Upgrading event driven Monte Carlo simulations for molecule-based morphological control for battery and sensor applications

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Abstract

Multiphase polymeric materials and applications play a prominent role in our society. One of the key challenges is the design and modification of their macromolecules so that the composition and structuring of the phases as well as the interactions between them can be controlled from the molecular scale onwards. In the present contribution, it is highlighted that more recently developed event driven (kinetic) Monte Carlo models provide an interesting framework to grasp molecular variations over various length scales. The strength lies in the tracking of individual molecules per phase of interest so that interphase transfer events can be sampled based on the distributed nature of the (macro)molecules present. Hence, the micro-scale of local concentrations and temperatures can be connected to the meso-scale defining interphase transport and morphological variations, with an additional connection to the macro- or application scale within reach by adding macro-scale transfer events to the overall sampling scheme. Starting from a benchmark coupled matrix based Monte Carlo (CMMC) study on the multiphase formation of engineering composites which explicitly acknowledges the type of (macro)molecules present in each phase, it is showcased that the CMMC framework can support the general field of energy and electronics applications. This is highlighted through (i) a case study devoted to the design of polymer electrolytes for batteries, and (ii) a case study on blend design for the regulated stretching of piezoresistive sensors.

Keywords: multiphase modeling; nanodomains: multi-scale design; stochastic algorithms; energy applications

Introduction

Multiphase polymeric materials play a crucial role in our society, with applications such as drug delivery, batteries, solar cells, high-tech engineering composites, and sensors [1-4]. A key challenge for these materials and their applications is the dedicated design of the morphology [5], e.g. core-shell, co-continuous, Janus shaped, or fibrillose alignment, allowing to optimize the final properties in several directions, e.g. strength, conductivity, permeability, transparency, and/or capacity [6-8].

Important research questions that arise to facilitate such design are: (i) Which type of polymeric phases are needed to obtain multi-functionality?; (ii) Which amount is required of each phase to obtain a certain morphology?; (iii) What is the most optimal (nano)structuring of the phases involved?; (iv) How to obtain (dynamic) control over the phase (nano)structuring?; (v) Which macromolecular structures allow proper phase interconnectivity to guarantee specifically stability and optimal macroscopic performance?; (vi) Which multiphase polymer engineering technique (*e.g.* emulsion or precipitation polymerization; extrusion or reactive extrusion) and process conditions (*e.g.* temperature, concentration ratios and compound/reactant types) are most suited to obtain a high material performance in an economic framework?

To address these questions a combination of experimental and modeling research is the most recommended pathway, recognizing that many phenomena at different length and time scales are at play during multiphase polymerization and processing [9-11], and that the link between the reaction conditions and the final material morphology is often very complex [12-14]. Most combined studies are however directed toward single phase systems and if one acknowledges multiple phases the distributed nature of polymer molecules with respect to chain length, composition, and architecture (or topology) is often replaced by a simplified average molecular description [9, 15, 16]. The molecular scale although constitutes the core of any (multi)material build-up but is often hidden, or seen as fixed, once manipulations at the material or application scale are performed. The current work therefore aims at making clearer to a broader community that engineering tools exist that are paramount to still include a (macro)molecular scale driven design at any moment of the value chain, pushing forward the realm of polymeric materials and applications.

In what follows, it is first explained how single phase oriented models can be upgraded to multiphase ones accounting in detail for the molecular scale, i.e. by embedding event driven stochastic modeling approaches in a multi-scale context. Next, two case studies connecting the molecular and material scale by means of bridging experiments and modeling results are included, considering for illustration purposes the overall field of energy and electronics applications. A differentiation is made between a first case study on polymer electrolyte design for batteries and a second case study on the compositional control of stretchable piezoresistive sensors.

Upgrading engineering knowledge on single phase polymeric material applications to multiphase systems

From an engineering point of view the largest level of molecular (modeling) detail is often taken up in single phase polymeric synthesis and material processing studies. For example many investigations on single-phase polymerization kinetics exist but as soon as *e.g.* precipitation takes place leading to a dispersed phase polymerization the modeling output is more limited. This is illustrated for emulsion polymerization in Figure 1 (left) [17-19], for which kinetic modeling approaches accounting for multiple reaction loci, being the aqueous phase and many organic nanoparticles, are well established but a coupling of these models to morphological variations in such particles (Figure 1; right) is still less developed [20-23]. For example, Marien *et al.* [24, 25] could predict for each miniemulsion nanoparticle which molecules (e.g. as defined by the chain length and overall comonomer composition) are present but did not describe the interactions between them to create a certain particle morphology. Hamzehlou *et al.* [21] in turn modeled such morphological variations within particles but treated the molecular scale in a lumped format, describing the overall conversion driven morphology behavior without explicitly accounting for a detailed set of elementary reactions. Similarly, for the field of extrusion-based polymer blending, e.g. for manufacturing of pharmaceutics and mechanical recycling, Edeleva *et al.* [26] highlighted that in most cases only the phenomena/properties at one scale are modeled with a high level of detail, while assuming an idealized or averaged description of the phenomena/properties at the other scales.

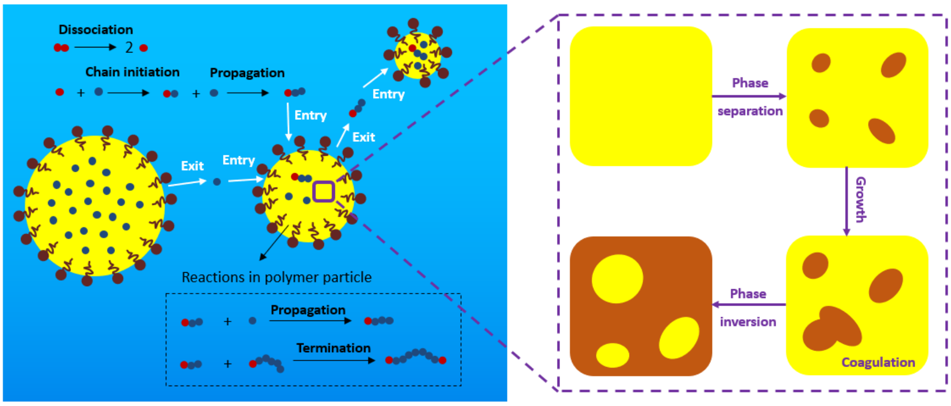

Figure 1. Left: Multi-scale character of dispersed phase polymerization (here illustrated for aqueous emulsion polymerization), resulting from the interplay between chemistry and interphase mass transfer, defining chain length and particle size variations. Right: the challenge to access morphological variations within such particles, while recognizing the molecules defining the morphology. The state-of-the-art either accounts for detailed reactions and particle size variations, ignoring morphological variations, or accounts for the latter but includes a basic chemistry description.

