Electronic and Spintronic Open-Shell Macromolecules, *Quo Vadis*?

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Abstract.

Open-shell macromolecules (i.e., polymers containing radical sites either along their backbones or at the pendant sites of repeat units) have attracted significant attention owing to their intriguing chemical and physical (e.g., redox, optoelectronic, and magnetic) properties, and they have been proposed and/or implemented in a wide range of potential applications (e.g., energy storage devices, electronic systems, and spintronic modules). These successes span multiple disciplines that range from advanced macromolecular chemistry through nanoscale structural characterization and on to next-generation solid-state physics and the associated devices. In turn, this has allowed different scientific communities to expand the palette of radical-containing polymers relatively quickly. However, critical gaps remain on many fronts, especially regarding the elucidation of key structure-property-function relationships that govern the underlying electrochemical, optoelectronic, and spin phenomena in these materials systems. Here, we highlight vital developments in the history of open-shell macromolecules to explain the current state of the art in the field. Moreover, we provide a critical review of the successes and bring forward open opportunities that, if solved, could propel this class of materials in a meaningful manner. Finally, we provide an outlook to address where it seems most likely that open-shell macromolecules will go in the upcoming years. Our considered view is that the future of radical-containing polymers is extremely bright, and that the addition of talented researchers with diverse skills to the field will allow these materials, and the end-use devices in which they are utilized, to have a positive impact on the global science and technology enterprise in a relatively rapid manner.

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1. Introduction

Open-shell organic compounds (i.e., carbon-based molecules bearing radical groups) are an essential component of modern chemistry, materials science, and emerging applications. For instance, the revelation regarding the significant role of organic radicals in living organisms (e.g., redox signaling and metabolism) has driven the synthesis of stable organic radicals that have been useful in multiple applications (e.g., radical-mediated polymerization, biological detection, and ecological capture).[1–4] In these open-shell materials, ambient stability is promoted by kinetic stabilization (e.g., steric protection and spin delocalization) to avoid potential radical quenching.[5,6] Moreover, the manipulation of the singly-occupied molecular orbital (SOMO) characteristics through synthetic design also brings about many interesting properties that have great potential in electronic and spintronic devices. Incorporating these open-shell species within macromolecules makes them an intriguing subclass of materials that has a large chemical design space; versatile processing properties that are consistent with roll-to-roll manufacturing techniques; and modular mechanical, thermal, spin, and transport properties. The inspiration for these manifold opportunities can be traced to first synthesis and observation of paramagnetic behavior in nitroxide-containing radical polymers by Griffith et al. in 1967,[7] as well as the evidence of electron exchange first discovered by Kishita and co-workers in 1982.[8] In the decades that has followed these seminal discoveries, many developments have occurred in terms of increased understanding of radical-containing macromolecules, their potential applications, as well as existing challenges. In this Perspective, we will summarize the development of radical-containing macromolecules and their applications in electrochemical, electronic, and spintronic devices, and we will provide our own assessment of the current state of the art and the open opportunities of this growing field.

Over the past 50 years, the chemical constructs of open-shell macromolecules have expanded in terms of their macromolecular architectures, range of stable radical groups, and the covalent linkages between the closed-shell and open-shell components of these molecules. Moreover, this class of materials can leverage many of the same advances in polymer synthesis that have occurred for their closed-shell analogs during these years. For instance, many synthetic efforts have been drawn to nitroxide-based radical polymers due to the stability and relative synthetic robustness of this open-shell class. As such, a variety of polymerization methods and molecular design modifications have been implemented. Besides, these advances have propelled structural diversity in other polymer types. Additionally, by altering the manner of the radicals incorporated into the macromolecular structure, the establishment of open-shell macromolecules with novel characteristics have been realized, and this is the focus of the first section of the current effort.

To bridge the molecular design to end-use applications divide, researchers are actively elucidating structure-function relationships of these next-generation macromolecules. Importantly, these relationships are impacted by fundamental transport processes that occur within many end-use systems (e.g., charge and mass transport) whose details are still to be fully resolved. At the molecular level, it is generally believed that hopping dominates the charge transfer process, and Marcus theory is widely utilized to predict pair-wise charge transfer rates. At longer length scales, charge transport is also influenced by the nanoscale structure and local morphology, radical distribution, and energy variations. Moreover, in electrolyte-supported device scenarios, the presence of solvents and salts and the potential for chain diffusion further complicate the description of charge and ion transport. Thus, the second section of this effort focuses on connecting molecular structure properties with nanoscale transport phenomena in radical-containing polymers.

