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Coarse-grained simulations of the effects of chain length, solvent quality, and chemical defects on the solution-phase morphology of MEH-PPV conjugated polymers

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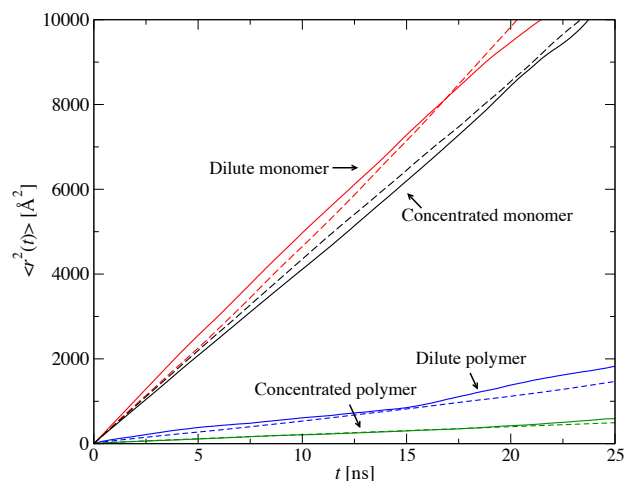


Figure 6: Mean-squared displacement (MSD) of atomistic (solid lines) and CG (dashed lines) monomers and decamers in THF at concentrations of 0.022 g/mL (dilute) and 0.252 g/mL (concentrated). The friction coefficient in the CG simulations was $\gamma = (95 \text{ fs})^{-1}$.

In any case, it was found that the choice of γ (for values up to 10 times larger) did not significantly affect the calculated structural probability distributions.

Impact of Solvent and Defects on Mesoscale Morphology

Figures 7 and 8 depict typical simulation configurations of MEH-PPV polymers with 300 and 1000 monomers, respectively, per chain for different defect concentrations and solvent conditions. For both chain lengths, the polymers have extended configurations in THF. In the simulation trajectories, chain segments were found to come together transiently in THF, but they inevitably came apart again. These results are consistent with experiments,^[4,10] which indicate that THF is a reasonable, but not very good, solvent for MEH-PPV at room temperature. The extended chain configurations in THF are qualitatively similar for chains with different defect concentrations, although kinks are evident at the positions of the saturation defects, where the chains have greater conformational flexibility. The difference between the chain configurations was quantified in terms of the radius of gyration R_g , which was calculated using

$$R_g^2 = \frac{1}{N_{\text{mon}}} \sum_{i=1}^{N_{\text{mon}}} |\mathbf{r}_i - \mathbf{r}_{\text{com}}|^2, \quad (2)$$

where \mathbf{r}_i and \mathbf{r}_{com} are the coordinates of monomer i and the polymer centre-of-mass, respectively. The root-mean-squared (RMS) radius of gyration, $\sqrt{R_g^2}$, decreases slightly with defect content for the 1000-monomer chains from 45 to 41 nm for 0 to 10% defects. The calculated radius of gyration of the 10%-defect polymers agrees with the measured hydrodynamic radius R_h of 29.5 nm for MEH-PPV chains with $N_{\text{mon}} = 1000$ in THF,^[20] using the relationship that $R_g/R_h \approx 1.3$ for linear monodisperse polymers in a θ -solvent.^[47]

In the poor solvent, the polymer chains aggregate into compact structures. For the shorter 300-monomer chains, the aggregated structures change qualitatively with defect