Interestingly, the strengths of more recently developed event driven (stochastic) algorithms are that they allow (i) to map many competing phenomena at the level of the smallest entity of interest, e.g. a molecule or a particle, and (ii) to screen complex design protocols, provided that dedicated parameter tuning is performed and scales are properly connected [2, 27, 28]. Ideally, one employs a multi-scale (stochastic) model that predicts physicochemical phenomena from sufficiently detailed first principles calculations at both (i) the micro-scale, being the scale of chemical reactions, concentrations, and diffusivities, (ii) the morphological or meso-scale, being the scale of particles, phases and interfaces, and (iii) the reactor/equipment or macro-scale, being the industrial implementation scale. Appropriate mass, momentum and energy equations per phase are additionally needed in combination with fundamental transfer terms to connect phases and thus scales [29]. Multi-scale model parameters should ideally follow from specific experiments, first under lab-scale bulk/solution conditions, allowing the determination of micro-scale parameters, and in a second step under multi-phase conditions allowing to obtain the remaining larger scale (e.g. meso and/or macro-scale) parameters.

It should be although admitted that mature multi-phase polymerization and processing multi-scale modeling tools that fundamentally address the coupling between the micro-, meso, and macro-scale, while acknowledging molecular scale driven morphological information, are still lacking. The most critical or first priority research task in the polymer multiphase modeling field is therefore the better connection of the micro- and meso-scale, particularly the enriching of (dynamic) morphological models with molecular features.

As shown in Figure 2, two main types of models have been applied to obtain meso-scale dynamic morphological information, namely dissipative particle dynamics (DPD) and Cahn-Hilliard (CH) models. In DPD models (top part of Figure 2), which can be seen as coarse-grained molecular dynamics simulations, the movement of beads under the influence of forces is the main output, allowing the implicit identification of regions in which polymer chains of a certain composition cluster and aggregate [30-33]. A coupling of DPD models to a simple stochastic reaction model has been applied, although a proper reflection of time-dependent reaction probabilities linked to fundamental rate laws and experimentally measurable macroscopic rate coefficients has not been achieved yet.

In CH models (bottom part of Figure 2), which are phase-field models, local material balances for individual species are solved, expressing diffusion and phase segregation as a result of chemical potential gradients, which can be evaluated by for instance the Flory-Huggins equation [34-37]. In any situation, it is non-trivial to keep track of reaction rate differences between certain phase entities, e.g. particles or (nano)domains, while simultaneously recognizing detailed chain-by-chain information, e.g. the structuring of comonomers units and the position and length of branches in a given chain.

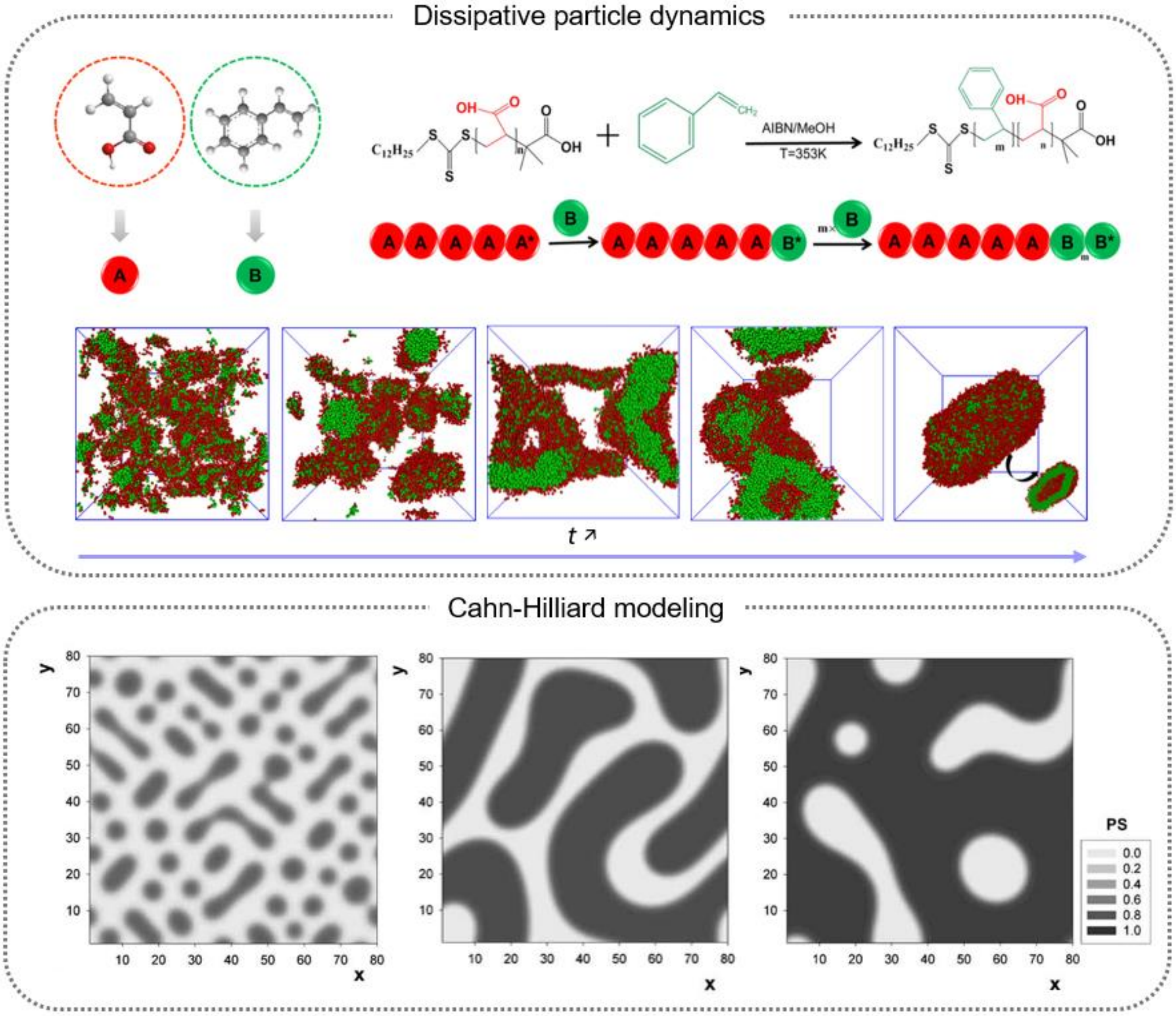

Figure 2. Concept of top dissipative particle dynamics (DPD) and (bottom) Cahn-Hilliard (CH) modeling to obtain dynamic meso-scale morphological information. Focus is on (top) the self-assembly of a poly(acrylic acid) macro-RAFT (reversible addition fragmentation chain transfer) agent during its extension with styrene in methanol (solvent beads are not shown; Figure adapted from Yan *et al.* [30], copyright (2019), with permission from the American Chemical Society) and (bottom) the phase inversion process during the production of high-impact polystyrene (Figure adopted from Vonka *et al.*

[38], Copyright (2011), with permission from Wiley). A challenge is to enrich such type of model outputs with molecular features.

A promising modeling route to implement such chain-by-chain information is to extend the application range of (Gillespie) event driven kinetic Monte Carlo (*k*MC) simulations, the principles of which are outlined in the next section. Such *k*MC simulations have already been upgraded to couple chain length and particle size variations in representative polymer engineering cases but only recently have been further upgraded to also account for morphological variations although in more composite engineering applications only [39]. Having access to the composition and topology of individual molecules at the micro-scale opens the door to make meso-scale parameters explicitly dependent on molecular information, whereas the more commonly applied reverse engineering approach with a posteriori sampling, e.g. conditional Monte Carlo, [40] or hybrid modeling [41], is by default more pragmatic and thus less generic.

