times (microseconds).
  - Reduction of the accumulated trajectories to ensembles of primitive paths (PPs) by applying the so called CReTA algorithm (Contour Reduction Topological Analysis).[5]
  - Detailed geometric analysis[6] of PPs to identify threading events between ring molecules and compute their characteristic time scales.

METHODOLOGY DETAILS

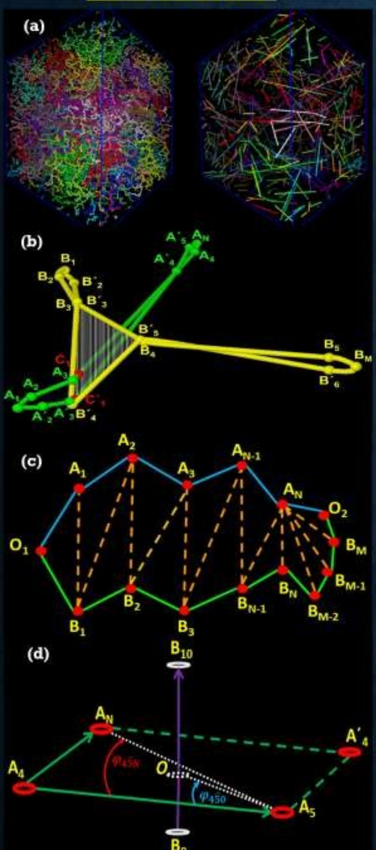
MODEL SYSTEM: PolyEthyle Oxide[7]

Melts		2k	5k	10k	20k
Atoms per chain		123	342	684	1368
Mw (g/mol)	ring	1806	5022	10044	20088

CRETA METHODOLOGY[5]



GEOMETRIC ANALYSIS[6]



RESULTS

ATOMISTIC SIMULATION OF PURE RING MELTS

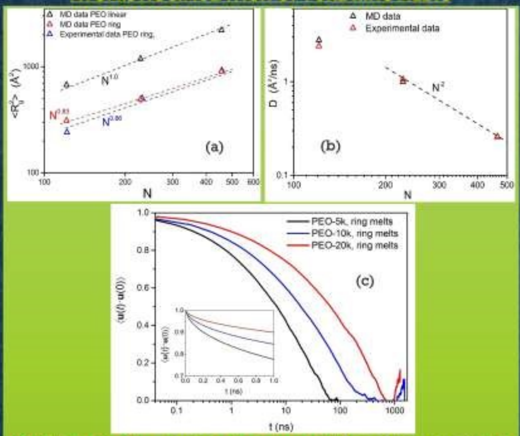


FIGURE 1: (a) $\langle R_g^2 \rangle$ versus chain length N from the present MD simulations and comparison with experimental data[8,9]. (b) Predicted and experimentally measured self-diffusion coefficients versus N. (c) Time decay of the ACF $\langle u(t) \cdot u(0) \rangle$ quantifying terminal relaxation.

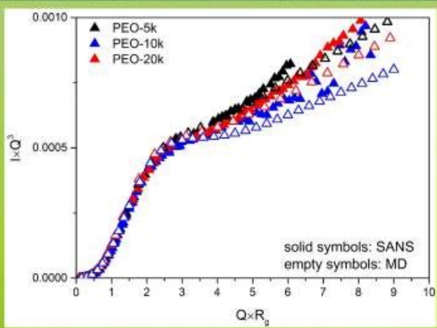


FIGURE 2: Direct comparison of SANS data[8,9] with our MD simulation predictions.

