A generic combined matrix- and lattice-based kinetic Monte Carlo modeling tool to tune surface-initiated polymerization

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Scope

One of the most important challenges to face during the preparation of biofunctionalized polymer interfaces through the deposition of bio-derived polymeric layers to flat substrates is to perform a thorough characterization based on the molar mass and dispersity on the individual chain level, as well as the variation of its thickness as a function of the polymerization time and the grafting density, which define the mushroom/brush character of the biofunctionalized polymer interface as well as the physicochemical properties of the substrates, thus, outlining their suitability for applications covering areas such as sample purification, biosensing platforms, antifouling coatings, platforms for controlled cell culture as well as drug and gene delivery.

The present work [1,2] puts forward a new advance matrix- and lattice based kinetic Monte Carlo platform with and implicit reaction scheme capable of evaluating the growth pattern of individual free and tethered chains in three-dimensional format during surface-initiated reversible deactivation radical polymerization (SI-RDRP) and, consequently, allows for a detailed study of the conformation of the polymer chains and other relevant molecular properties, enabling a thorough characterization of the biofunctionalized polymer interface and the optimization of the synthesis conditions and control strategies for the production of well-defined polymer interfaces.

[1] Arraez, F. J.; Van Steenberge, P. H. M.; D'hooge, D. R., Macromolecules 2020, 53 (12), 4630 – 4648.
[2] Arraez, F. J.; Van Steenberge, P. H. M.; D'Hooge D, R., Polymers 2020, 12 (6), 1409.

Principles of kinetic Monte Carlo (kMC) model

➢ Lumped chemical reactions to model SI-RDRP

- **Chain initiation**

$$R_{0,surf}X + M_{lat} \xrightarrow{k^{app}_{i,lat-surf}} R_{1,surf}X$$
$$R_{0,lat}X + M_{lat} \xrightarrow{k^{app}_{i,lat}} R_{1,lat}X$$

- **Propagation**

$$R_{i,surf}X + M_{lat} \xrightarrow{k^{app}_{p,lat-surf}} R_{i+1,surf}X$$
$$R_{i,lat}X + R_{j,lat}X \xrightarrow{k_{td,lat}} P_{i,lat} + P_{j,lat}$$

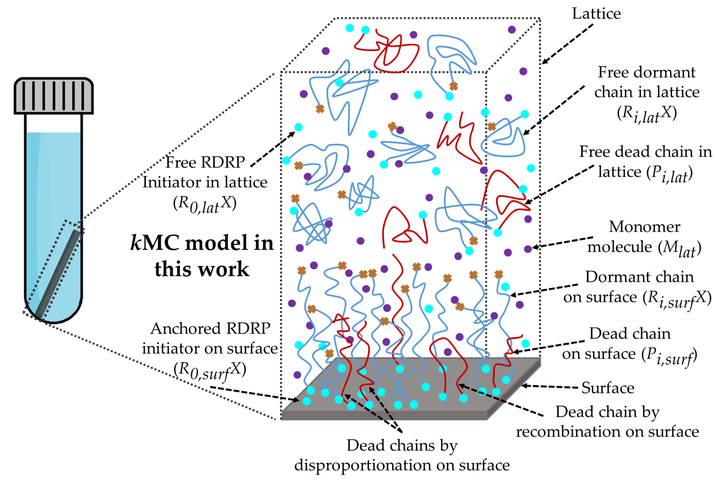
- **Recombination**

$$R_{i,surf}X + R_{j,surf}X \xrightarrow{k^{app}_{tc,surf}} P_{i+j,surf}$$
$$R_{i,surf}X + R_{j,lat}X \xrightarrow{k^{app}_{tc,lat-surf}} P_{i+j,surf}$$
$$R_{i,lat}X + R_{j,lat}X \xrightarrow{k^{app}_{tc,lat}} P_{i+j,lat}$$