Multi-scale kinetic Monte Carlo principles

Event driven *k*MC modeling relies on the sampling of events between species in a discrete manner according to probabilities as defined by fundamental rate laws [27]. Originally such stochastic modeling has been applied to describe the concentration changes for single phase chemical systems consisting of elemental species considering a limited amount of reactions. For example, emphasis has been on the reaction between A and B to C in competition with the reaction between A and A to D, this for simplicity in the absence of concentration or temperature gradients so that the micro- and macro-scale are the same; note that no meso-scale is needed as a single phase system is considered. A prerequisite is a sufficiently large ensemble size, which for the example given implies a high amount of A and B molecules at the start so that the reaction probabilities are accurately represented.

For polymerization kinetics, the amount of reaction events is much larger as a complex reaction mechanism is likely active and the chain length *i* is an unavoidable parameter with many possibilities [42-45], e.g. a basic (chain-growth) homopropagation reaction occurs with R_i (i=1 to i_{max}, e.g. 10^5). Moreover, for multiphase systems, reaction events occur per phase and one also has to sample meso-scale transfer events to address the crossing of species over the interphase border or interface. In general, for a multiphase polymer-based system, a very high number of reaction and physical events needs to be considered. Next to that a high amount of matrices are needed if one wants to describe in high level of detail the chemical build-up of the macromolecules formed.

To make clearer the order of magnitude of the mathematical modifications at hand for multiphase polymeric systems we again refer to Figure 1 (left), in which focus is only on a basic free radical homopolymerization (FRP) in miniemulsion, with reactions such as chain initiation, propagation and termination (by recombination) inducing in a given particle with a maximum chain length of 10^5 already 10^{10} reaction events. With a typical ensemble size of 1000 droplets/particles, while including meso-scale entry/exit events, this implies on overall amount of 10^{13} micro- and meso-scale events. In case macro-scale variations exist as well, at least per “isolated” compartment with given macro-scale characteristics (e.g. a region close to the impeller or reactor inlet) all the relevant lower scale events need to be sampled and additional macro-scale transfer events are required to account for variations in bulk concentration and temperature. One easily thus goes from 10^{13} micro- and meso-scale events to 10^{14} micro-, meso-scale and macro-scale events. Furthermore, every monomer unit in a given (general) macromolecule can possess a certain nature, and branches can be present of a certain size and at a given backbone position, so that for very detailed molecular scale driven *k*MC models the overall mathematical complexity is even higher (e.g. in total 10^{18} possibilities).

The mathematical complexity also depends on the degree of phase coupling. For example, for Figure 1, only dealing with homopolymer chains, already a strong interaction between the micro- and meso-scale is active. A different particle nucleation mechanism leads here to different distributions of nanoparticle sizes, with the kinetics in the nanoparticles strongly dependent on the size, largely due to the particle size dependence of the rate coefficients for entry and exit events of species to and from the (nano)particles and due to so-called (kinetic) compartmentalization effects [20, 46-49]. The associated coupled matrix based Monte Carlo (CMMC) model allows the coupled calculation of the chain length distribution (CLD) at the micro-scale and the particle size distribution (PSD) at the meso-scale [24, 25]. Instead of averaging (e.g. monomer) concentrations over particles, fluctuations in concentrations for all types of species are acknowledged per nanoparticle size, proving the incorrectness, at least under general conditions delivering various active species, of more simplified average-based models, hence, creating a huge step forward in emulsion process design.

In any case, for polymer engineering applications, advanced multi-scale *k*MC modeling demands the development and use of advanced storage and search algorithms [50], with the main micro-scale mathematical principles explained in the recent review of Trigilio *et al* [27]. and the details for more advanced complex multiphase topologies, hence, micro- and meso-scale influenced systems given in the work of De Keer *et al* [2] and Figueira *et al* [39].

Figure 3 highlights a key result of the recent work of Figueira *et al.* [39], in which the top left part conceptually shows how a single phase model is too simplified as a so-called salami morphology is eventually formed in high-impact polystyrene (HIPS) production. The polymerization is started with styrene monomer and polybutadiene (PB) polymer to create in one phase PS and grafted copolymer (GC), with PB backbones and styrene grafts. Once a certain amount of PS is formed phase separation occurs (first vertical line in top right plot in Figure 3), with a PS-rich being a dispersed phase and a PB-rich phase being a continuous phase. The situation changes once the contributions of PS and PB are similar (second vertical line in top right plot in Figure 3) and becomes even more complex with freshly formed PS remaining trapped as occlusion particles in the PB-rich phase. The bottom part of Figure 3 displays the associated log-molar mass distributions (log-MMDs) for PS, highlighting which type of PS chain lengths are defining each of the aforementioned three phases. Such a unique classification is only possible by tracking individual chains per phase and accounting for both micro- and meso-scale events, highlighting the CMMC relevance and novelty.