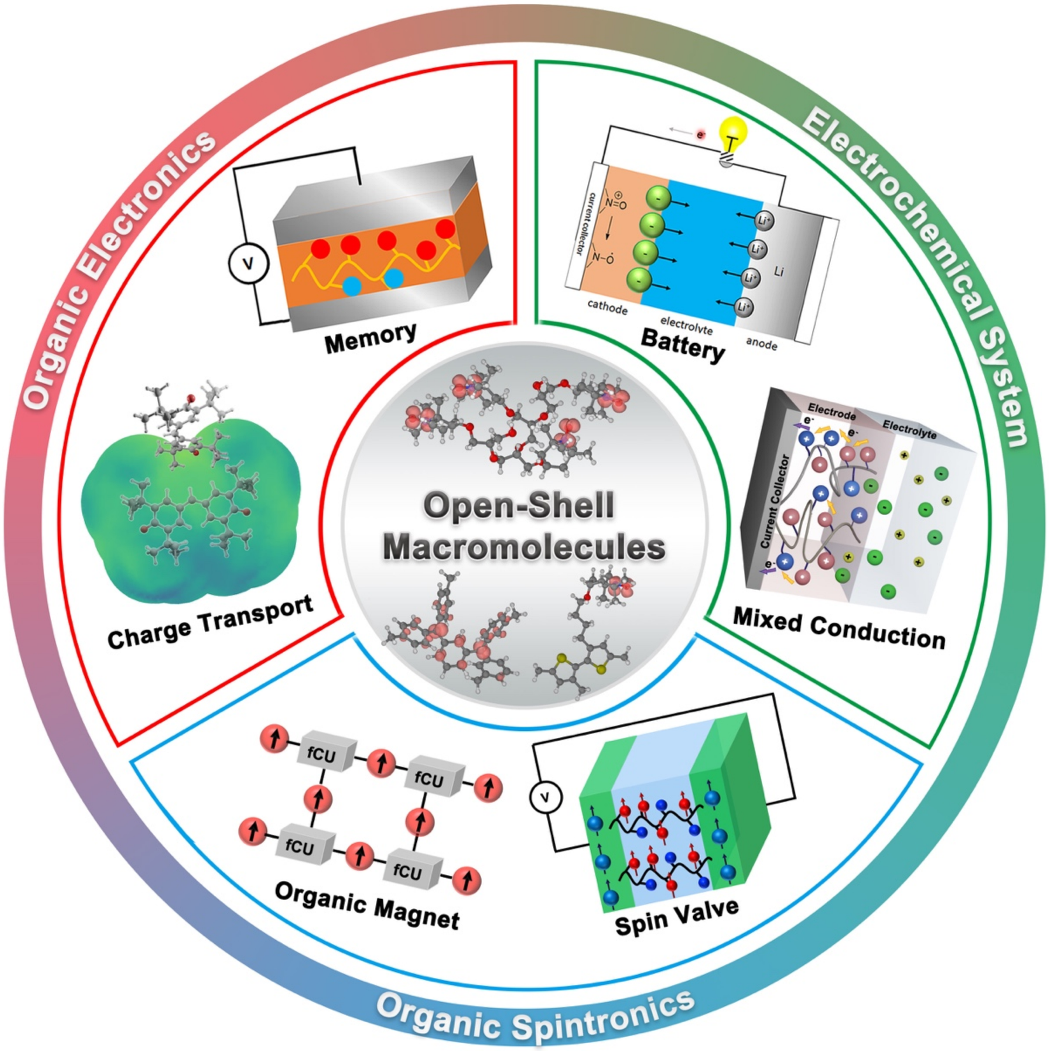

Figure 1. Schematic illustration of open-shell macromolecules in organic electronics, electrochemical systems, and organic spintronics, as discussed within the scope of this perspective. Representative frameworks of open-shell macromolecules and their spin density are visualized in the center circle. Organic electronic applications (e.g., memristors) and a molecular charge transport isosurface of the galvinoxyl radical are in the left arc. A cartoon of an electrochemical system and the mixed conduction phenomenon are shown in the right arc. Organic spintronic devices (e.g., organic magnets and spin valves) are in the bottom arc. The electronic coupling isosurface of the galvinoxyl radical is adapted from ref 66. Copyright 2021 American Chemical Society.