- **Disproportionation**

$$R_{i,surf}X + R_{j,surf}X \xrightarrow{k^{app}_{td,surf}} P_{i,surf} + P_{j,surf}$$
$$R_{i,surf}X + R_{j,lat}X \xrightarrow{k^{app}_{td,lat-surf}} P_{i,surf} + P_{j,lat}$$
$$R_{i,lat}X + R_{j,lat}X \xrightarrow{k_{td,lat}} P_{i,lat} + P_{j,lat}$$

- ✓ Reference polymerization case: MMA @ 353 K
- ✓ RDRP initiator molecules $N_{R_{0,lat}X} = N_{R_{0,surf}X} = 1\times10^5$
- ✓ TCL of 100 per phase ($N_{M,0} = 2\times10^7$)
- ✓ Average surface coverage $\theta_{R_{0,surf}X} = 2.5\times10^{-1}$



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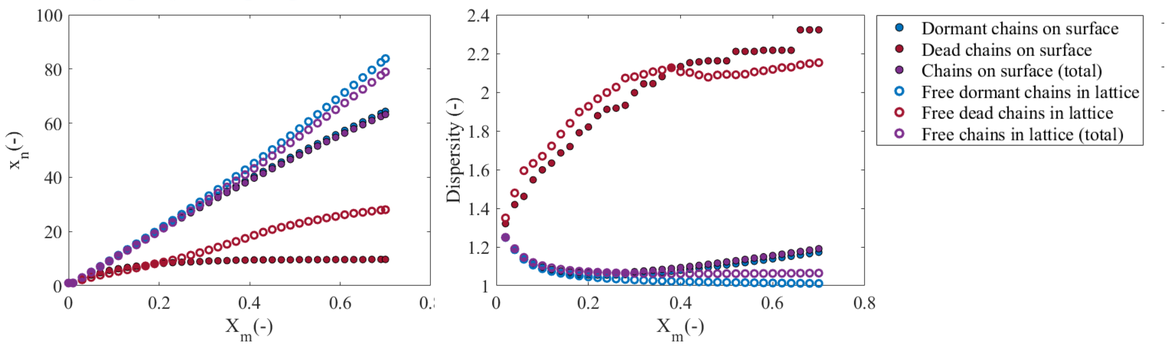
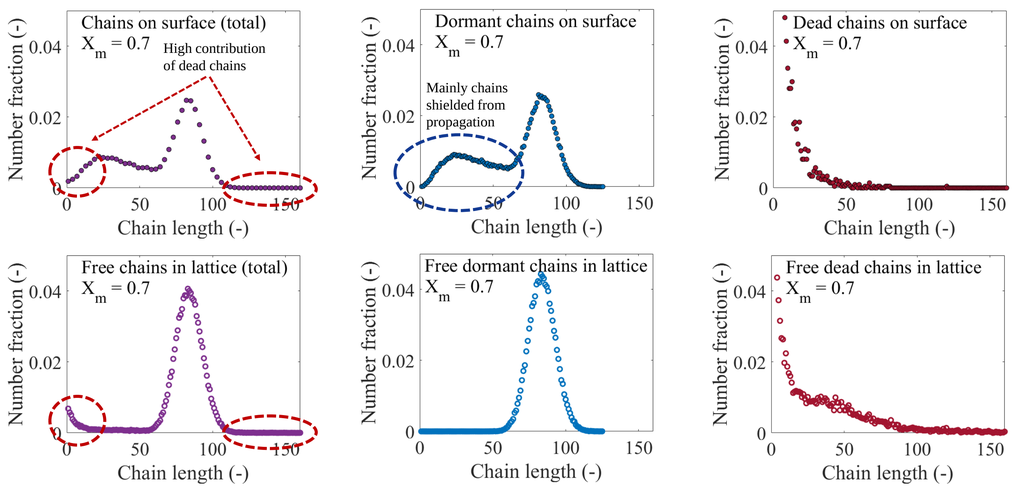
Conventional molecular properties

➢ Average polymer properties



➢ Number chain length distributions



The model predicts the evolution of bimodal chain length distributions due to shielding effects