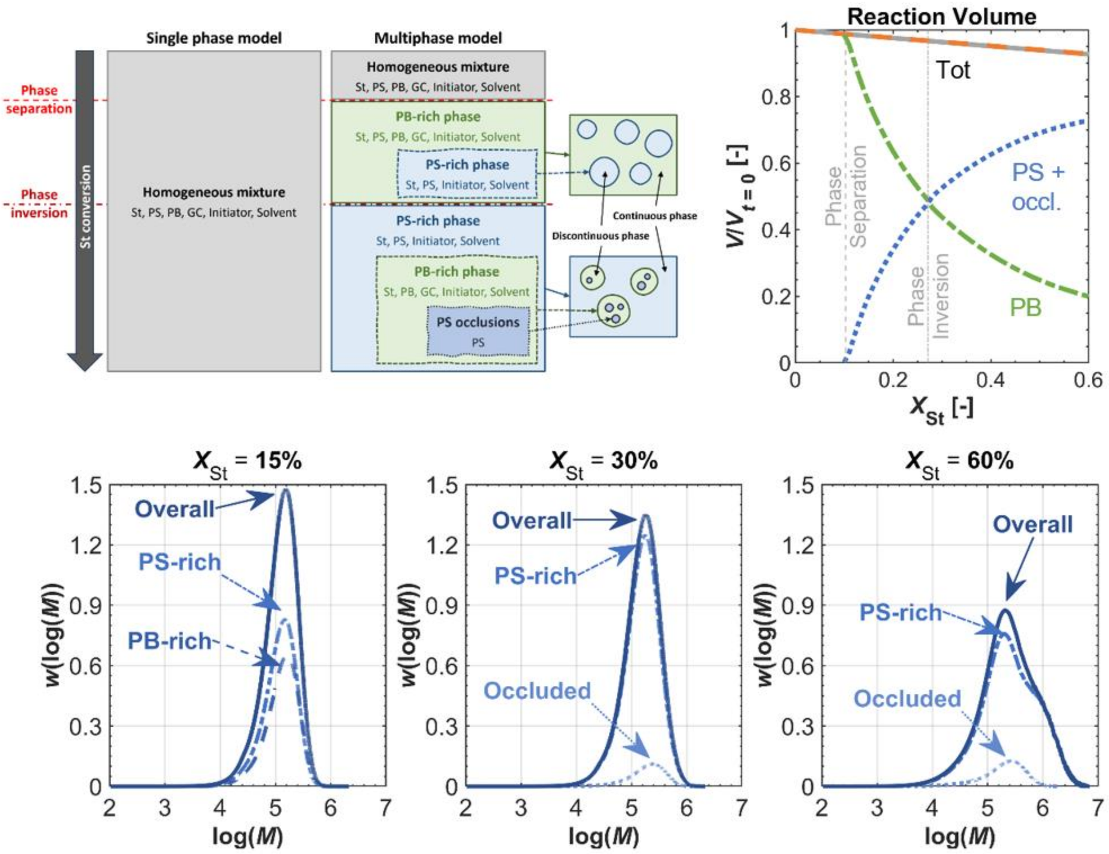

Figure 3. The application of coupled matrix-based Monte Carlo (CMMC) for multiphase polymerization generating a multiphase morphology in the absence of macro-scale variations; example of morphology development for high-impact polystyrene (HIPS) production with a polystyrene (PS)-rich phase, a polybutadiene (PB)-rich phase, and PS occlusion (occl.) phase; GC: graft copolymer. Top: simplified single phase vs. advanced multiphase modeling, with a comparison of phase volumes (grey line: single phase; colored lines: multiple phase); bottom: example of log-molar mass distributions (log-

MMDs) at three styrene (St) conversions distinguishing contributions per phase (if phase not shown: negligible contribution). This type of modeling approach connects the phase formation to the dynamics and structure of individual molecules and is applicable to other fields than engineering composites, as illustrated in the present work for the field of energy and electronics applications. Data taken from Figueira [39]. Copyright (2024), with permission from Elsevier. Permission

Hence, it is very worthwhile to develop stochastic modeling strategies not only allowing the sampling of reactions and transfers but also of morphological phenomena (e.g. phase contribution and particle size variations). Overall, the state-of-the art of such implementations is still rather basic with only a handful of scientific contributions. One has e.g. the already discussed work of Figueira *et al* [39]. but also the simulations of for instance Stubbs *et al* [23]. for radical gradients in nanoparticles during emulsion polymerization. However, a single nanoparticle size was assumed by the latter authors so that the effect of particle size variations was neglected. Dedicated molecular driven simulations of multiphase morphologies are thus still largely lacking, although recently some deterministic attempts have been made, however, without a fundamental coupling to the micro-scale [22, 51, 52]. Similar to the desired evolution of (stochastic) kinetic modeling studies to acknowledge the complete CLD and PSD in emulsion polymerization instead of only the average chain length and particle size, a transition needs to be therefore made from pseudo-single-phase models to genuine multiphase models acknowledging the complete morphology portfolio. This will allow to understand and control the effect of the make-up of individual macromolecules on morphological variations, which in turn allows to better regulate the (interfacial) macroscopic properties for various applications.

In what follows, the potential of such molecular scale driven morphological description is further highlighted for two case studies in the energy and electronics application field, differentiating between (i) a case study on polymer electrolytes for batteries and (ii) a case study for blend design for piezoresistive sensors.

Case study 1: Design of polymer electrolytes for battery applications

An important societal challenge is meeting the increasing energy consumption with renewable or sustainable energy sources, using technological advances. For example, electrical energy can be sustainably produced by harvesting solar energy via photovoltaic cells, converting it into electrical energy and storing it via electrical batteries [53, 54]. Notably, high-tech polymeric materials are important candidates for both organic PV cells and electrical batteries, avoiding the use of rare-earth metals in inorganic solar cells[55, 56]. In the past decades, the photon efficiency of organic PV cells has approached the efficiency of existing commercial inorganic photovoltaic cells, at least under laboratory conditions. Furthermore, electrical batteries based on solid polyelectrolytes are expected to achieve superior energy storage compared to non-polymer technology. However, large efficiency gains are expected by optimizing molecular and morphological parameters [57, 58]. In this context, a multi-scale modeling approach recognizing micro- and meso-scale interactions is highly recommendable.

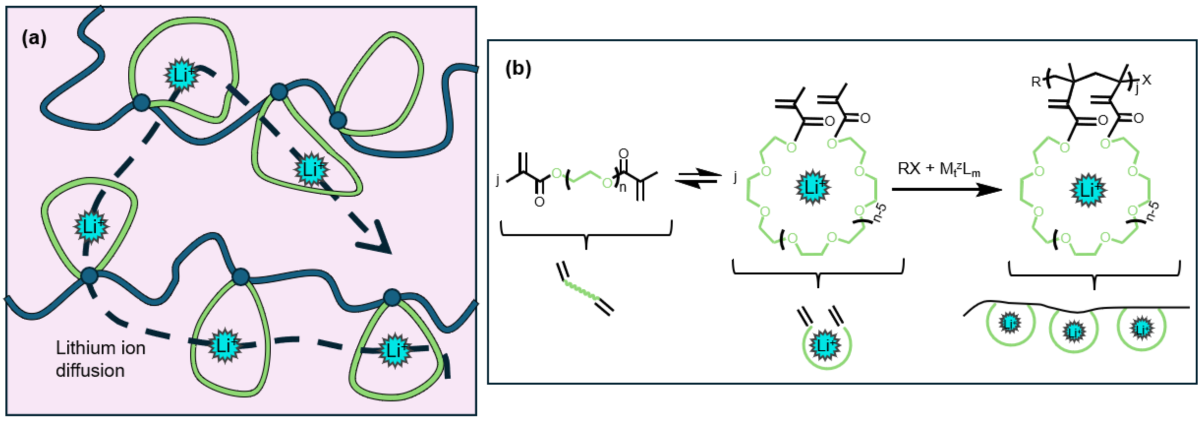

Figure 4. Molecular and morphology control for cyclopolymer electrolytes. (a) Conceptual illustration of diffusion channels enhancing the ion conductivity of cyclopolymers. (b) Cation template-assisted controlled radical cyclopolymerization (CCP) leading to linear polymeric pseudo-crown ethers [59, 60].

Indeed, as e.g. shown in **Figure 4(a)**, the efficiency of ion transport for cyclopolymer electrolytes depends on how the chains fold and define a nanomorphology. More in detail, as shown in Figure 4(b), it follows that a bifunctional monomer can be polymerized under radical conditions in such a way that cyclization is possible (green loops), i.e. an intramolecular interaction first takes place so that the dangling double bond of the incorporated functional monomer is aligned for a linear propagation (instead of crosslinking) [59]. With a mediating agent, control over the molar mass distribution is also possible and chains can be capped with halogen ends [60]. The loops are so-called (pseudo)crown ethers recognizing certain cations thus enabling tunneling and charge transport for which CMMC modeling as displayed in Figure 3 would be highly beneficial to search for fine dispersions. Note that a CMMC-based morphology design of recently proposed self-healing pseudo-cyclic vitrimers [61] would also be highly advantageous.