The combination of synthetic design and theoretical understanding have propelled the successful design of diverse functionalities for device applications. Among them, research on organic radical batteries is the most extensive, which is essentially an application originating from mixed conduction. By modulating the charge transport properties (charge injection and accumulation), memory devices have been developed. Additionally, the doublet emission characteristic renders efficient light-emitting diodes. The new field of organic spintronics also emerges due to the spin properties associated with these macromolecular systems, although it ais at an earlier state compared to the aforementioned applications. However, all of these efforts will be detailed in the final section of this work.

That is, this Perspective has been organized to quickly bring synthetic and computational researchers in adjacent fields to speed on the state-of-the-art in open-shell macromolecular materials and emerging opportunities. The scope of this Perspective is illustrated in Figure 1. We begin with a brief discussion regarding the syntheses of different categories of open-shell macromolecules (Section 2). Then, we then discuss the mechanisms associated with charge transfer and mixed conduction (Section 3). We subsequently review device applications for open-shell macromolecular materials, including electrolyte-supported electrochemical systems and solid-state organic electronic and spintronic devices (Section 4). By focusing on areas of opportunity at the leading edge of the research enterprise, we aim to have this effort generate new interest in the development of open-shell macromolecules such that the most pressing opportunities can be solved by a diverse group of interdisciplinary researchers in a ready manner.

2. Synthesis of Open-Shell Macromolecules

A primary tenet in the design of synthetic routes for open-shell macromolecules is to ensure that the presence of the open-shell sites is retained when the radical groups are placed within the macromolecular architecture, either during or after the formation of the bonds that form the macromolecular skeleton (e.g., the polymerization reaction). Based on the way the radicals are incorporated into the macromolecular structure, they can be divided into the following three categories: (1) nonconjugated radical polymers; (2) conjugated radical polymers (CRPs); and (3) polyradicals. Given the diversity of radical chemistries (most heteroatom-based, with carbon, nitrogen, oxygen and sulfur as spin density carriers),[5,9,10] our scope has been intentionally narrowed to focus on electronically-neutral, stable open-shell functionalities that have been commonly-incorporated into macromolecular structures, including nitroxide groups [e.g., 2,2,6,6-tetramethylpiperidin-1-yl)oxyl) (TEMPO), 2,2,5,5-tetramethyl-1-pyrrolidinyloxy (PROXYL), styrenic nitroxide, and nitronyl nitroxide radicls]; the nitrogen-based verdazyl radical, oxygen-based organic radicals (e.g., phenoxyl, galvinoxyl), and carbon-centered radicals (e.g., triphenyl methyl radical and derivatives).[11–16]

2.1 Nonconjugated Radical Polymers

Generally, a nonconjugated radical polymer is composed of an aliphatic polymeric backbone, which significantly influences the thermomechanical properties, and pendant open-shell moieties that impart the redox-active and end-use functional (e.g., electrochemical) properties. Their syntheses can be achieved through a direct polymerization of monomers bearing open-shell pendant groups. Additionally, polymerization of a closed-shell, protected monomer (i.e., a radical precursor) is also feasible, but an additional step of post-polymerization modification is required to yield the open-shell macromolecules. Finally, radical polymers can also be synthesized by attaching open-shell groups to pre-synthesized polymer structures. Here, we discuss the primary means by which these techniques are implemented; however, the interested reader is encouraged to review efforts that summarize these synthetic considerations in a more comprehensive manner.[6,11–17]