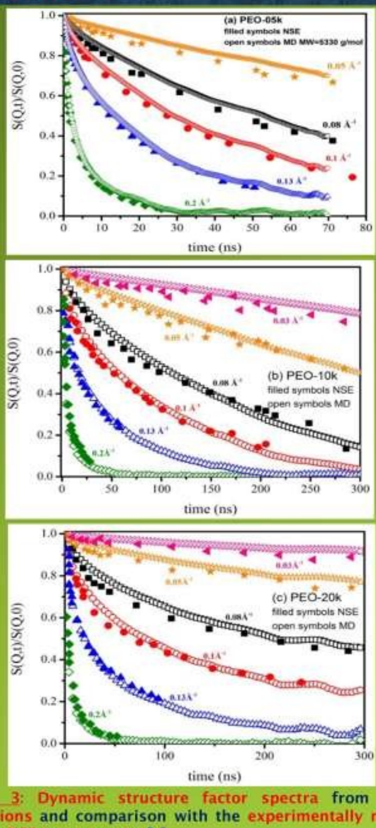


FIGURE 3: Dynamic structure factor spectra from the MD simulations and comparison with the experimentally measured ones by NSE spectroscopy.[8, 9]

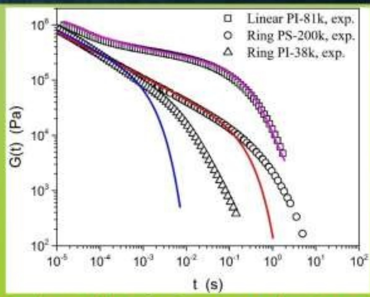


FIGURE 4: Experimental data for the stress relaxation modulus G(t) of linear and ring polyisoprene and polystyrene ring melts. Solid lines correspond to best fits with Eqs. (1) and (2) below.

Linear melts fits:
$$G(t)=G_N^0\left(\frac{\tau_e}{t}\right)^{\frac{1}{2}}+G_N^0\sum_{p:odd}\frac{8}{p^2\pi^2}\exp\left(-\left(\frac{p^2 t}{\tau_d}\right)^{\beta}\right) \quad \text{Eq. (1)}$$

Ring melts fits:
$$G(t)=G_N^0\left(\frac{t}{\tau_e}\right)^{-\frac{2}{5}}\exp\left(-\frac{t}{\tau_{Ring}}\right) \quad \text{Eq. (2)}$$

TOPOLOGICAL ANALYSIS OF PURE RING MELTS

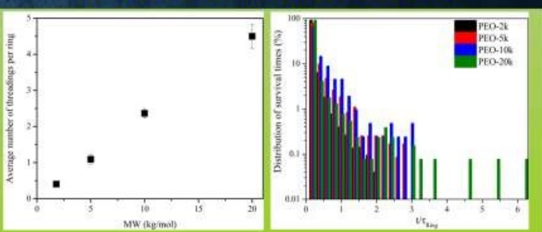


FIGURE 5: (a) Dependence of the average number of threadings per ring on N. Linear dependence agrees with a recent simulation study assuming fixed obstacles.[10] (b) Distribution of the corresponding survival times for ring-ring penetrations.

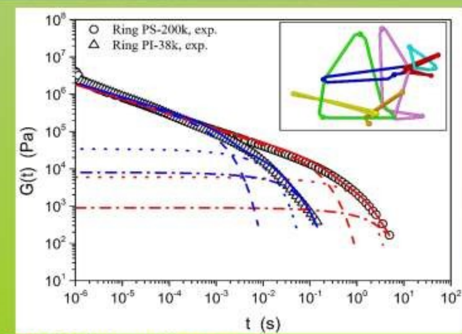


FIGURE 6: G(t) fittings with new eq. (3).

$$G(t)=G_N^0\left(\frac{t}{\tau_e}\right)^{-\frac{2}{5}}\exp\left(-\frac{t}{\tau_{Ring}}\right)+G_{N,RR}\sum_{p:odd}\frac{8}{p^2\pi^2}\exp\left(-\frac{p^2 t}{\tau_{d,RR}}\right)+ G_{N,RL}\sum_{p:odd}\frac{8}{p^2\pi^2}\exp\left(-\frac{p^2 t}{\tau_{d,RL}}\right) \quad \text{Eq. (3)}$$

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