More in general well-defined multi-phase nanostructured polymer electrolytes are promising solid-state electrolytes for high energy density lithium metal batteries [62, 63]. In contrast to the currently available Li ion batteries (LIB), metallic lithium is used as anode material in lithium metal batteries (LMB), thereby achieving the highest possible cell voltage and energy density [64, 65]. Notably, liquid electrolytes used in LIBs cannot be used in LMBs as electrodeposition of lithium on the negative electrode would lead to dendrite formation and thus an undesired micro- and meso-scale interaction. The presence of these dendrites not only consumes the electrolyte but also leads to short-circuiting with potential fire and explosion hazards. A very interesting alternative is to employ a mechanically robust solid polymer electrolyte that suppresses the formation of dendrites.

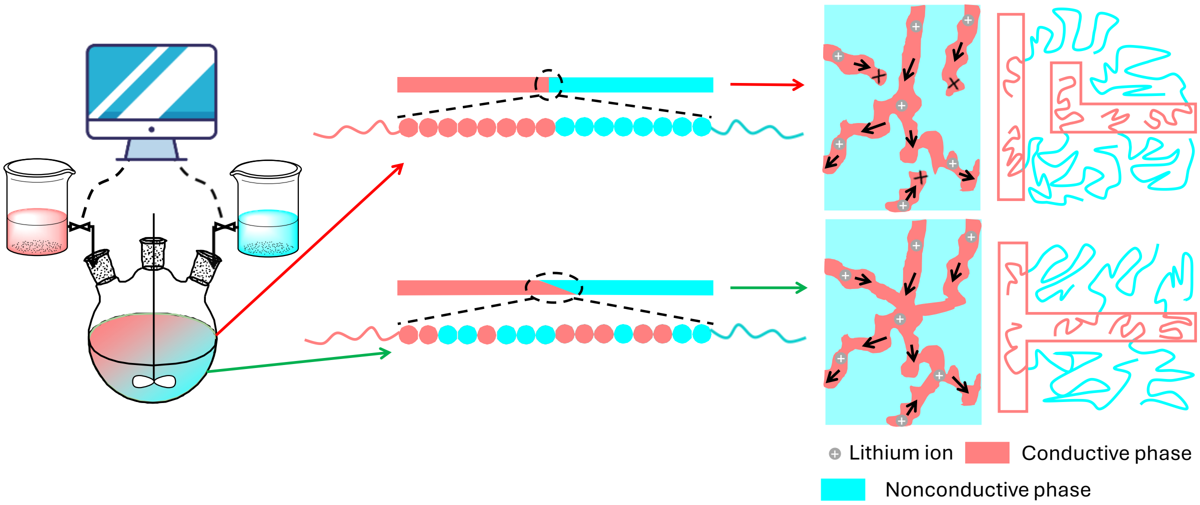

Figure 5. Model-based strategy to avoid dead ends in the conductive pathways of solid polymer electrolytes via the design of tapered block copolymers (green arrows) instead of conventional block copolymers (red arrows) [66, 67].

Currently, most research efforts have been devoted to block copolymer-based electrolytes based on ion-conducting poly(ethylene oxide) (PEO) and mechanically robust polystyrene (PS) [68, 69]. Interesting is to also deal with poly(oligo-oxyethylene methacrylate) (POEM) in view of its superior conductivity at room temperature compared to PEO. Another advantage of considering POEM is that tapered block copolymers (*i.e.* diblock copolymers with a gradient section in between the two blocks; see Figure 5 (middle) can be synthesized via controlled radical polymerization and appropriate feeding strategies. Notably, it has been anticipated that the smooth transition between the polar and non-polar block in tapered block copolymers allows to obtain a more continuous morphology (Figure 5; bottom right) compared to conventional block copolymers for which the sharp transition between the block leads to bending of domains (Figure 5; top right) [66, 67].

Tapered POEM-PS block copolymers could thus be designed by applying appropriate feeding strategies, which depend on the monomer reactivity ratios. Macromolecular structures simulated via CMMC can then be validated based on gel permeation chromatography and nuclear magnetic resonance data. This allows in a next step to quantify *in silico* the degree at which the actual macromolecular structure corresponds to the targeted one via the so-called structural deviation calculation, an approach which has very recently been extended for various macromolecular structures by stochastic means [70]. The morphology evolution can be simulated based on nanodomain nucleation and coagulation kernels depending on the segregation strength χ N (χ: Flory-Huggins interaction parameter and N: chain/segment length), consistent with the principles outlined in Figure 3 and to be correlated to the structural deviation parameter which characterizes the macromolecular structure. A morphology validation can be performed via transition electron and atomic force microscopy, and the effect on the ion-conductivity can be measured and tuned by model-based design.

Case study 2: Polymer blend design for stretchable piezoresistive sensors

Stretchable piezoresistive sensors display a morphology that is altered upon mechanical strain so that they can be used to detect damage or translate deformation in other signals enabling for instance motion, e.g. for smart textile applications or other electronic applications [71, 72].

In contrast to an assembly based on more expensive structural engineering, a cheap way to manufacture prototypes of stretchable piezoresistive sensors is through extrusion in which a polymer blend is loaded with a filler system creating a particle-driven network morphology. Upon a well-defined control of the meso-scale filler matrix interactions, close to the percolation limit, mechanical forces move the particles in such manner that tunneling resistances are altered and thus the conductivity is changing. Ideally a linear response is obtained for the variation in the resistance relative to the original resistance (r) versus the applied strain, and applicability is obtained for either lower or larger strains. The sensitivity is typically captured by the calculating the gauge factor GF defined as the ratio of r and the strain.

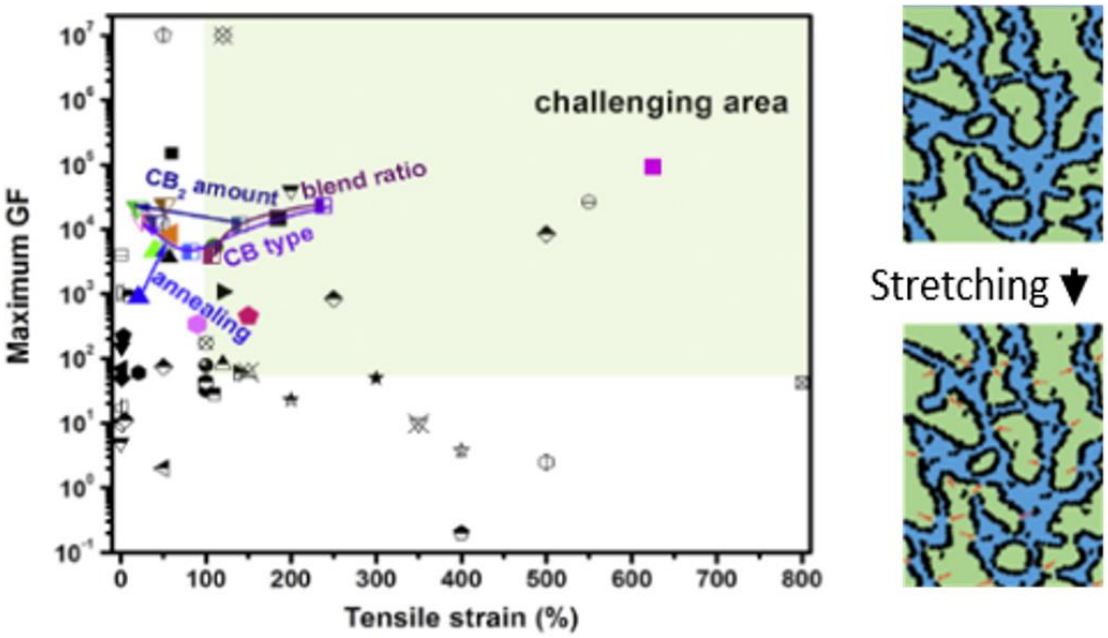

Figure 6: (left) Literature data on sensitivities expressed by gauge factor (GF) as a function of applied strain for structural engineered assemblies and conductive polymer composites; (right) Principle of morphology control via ternary blend design. Data taken from Duan [73, 74]. Copyright (2024), with permission from American Chemical Society and Elsevier.