The aforementioned direct polymerization routes include ionic (i.e., either cationic or anionic) polymerizations, group transfer polymerizations, ring-opening polymerizations, and metal-catalyzed polymerizations (Figure 2).[7,18–29] The first successful synthesis of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) was achieved through a Grignard reagent-catalyzed anionic polymerization scheme using the TEMPO-functionalized methacrylate monomer, and this scheme yielded a macromolecule with a modest chain length (i.e., M_n ~1 kg mol^{-1}) (Figure 2a).[7] Subsequently, a moderately nucleophilic lithium initiator, 1,1-diphenylhexyllithium (DPHLi)-capped methyl methacrylate (MMA) was used to produce higher molecular weight PTMA while maintaining a relatively narrow molecular weight distribution ($M_n \leq 30.4$ kg/mol and $Đ \leq 1.1$) (Figure 2a).[21] In a similar manner, anionic or anionic coordinated polymerization can also be implemented to facilitate ring opening (ACROP) of nitroxide-functionalized cyclic ethers to generate radical polyethers.[23,24] For instance, potassium *tert*-butoxide performs well as an initiator in bulk for the polymerization of the 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEO) monomer to produce poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO).[22] Moreover, a $ZnEt_2/H_2O$ initiator functions better with an unsaturated proxyl-bearing epoxide at room temperature via the anionic-coordinated polymerization, resulting in full radical content (i.e., 1 spin per repeat unit) and a large molecular weight was achieved for the poly(PROXYL EO) polymer in Figure 2d.[23] These different preferences of initiators are highly dependent on the radical stability and compatibility, and in general, anionic polymerization serves as a feasible solution to directly produce radical polymers with high radical contents.