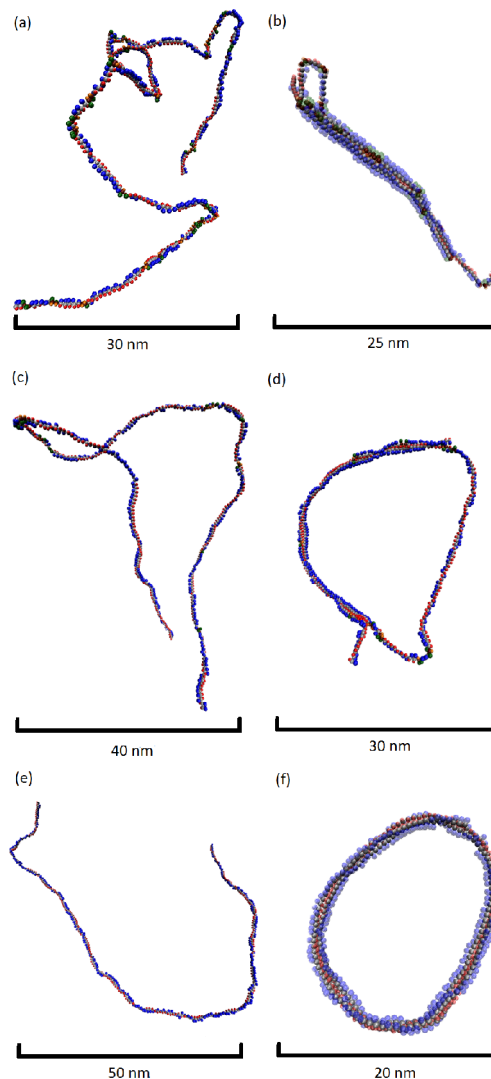


Figure 7: Snapshots of typical simulation configurations of CG polymers with $N_{\text{mon}} = 300$ for defect concentrations of (a) 10%, (c) 5%, and (e) 0% in THF and (b) 10%, (d) 5% and (f) 0% in the model poor solvent.

concentration. The 0%-defect chains form toroidal structures roughly 20 nm in diameter, while the 10%-defect chains form cylindrical structures roughly 30 nm long. The 5%-defect chains form both toroids and cylinders (only the toroid is shown in Figure 7), with the cylinders roughly twice as long and consisting of half as many loops as in the 10%-defect case. On the other hand, the aggregated structures are qualitatively similar for the longer 1000-monomer chains with 0% and 10% defect concentrations, with cylinders formed in both cases. The loops formed by the longer chains with 0% defects are slightly wider than those with 10% defects, due to the higher stiffness of the non-defect chain segments.

The results for the 300-monomer chains are qualitatively consistent with those of Monte Carlo simulations of 0%- and 6%-defect 250-monomer chains using a simple lattice model of MEH-PPV. In this model, each 2.5 monomers was represented by a single site and model parameters were simply set to physically reasonable values.^[8] These simulations found distinct toroidal and cylindrical structures respectively for

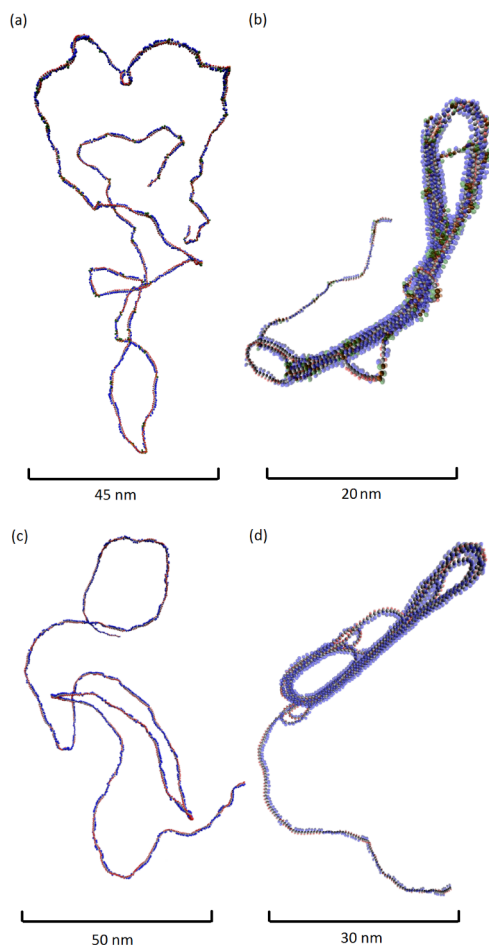


Figure 8: Snapshots of typical simulation configurations of CG polymers with $N_{\text{mon}} = 1000$ for defect concentrations of (a) 10% and (c) 0% in THF and (b) 10% and (d) 0% in the model poor solvent.