Duan et al. [73, 74] for instance tuned blends based on thermoplastic polyurethane (TPU), olefin block copolymer (OBC) and carbon black (CB) filler using extrusion technology, therefore, enabling a straightforward manufacturing technique for sensor design. Binary blends of one polymer and CB, and ternary blends of both polymers and CB have been explored, playing with the mixing order and extrusion design parameters. Furthermore, two types of CB have been considered, including even a hybrid situation. As shown in Figure 6(left), the (maximum) GF could be regulated by blend design in the more challenging region of high strains and high sensitivities. However, only a couple of material blends can be seen as successful and still significant tuning of polymer blends design is required, also taking into account mechanical strength specifications.

As shown in Figure 6 (right), this comes to dedicated morphology control considering variations in the number of blending partners thus material phases as well as processing conditions (*e.g.* masterbatch approach with further blending or direct blending). Another point of attention is the minimization of hysteresis, being drifting upon cyclic strain loading, this for both low and high strains which is related to the application range of the final sensor. As many parameters can be varied a model-driven approach making a link to the molecular scale is highly recommended. In that way it can be better screened which material specifications are needed to enable a certain interaction scheme from the molecular to the material scale level, with again a core research item a more molecular driven interpretation of Flory-Huggins driven parameters.

Summary and outlook

Event driven (kinetic) Monte Carlo simulations, especially those based on coupled matrices (e.g. coupled matrix Monte Carlo (CMMC)), are a powerful modeling tool to support the molecule-based morphological design and control of multiphase polymeric materials and applications. These simulations rely on discretely sampling micro-scale (*e.g.* reactions after molecular diffusion) and meso-scale (*e.g.* interphase transfer and nucleation) events based on probabilities derived from rate laws.

The strength of these modeling tools lies in the tracking of individual (macro)molecules in each phase such that the rate of meso-scale phase transfer and morphological phenomena (e.g. nucleation or coagulation) and their corresponding probabilities can be made a function of the properties (e.g. chain length and comonomer composition) of the (macro)molecules present in the participating phases. Hence, these modeling tools allow to describe morphological dynamics based on time dependent (macro)molecular property variations. This enables the design and control of the morphology from the molecular scale onwards, ultimately allowing to improve the macroscopic material/application properties.

The ability of CMMC to connect the dynamics of the formation of individual macromolecules to the phase formation dynamics has first been demonstrated for high-impact polystyrene production, thus for multiphase engineering composites. Here, it has in particular been shown that different log-molar mass distributions are obtained in different phases, which is important to understand the contribution of the different phases to the overall macroscopic material properties.

Next, the potential of CMMC has been illustrated for the combined molecular and morphological design of solid polymer electrolytes for batteries. In particular, the potential of CMMC to design (i) fine dispersions of pseudo-crown ether rings and (ii) tapered block copolymers avoiding dead ends in the ion conducting pathways of solid polymer electrolyte materials has been highlighted. Moreover, it has been put forward that CMMC can help to optimize the blend design for stretchable piezoresistive sensors by coupling molecular variations to meso-scale phase interactions. Notably, upon doing so, a more molecular driven interpretation of Flory-Huggins parameters can be obtained.

It can be expected that the event driven Monte Carlo approach, which couples in a first stage the molecular (micro-) and morphological (meso-) scale and in a next stage also ensures a connection to the process/material (macro-) scale, will allow the advancement of multiphase polymer materials, specifically in the fields of energy and electronics.

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Conflicts of interest

The authors declare no conflicts of interest.

Data availability statement

Data sharing is not applicable as no data sets were generated.

References

1. Thompson, R.B., V.V. Ginzburg, M.W. Matsen, and A.C. Balazs, *Predicting the Mesophases of Copolymer-Nanoparticle Composites.* Science, 2001. **292**(5526): p. 2469-2472.
2. De Keer, L., et al., *Computational prediction of the molecular configuration of three-dimensional network polymers.* Nature Materials, 2021. **20**(10): p. 1422-1430.
3. Zarzar, L.D., et al., *Dynamically reconfigurable complex emulsions via tunable interfacial tensions.* Nature, 2015. **518**(7540): p. 520-524.
4. Eckmann, D.M., R.J. Composto, A. Tsourkas, and V.R. Muzykantov, *Nanogel carrier design for targeted drug delivery.* Journal of Materials Chemistry B, 2014. **2**(46): p. 8085-8097.
5. Röding, T., et al., *A review of polyethylene-based carbon fiber manufacturing.* Applied Research, 2022. **1**(3): p. e202100013.
6. Meereboer, N.L., I. Terzić, G. Portale, and K. Loos, *Improved energy density and charge-discharge efficiency in solution processed highly defined ferroelectric block copolymer-based dielectric nanocomposites.* Nano Energy, 2019. **64**: p. 103939.
7. Karagoz, B., et al., *Polymerization-Induced Self-Assembly (PISA) – control over the morphology of nanoparticles for drug delivery applications.* Polymer Chemistry, 2014. **5**(2): p. 350-355.
8. Zhang, Q., K. Liu, F. Ding, and X. Liu, *Recent advances in solid polymer electrolytes for lithium batteries.* Nano Research, 2017. **10**(12): p. 4139-4174.
9. D’hooge, D.R., P.H.M. Van Steenberge, M.-F. Reyniers, and G.B. Marin, *The strength of multi-scale modeling to unveil the complexity of radical polymerization.* Progress in Polymer Science, 2016. **58**: p. 59-89.
10. Bates, F.S., *Polymer-Polymer Phase Behavior.* Science, 1991. **251**(4996): p. 898-905.
11. Oosterhout, S.D., et al., *The effect of three-dimensional morphology on the efficiency of hybrid polymer solar cells.* Nature Materials, 2009. **8**(10): p. 818-824.
12. Sau, T.K. and A.L. Rogach, *Nonspherical Noble Metal Nanoparticles: Colloid-Chemical Synthesis and Morphology Control.* Advanced material, 2010. **22**(16): p. 1781-1804.
13. Mann, S., *The Chemistry of Form.* Angew Chem Int Ed Engl, 2000. **39**(19): p. 3392-3406.
14. Pearce, A.K., T.R. Wilks, M.C. Arno, and R.K. O’Reilly, *Synthesis and applications of anisotropic nanoparticles with precisely defined dimensions.* Nature Reviews Chemistry, 2021. **5**(1): p. 21-45.
15. Zhou, Y.-N., J.-J. Li, Y.-Y. Wu, and Z.-H. Luo, *Role of External Field in Polymerization: Mechanism and Kinetics.* Chemical Reviews, 2020. **120**(5): p. 2950-3048.
16. D'Hooge, D.R., et al., *Model-based design of the polymer microstructure: bridging the gap between polymer chemistry and engineering.* Polymer Chemistry, 2015. **6**(40): p. 7081-7096.
17. Edeleva, M., et al., *Chapter 2 - Multiscale theoretical tools for in silico macromolecular chemistry and engineering*, in *In silico Approaches to Macromolecular Chemistry*, M.E. Thomas, J. Thomas, S. Thomas, and H. Kornweitz, Editors. 2023, Elsevier. p. 17-69.
18. Aguirre, M., et al., *Polymer Colloids: Current Challenges, Emerging Applications, and New Developments.* Macromolecules, 2023. **56**(7): p. 2579-2607.