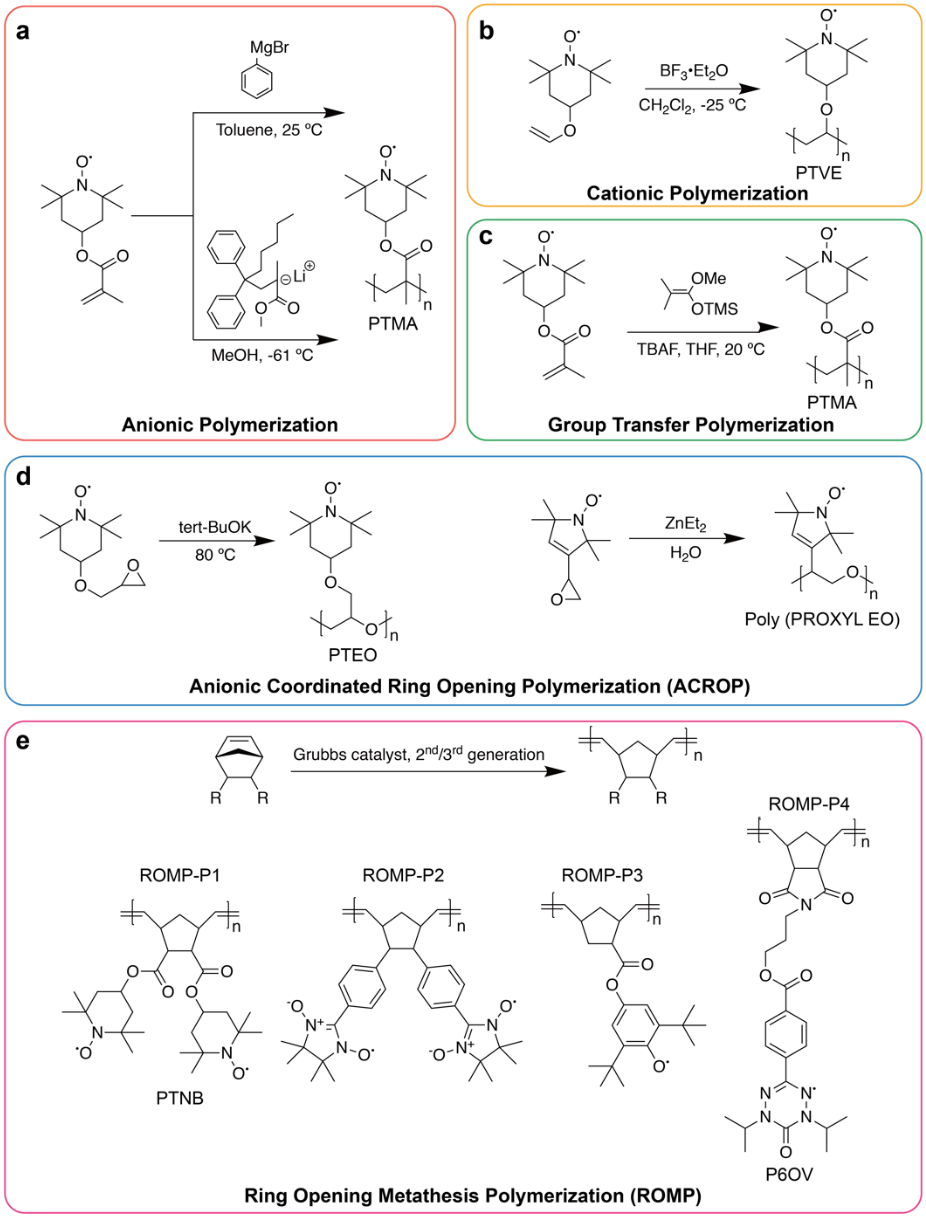

Figure 2. Nitroxide-based radical polymers synthesized from radical-containing monomers using (a) anionic, (b) cationic, (c) group transfer, and (d) anionic coordinated ring-opening polymerization techniques. (e) Furthermore, ring-opening metathesis polymerization allows for the synthesis of various radical polymers using open-shell monomers as the starting materials.

As with closed-shell macromolecules, there are fewer reports on cationic polymerization of nitroxide-based monomers relative to anionic polymerization schemes, and this is partially due to the oxidative susceptibility of the nitroxide group to cationic initiators. Importantly, low temperatures are generally required for the cationic polymerization of nitroxide-containing monomers. For instance, the polymerization of poly(TEMPO vinyl ether) (PTVE) catalyzed by boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) is executed at –25 ºC, offering an insoluble, gel product (Figure 2b).[25] Group transfer polymerization (GTP) has also been implemented to polymerize PTMA (M_n = 13.9 kg mol^{-1} and $Đ$ = 2.97) with 1-methoxy-2-methyl-1-trimethylsilyloxy-propene as the GTP agent (Figure 2c).[18] Although the high dispersity indicates that this was not a living polymerization, the GTP method performs well in terms of high radical content (i.e., ~100% relative to the theoretical amount) and good tacticity control (84% isotactic triads contributing to reversible redox processes).[27] Despite these initial successes, we stress that there is still a large design space to be had for polymer chemists in implementing cationic polymerization and GTP to radical polymer systems.

The above-mentioned ionic and group transfer polymerization methods are currently limited to nitroxide-based radicals. In comparison, polymerizations catalyzed by organometallic complexes are more versatile. For instance, the ring-opening metathesis polymerization (ROMP) of norbornene-based monomers has been implemented to afford polymers bearing different open-shell moieties [e.g., poly(2,3-bis(2’,2’,6’,6’-tetramethylpiper-idinyl-N-oxyl-4’-oxycarbonyl)-5-norbornene) (PTNB) and poly-[1,5-diisopropyl-3-(cis-5-norbornene-exo-2,3-dicarboxiimide) 6-oxoverdazyl] (P6OV)] as shown in Figure 2e.[26,30–32] This polymerization reaction is catalyzed by either 2nd and 3rd generation Grubbs catalysts, and these ROMP reactions yield polymers with high molecular weight and high radical content as well. However, as with many polynorbornene-based systems, a practical limit exists for this method as *-endo* and *-exo* conformations can drastically affect solubility. Thus, care must be taken in terms of the polymerization of these species if solution-based processing is desired for the end-use applications. Overall, direct polymerization has the advantage of maintaining high radical content, but it should be noted that undesired chain transfer or termination reactions may occur with radical species present.

The implementation of free and controlled radical polymerization is a natural means to create nonconjugated radical polymers due to the relatively versatile and robust nature of these synthetic methods that have been well-established in the closed-shell polymer literature.[6,20,26,33–39] Here, we classify radical-mediated polymerization schemes as indirect polymerization reactions, because the mechanism of the polymerizations requires the use of closed-shell, protected monomers that are then deprotected after the polymerization step to generate stable radical sites along the macromolecular pendant groups.[20,26,33–40] Open-shell bearing monomers are avoided, otherwise unfavorable chain transfer or termination reactions will occur during the polymerization process. The earliest successful example of this polymerization method was also aimed at synthesizing PTMA, through the conventional radical polymerization of the 2,2,6,6-tetramethylpiperidin-4-yl methacrylate (TMA) precursor monomer where the initiator was azobisisobutylonitrile (AIBN). After polymerization of the protected polymer, a H_2O_2-methanol solution was used to oxidize the polymer in the presence of catalytic Na_2WO_4 to yield the final PTMA product.[34] In this study, the copolymerization of TMA with styrene and MMA offered polymers with $49 \text{ kg mol}^{-1} \leq M_n \leq 111 \text{ kg mol}^{-1}$.