0% and 6% defects. The so-called "defect cylinder" structure formed by the 6%-defect chains was found to match the distribution of modulation depths from single-molecule polarization spectroscopy experiments.^[8] Our results for chain lengths of 1000, which is more typical of the chain lengths used experimentally, suggest that longer chains with 1000 or more monomers form similar aggregated structures in poor solvent for defect contents up to 10%. Such chains are many times longer than the persistence length, even for defect-free segments, and so they are less constrained in the way they aggregate than the shorter 300-monomer chains. Thus, regardless of defect concentration, they can loop back on themselves to form compact cylindrical structures in which adjacent chain segments are parallel to each other, with some difference in the curvature of the loops at the ends of the cylinders depending on the defect concentration. The persistence length l_p was estimated from $l_p = 3R_g^2/R_{\text{max}}$,^[13] where R_{max} is the chain contour length, to be 7.7 nm and 9.3 nm or roughly 12 and 14 monomers, respectively, for the 0%- and 10%-defect polymers with $N_{\text{mon}} = 1000$.

These results have implications for energy transfer in MEH-PPV, which is critical for many applications of these polymers, because energy transfer rates are sensitive to the

polymer morphology. To a first approximation, energy transfer occurs between quasi-localized chromophore units into which the polymer chain is divided by conformational distortions or chemical defects; the transition dipoles of these chromophores are aligned parallel to the chromophore axis.^[48] The transfer rate depends on the absorption and emission spectra of the donor and acceptor chromophores. It also decreases with increasing donor-acceptor distance and as the relative orientation of their transition dipoles changes from parallel to perpendicular. The rate of energy transfer is, not surprisingly, expected to change as a polymer goes from an extended conformation in a good solvent to a compact structure in a poor solvent. Our results also suggest that the energy transfer rates in aggregated structures should be more sensitive to the saturation defect concentration for shorter chains than for longer chains, due to the stronger dependence of the mesoscale polymer morphology on the defect concentration in shorter chains.

The ultimate goal of this work is to elucidate the molecular-level mechanisms for variations in photophysical properties of conjugated polymers such as energy transfer and fluorescence with solvent- or defect-induced changes in the polymer morphology. In work to be published, we couple of CG simulation configurations of MEH-PPV with a morphology-dependent model of energy transfer dynamics between weakly coupled chromophores^[49] to achieve this goal.

Conclusions

The systematically coarse-grained model of MEH-PPV that has been developed in this work improves on previously developed models by reparametrizing unphysical bond-angle potentials, by parametrizing inter-monomer torsions using quantum chemical calculations, by systematically coarse-graining saturation defects, and by treating polymers with random rather than regularly spaced defect positions. The model gives good agreement with experiment for the radius of gyration of MEH-PPV in THF. Simulations of MEH-PPV polymers with 300 and 1000 monomers per chain for saturation defect concentrations of 0 to 10% in THF and in a model poor solvent show that the polymers are extended in THF, a moderately good solvent. These extended configurations are qualitatively similar for different defect concentrations, although the radius of gyration decreases slightly with the number of defects. The polymers collapse into compact structures in the poor solvent. The structures formed by the 300-monomer chains change significantly with defect concentration, with toroids formed for 0% defects, cylinders for 10% defects, and a combination of the two for 5% defects, in qualitative agreement with previous simulations of a simple lattice model of MEH-PPV. On the other hand, the 1000-monomer chains form cylinders for both 0 and 10% defect concentrations.

Accessory Publication

The atomistic simulation model parameters for MEH-PPV, PPV, and THF and the coarse-grained simulation model parameters for MEH-PPV in implicit THF are given in the Accessory Publication, which is available from the journal website.

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