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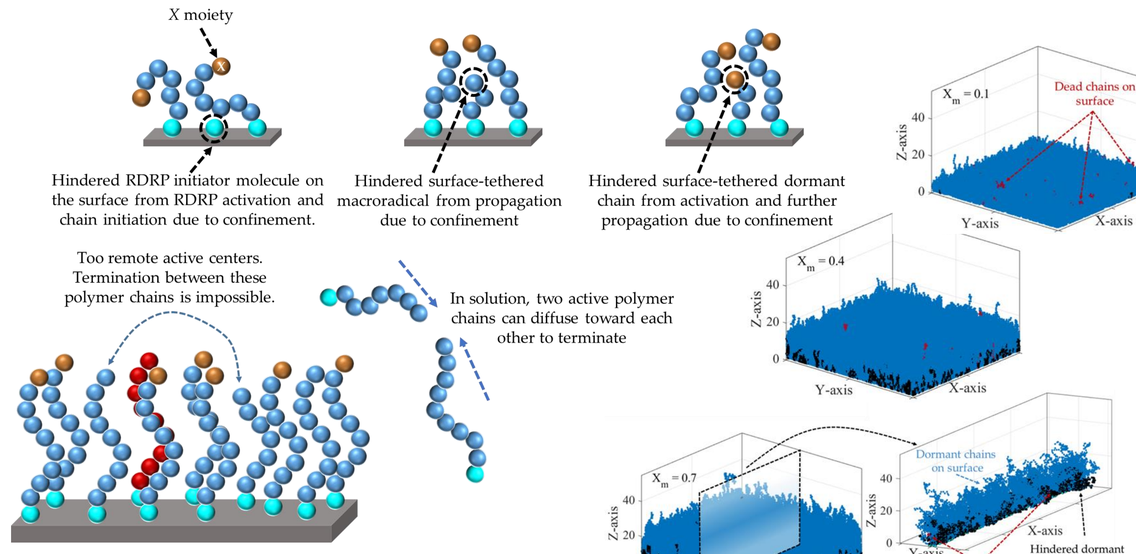
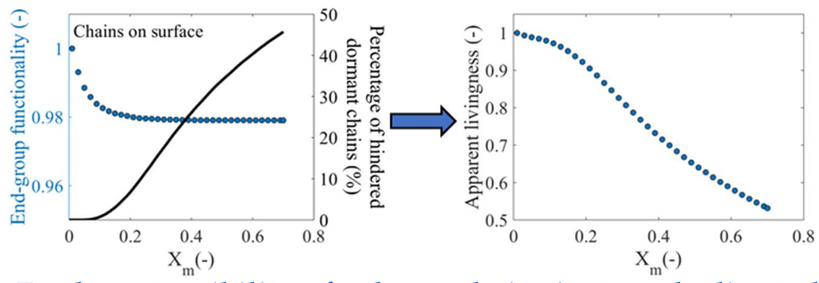
Effect of confinement on surface reactions

➢ Visualization of confinement



➢ Definition of apparent livingness of the polymer layer



Further extensibility of polymer chains is strongly dictated by shielding and to a lesser extent by classical EGF.

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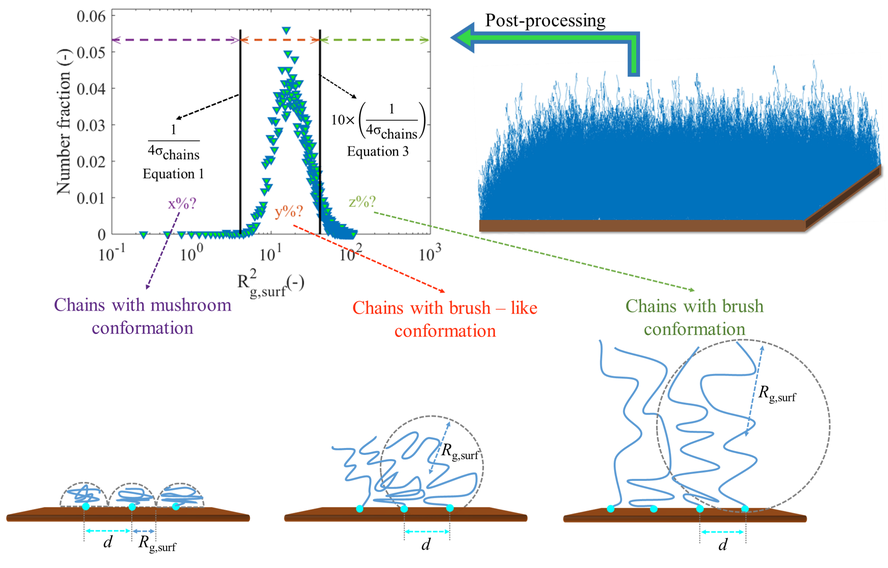
Conformational character of the polymer layer