Many efforts followed from this initial foray into the radical-mediated polymerization of nonconjugated open-shell macromolecules, and these studies led to the creation of nitronylstyrene-, phenoxyl-, galvinoxyl- [e.g., poly-(4-(2,6-di-*tert*-butyl-R-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy)styrene (PGSt)], and verdazyl-based radical polymers generated from free radical polymerization techniques (Figure 3). The primary difference is only the post-polymerization oxidation step, which depends on the desired radical type (e.g., AgO_2 for the nitronylstyrene radical,[33] *p*-benzoquinone for the verdazyl radical,[38] lead oxide for the phenoxyl radical,[26] and $K_3Fe(CN)_6$ for the galvinoxyl radical).[20,37]

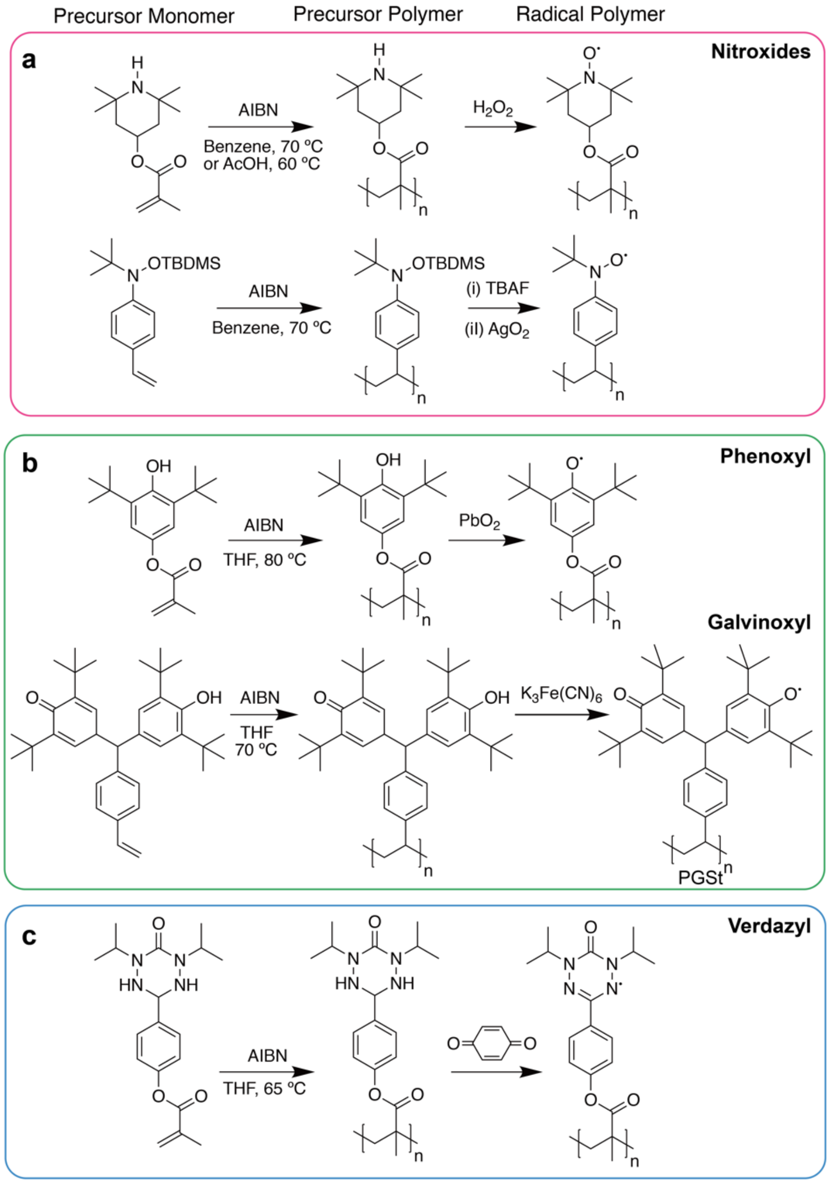

Figure 3. Representative schemes of free radical polymerization reactions used to generate radical polymer precursors followed by post-polymerization functionalization of the macromolecules to generate nonconjugated radical polymers. These schemes allow for the creation of (a) nitroxide-based radical polymers, (b) phenoxyl- and galvinoxyl-, and (c) verdazyl-based radical polymers.