19. Lovell, P.A. and F.J. Schork, *Fundamentals of Emulsion Polymerization.* Biomacromolecules, 2020. **21**(11): p. 4396-4441.

20. Zetterlund, P.B. and D.R. D'hooge, *The Nanoreactor Concept: Kinetic Features of Compartmentalization in Dispersed Phase Polymerization.* Macromolecules, 2019. **52**(21): p. 7963-7976.

21. Hamzehlou, S., J.R. Leiza, and J.M. Asua, *A new approach for mathematical modeling of the dynamic development of particle morphology.* Chemical Engineering Journal, 2016. **304**: p. 655-666.

22. Rajabalinia, N., S. Hamzehlou, J.R. Leiza, and J.M. Asua, *Experimental validation of a mathematical model for the evolution of the particle morphology of waterborne polymer-polymer hybrids: Paving the way to the design and implementation of optimal polymerization strategies.* Chemical Engineering Journal, 2019. **363**: p. 259-269.

23. Stubbs, J., R. Carrier, and D.C. Sundberg, *Monte Carlo Simulation of Emulsion Polymerization Kinetics and the Evolution of Latex Particle Morphology and Polymer Chain Architecture.* Macromolecular Theory and Simulations, 2008. **17**(4-5): p. 147-162.

24. Marien, Y.W., P.H.M. Van Steenberge, D. R. D'hooge, and G.B. Marin, *Particle by Particle Kinetic Monte Carlo Tracking of Reaction and Mass Transfer Events in Miniemulsion Free Radical Polymerization.* Macromolecules, 2019. **52**(4): p. 1408-1423.

25. Marien, Y.W., P.H.M. Van Steenberge, A. Pich, and D.R. D'Hooge, *Coupled stochastic simulation of the chain length and particle size distribution in miniemulsion radical copolymerization of styrene and N-vinylcaprolactam.* Reaction Chemistry & Engineering, 2019. **4**(11): p. 1935-1947.

26. Edeleva, M., et al., *Molecular scale-driven upgrading of extrusion technology for sustainable polymer processing and recycling.* Current Opinion in Green and Sustainable Chemistry, 2023. **43**: p. 100848.

27. Trigilio, A.D., Y.W. Marien, P.H.M. Van Steenberge, and D.R. D'hooge, *Gillespie-Driven kinetic Monte Carlo Algorithms to Model Events for Bulk or Solution (Bio)Chemical Systems Containing Elemental and Distributed Species.* Industrial & Engineering Chemistry Research, 2020. **59**(41): p. 18357-18386.

28. Figueira, F.L., et al., *Coupled matrix kinetic Monte Carlo simulations applied for advanced understanding of polymer grafting kinetics.* Reaction Chemistry & Engineering, 2021. **6**(4): p. 640-661.

29. De Smit, K., et al., *Multi-scale reactive extrusion modelling approaches to design polymer synthesis, modification and mechanical recycling.* Reaction Chemistry & Engineering, 2022. **7**(2): p. 245-263.

30. Yan, Y.-D., et al., *Insight into the Polymerization-Induced Self-Assembly via a Realistic Computer Simulation Strategy.* Macromolecules, 2019. **52**(16): p. 6169-6180.

31. Wang, J., et al., *Precise Mesoscopic Model Providing Insights into Polymerization-Induced Self-Assembly.* Langmuir, 2020. **36**(27): p. 8009-8016.

32. Zuo, S., et al., *Polymerization-induced self-assembly of side-chain liquid crystalline copolymers by dissipative particle dynamics simulation.* Polymer, 2023. **264**: p. 125530.

33. Wang, J., et al., *Dissipative Particle Dynamics Simulation: A Review on Investigating Mesoscale Properties of Polymer Systems.* Macromolecular Materials and Engineering, 2021. **306**(4): p. 2000724.

34. Vonka, M. and J. Kosek, *Modelling the morphology evolution of polymer materials undergoing phase separation.* Chemical Engineering Journal, 2012. **207-208**: p. 895-905.
35. Nauman, E.B. and D.Q. He, *Nonlinear diffusion and phase separation.* Chemical Engineering Science, 2001. **56**(6): p. 1999-2018.
36. Inguva, P.K., et al., *Continuum-scale modelling of polymer blends using the Cahn–Hilliard equation: transport and thermodynamics.* Soft Matter, 2021. **17**(23): p. 5645-5665.
37. Martínez-Agustín, F., et al., *3D pattern formation from coupled Cahn-Hilliard and Swift-Hohenberg equations: Morphological phases transitions of polymers, bock and diblock copolymers.* Computational Materials Science, 2022. **210**: p. 111431.
38. Vonka, M., L. Šeda, and J. Kosek, *Modelling of the High-Impact Polystyrene Morphogenesis.* Macromolecular Symposia, 2011. **302**(1): p. 151-160.
39. Figueira, F.L., et al., *Combining ternary phase diagrams and multiphase coupled matrix-based Monte Carlo to model phase dependent compositional and molar mass variations in high impact polystyrene synthesis.* Chemical Engineering Journal, 2024. **481**: p. 148349.
40. Hoefsloot, H.C.J. and P.D. Iedema, *A Conditional Monte Carlo Method to Determine the Architectures of Metallocene Catalyzed Polyethylene.* Macromolecular Theory and Simulations, 2003. **12**(7): p. 484-498.
41. Tripathi, A.K. and J.G. Tsavalas, *Ghost-Mirror Approach for Accurate and Efficient Kinetic Monte Carlo Simulation of Seeded Emulsion Polymerization.* macromolecular Theory and Simulations, 2020. **29**(5): p. 2000033.
42. Zhou, Y.-N., et al., *Precision polymer synthesis by controlled radical polymerization: Fusing the progress from polymer chemistry and reaction engineering.* Progress in Polymer Science, 2022. **130**: p. 101555.
43. Guo, J.-K., Y.-N. Zhou, and Z.-H. Luo, *Kinetic insight into electrochemically mediated ATRP gained through modeling.* AIChE Journal, 2015. **61**(12): p. 4347-4357.
44. Mätzig, J., M. Drache, G. Drache, and S. Beuermann, *Kinetic Monte Carlo Simulations as a Tool for Unraveling the Impact of Solvent and Temperature on Polymer Topology for Self-Initiated Butyl Acrylate Radical Polymerizations at High Temperatures.* Macromolecular Theory and Simulations, 2023. **32**(4): p. 2300007.
45. Tripathi, A.K., J.G. Tsavalas, and D.C. Sundberg, *Monte Carlo Simulations of Free Radical Polymerizations with Divinyl Cross-Linker: Pre- and Postgel Simulations of Reaction Kinetics and Molecular Structure.* Macromolecules, 2015. **48**(1): p. 184-197.
46. Zetterlund, P.B., *Controlled/living radical polymerization in nanoreactors: compartmentalization effects.* Polymer Chemistry, 2011. **2**(3): p. 534-549.
47. Zeinali, E., et al., *How phase transfer increases the number of kinetic regimes from three to seven in nitroxide mediated polymerization of n-butyl acrylate in aqueous miniemulsion.* Chemical Engineering Journal, 2023. **470**: p. 144162.
48. Tobita, H. and F. Yanase, *Monte Carlo Simulation of Controlled/Living Radical Polymerization in Emulsified Systems.* Macromolecular Theory and Simulations, 2007. **16**(4): p. 476-488.
49. Zeinali, E., et al., *Comparing SG1 and TEMPO for NMP of n-butyl acrylate in miniemulsion to optimize the average particle size for rate and molecular control.* Reaction Chemistry & Engineering, 2024.
50. Trigilio, A.D., et al., *Optimal search methods for selecting distributed species in Gillespie-based kinetic Monte Carlo.* Computers & Chemical Engineering, 2022. **158**: p. 107580.