The model indicates that the polymer layer can be described by a contribution of more than a single regime of 3D conformation

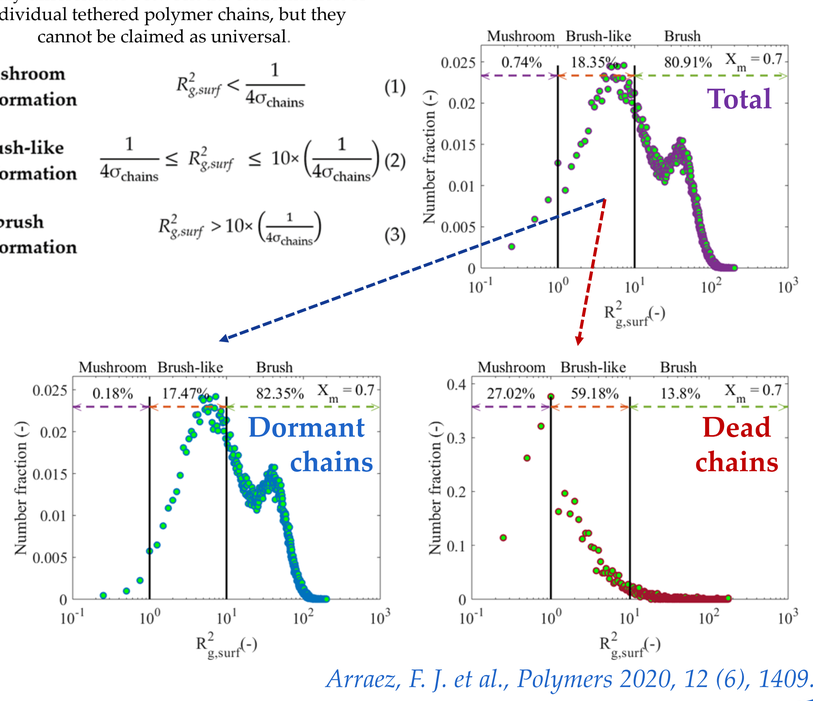


These equations are used for a guide-of-the-eye to quickly differentiate between the conformation of individual tethered polymer chains, but they cannot be claimed as universal.

mushroom conformation
$$R^2_{g,surf} < \frac{1}{4\sigma_{chains}} \quad (1)$$

brush-like conformation
$$\frac{1}{4\sigma_{chains}} \leq R^2_{g,surf} \leq 10\times\left(\frac{1}{4\sigma_{chains}}\right) \quad (2)$$

brush conformation
$$R^2_{g,surf} > 10\times\left(\frac{1}{4\sigma_{chains}}\right) \quad (3)$$



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Conclusions

- The developed *k*MC model offers new insights regarding the kinetic evolution of the molecular characteristics of individual polymer chains formed either on the surface or in the solution near this surface.
- The confinement kinetic effect for the surface-tethered polymer chains promotes the formation of a polymeric layer made up of shorter and more heterogeneously composed polymer chains compared to the free chains in solution.
- The concept of the apparent livingness of the polymer layer is introduced which considers not only dead chains formed via termination but also hindered dormant chains that have no direct space around the dormant moiety to enable further modification.
- The heterogeneous character of the polymeric layer puts forward that a distribution of regimes of conformation (*i.e.* mushroom, brush-like and brush) is needed for a thorough description of the conformation of the individual polymer chain at any given polymerization time.

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