While these synthetic strategies allow for facile polymerizations to occur, the drawback of the post-oxidation route is the possible inducement of solubility issues and excessive oxidation (i.e., over-oxidation by transferring two electrons forming ionic species). Thus, the radical content is difficult to control, and it may also induce unexpected doping processes.

Subsequent efforts to better control the molecular weight and control the molecular weight distribution of radical polymers were had by implementing controlled radical polymerization schemes (Figure 4). For instance, the utilization of metal-free reversible addition-fragmentation chain transfer (RAFT) polymerization yields a PTMA precursor with tunable molecular weights and relatively low dispersity values (M_n ~20 kg mol^{-1} and $Đ$ = 1.2) (Figure 4a)..[40] After removal of the chain transfer terminus through the addition of excess ABIN, *meta*-chloroperbenzoic acid (mCPBA) was used to convert the material to the PTMA nonconjugated radical polymer. Additionally, atom transfer radical polymerization (ATRP) has been utilized frequently to generate well-defined nonconjugated radical polymers. For instance, the polymerization of the precursor monomer, 4-methacryloyloxy-1-((1'-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (MPEOT), followed by an oxidative cleavage of C-ON bond, afforded PTMA with a low dispersity and controlled molecular weight (M_n ~30 kg mol^{-1} (tunable) and $Đ \leq 1.2$) (Figure 4b).[39] Although reported less frequently, nitroxide mediated polymerization (NMP) also has been employed. For instance, a random copolymer of poly[(styrene)-*co*-((4-*N*-carbazolyl)-2,6-dichlorophenyl]bis-(2,4,6-trichlorophenyl)methyl)] (PS-CzTTM) has been successfully synthesized (M_n = 38.7 kg mol^{-1} and $Đ$ =1.12) (Figure 4c).[19] In general, the implementation of free radical and living radical polymerizations allows for the production of more open-shell moieties, and the transition to living radical polymerization techniques, either using controlled radical or ionic mechanisms, has allowed for the creation of well-defined homopolymers and copolymers. This shows the power and versatility that polymer chemistry adds to the radical polymer community.