51. Zhu, C.-X., et al., *A two-phase method of moments model for high-impact polystyrene phase inversion conversion and molecular properties.* AIChE Journal, 2024. **70**(2): p. e18297.
52. Maffi, J.M. and D.A. Estenoz, *On the evolution of particle size distributions during the bulk synthesis of high-impact polystyrene using PBM: Towards morphology and phase inversion prediction.* Chemical Engineering Science, 2022. **247**: p. 117027.
53. Hosseini, T., I. Flores-Vivian, K. Sobolev, and N. Kouklin, *Concrete Embedded Dye-Synthesized Photovoltaic Solar Cell.* Scientific Reports, 2013. **3**(1): p. 2727.
54. Hoang, A.T., V.V. Pham, and X.P. Nguyen, *Integrating renewable sources into energy system for smart city as a sagacious strategy towards clean and sustainable process.* Journal of Cleaner Production, 2021. **305**: p. 127161.
55. Li, M., F. Igbari, Z.-K. Wang, and L.-S. Liao, *Indoor Thin-Film Photovoltaics: Progress and Challenges.* Advanced Energy Materials, 2020. **10**(28): p. 2000641.
56. Nielsen, T.D., et al., *Business, market and intellectual property analysis of polymer solar cells.* Solar Energy Materials and Solar Cells, 2010. **94**(10): p. 1553-1571.
57. Sanchez, C., P. Belleville, M. Popall, and L. Nicole, *Applications of advanced hybrid organic–inorganic nanomaterials: from laboratory to market.* Chemical Society Reviews, 2011. **40**(2): p. 696-753.
58. McIntosh, L.D., et al., *Evolution of Morphology, Modulus, and Conductivity in Polymer Electrolytes Prepared via Polymerization-Induced Phase Separation.* Macromolecules, 2015. **48**(5): p. 1418-1428.
59. Terashima, T., et al., *Polymeric pseudo-crown ether for cation recognition via cation template-assisted cyclopolymerization.* Nature Communications, 2013. **4**(1): p. 2321.
60. Moins, S., et al., *Potential of polymethacrylate pseudo crown ethers as solid state polymer electrolytes.* Chemical Communications, 2017. **53**(51): p. 6899-6902.
61. Liu, J., J.-J. Li, Z.-H. Luo, and Y.-N. Zhou, *Fast room-temperature self-healing vitrimers enabled by accelerated associative exchange kinetics.* Chemical Engineering Journal, 2023. **452**: p. 139452.
62. Su, G., et al., *Polymeric Electrolytes for Solid-state Lithium Ion Batteries: Structure Design, Electrochemical Properties and Cell Performances.* ChemCatChem, 2024. **17**(3): p. e202300293.
63. Wang, H., et al., *Reviewing the current status and development of polymer electrolytes for solid-state lithium batteries.* Energy Storage Materials, 2020. **33**: p. 188-215.
64. Shen, X., et al., *Beyond lithium ion batteries: Higher energy density battery systems based on lithium metal anodes.* Energy Storage Materials, 2018. **12**: p. 161-175.
65. Cheng, X.-B., R. Zhang, C.-Z. Zhao, and Q. Zhang, *Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review.* Chemical Reviews, 2017. **117**(15): p. 10403-10473.
66. Kuan, W.-F., R. Remy, M.E. Mackay, and I.I.I.T.H. Epps, *Controlled ionic conductivity via tapered block polymer electrolytes.* RSC Advances, 2015. **5**(17): p. 12597-12604.
67. Zheng, Z., X. Gao, Y. Luo, and S. Zhu, *Employing Gradient Copolymer To Achieve Gel Polymer Electrolytes with High Ionic Conductivity.* Macromolecules, 2016. **49**(6): p. 2179-2188.
68. Lu, G., et al., *Trade-offs between ion-conducting and mechanical properties: The case of polyacrylate electrolytes.* Carbon Energy, 2023. **5**(2): p. e287.

69. Wang, J., et al., *Structure Code for Advanced Polymer Electrolyte in Lithium-Ion Batteries.* Advanced Functional Materials, 2021. **31**(12): p. 2008208.
70. Conka, R., et al., *A unified kinetic Monte Carlo approach to evaluate (a)symmetric block and gradient copolymers with linear and branched chains illustrated for poly(2-oxazoline)s.* Polymer Chemistry, 2022. **13**(11): p. 1559-1575.
71. Duan, L., D.R. D'Hooge, and L. Cardon, *Recent progress on flexible and stretchable piezoresistive strain sensors: From design to application.* Progress in Materials Science, 2020. **114**.
72. Yao, S., et al., *Nanomaterial-Enabled Flexible and Stretchable Sensing Systems: Processing, Integration, and Applications.* Advanced material, 2020. **32**(15): p. 1902343.
73. Duan, L., et al., *Facile and Low-Cost Route for Sensitive Stretchable Sensors by Controlling Kinetic and Thermodynamic Conductive Network Regulating Strategies.* ACS Applied Materials & Interfaces, 2018. **10**(26): p. 22678-22691.
74. Duan, L., et al., *Designing formulation variables of extrusion-based manufacturing of carbon black conductive polymer composites for piezoresistive sensing.* Composites Science and Technology, 2019. **171**: p. 78-85.