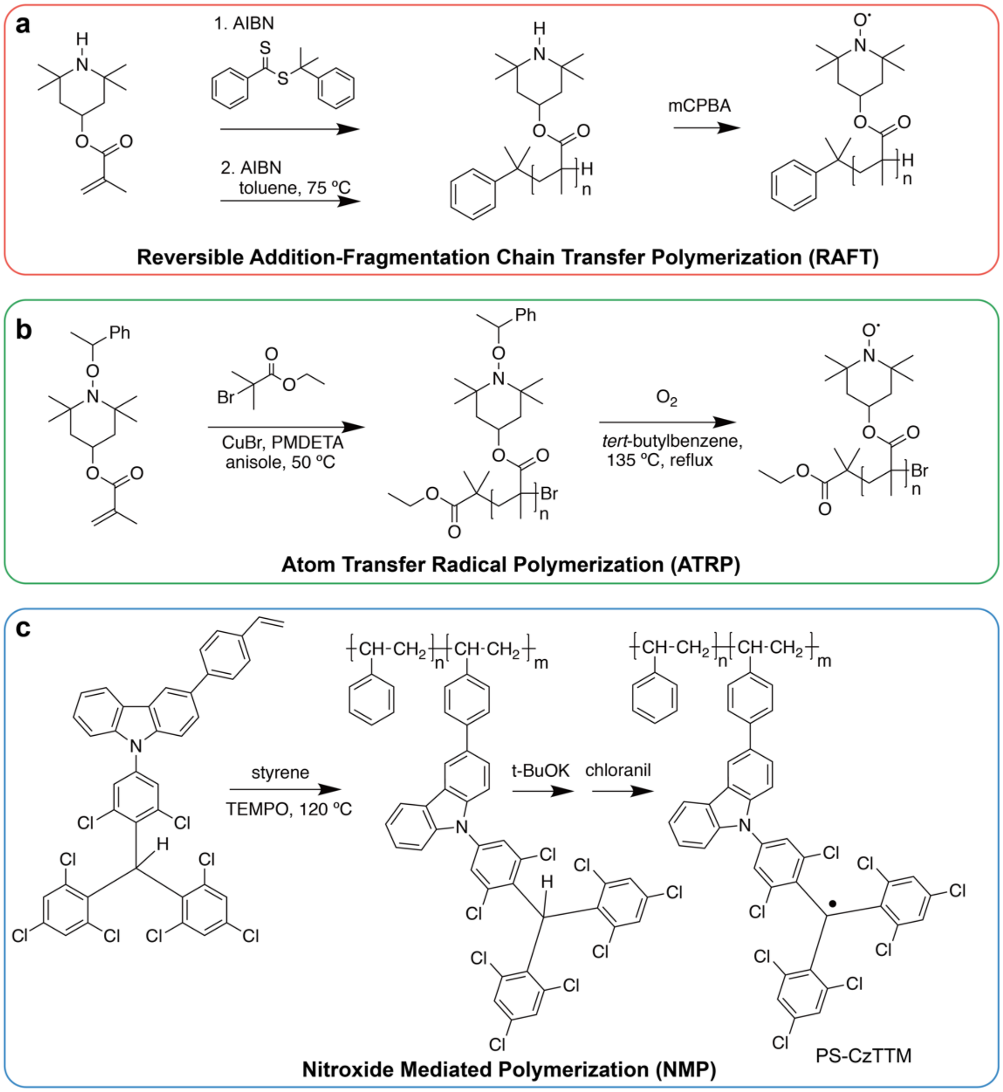

Figure 4. Representative controlled radical polymerization schemes for the synthesis of (a) PTMA using a RAFT mechanism, (b) PMTA using an ATRP mechanism, and (c) poly[(styrene)-*co*-(czTTM-styrene)] using an NMP mechanism.

Post-modification of existing polymers motifs (e.g., by grafting to a polymer backbone with a radical-containing side chain) through the attachment of open-shell units (or precursors) provides an additional alternative in the syntheses of advanced polymer architectures. For instance, coupling and click reactions (e.g., azide-alkyne cycloaddition, hydrosilylation, and amidation) have been employed and various pre-synthesized polymer structures (i.e., poly(methylsiloxanes), polyacrylamide, and cellulose) have been combined to yield nonconjugated radical polymers, which highlights the robust nature of this approach.[41–44] For example, an alkyne-substituted verdazyl radical was coupled with poly(3-azidopropylmethacrylate) (N3-P) to render a verdazyl-based radical polymer.[43] The synthesis of poly[2,6-di-*tert*-butyl-4-((3,5-di-*tert*-butyl-4-(λ^1-oxidaneyl)phenyl)(4-((3-(methoxydimethylsilyl)propoxy) methyl)phenyl)methylene)cyclohexa-2,5-dien-1-one] (PGMS) was carried out through hydrosilylation of poly(methylhydrosiloxane) with 4-allyl-galvinoxyl-H in toluene catalyzed by a platinum complex, followed by oxidation with $K_3Fe(CN)_6$ to produce the final radical polymer.[44] The post-modification method, in general, follows a statistical incorporation, as the radical per monomeric unit can be quantitively measured. Therefore, it is clear that many different techniques can be employed to generate a suite of advanced nonconjugated radical polymer designs; thus, the only limitation in advancing these materials systems is the creativity of polymer scientists and a clear vision of the requisite molecular design features that will yield the desired performance in targeted applications. To expand from this general synthetic construct, conjugated radical polymers are a more recently-established class of materials that do not have as many direct analogs to closed-shell polymerization techniques. As such, an important avenue that needs to be addressed in the near-term by the community is to establish new means to create an array of conjugated radical polymers in a controlled and scalable manner.

2.2 Conjugated Open-Shell Macromolecules

Most materials within the subclass of conjugated open-shell macromolecules are conjugated radical polymers (CRPs). As the name implies, the primary difference from their nonconjugated radical polymer counterparts is their replacement of the nonconjugated backbone with a repeat unit backbone that is π-conjugated in nature (Figure 5a).[45–50] Moreover, the polymerization methods described in Section 2.1 also must be modified for the syntheses of CRPs, as the polymer backbones typically associated with these materials [i.e., polyacetylenes, polythiophene, polypyrrole, polydithienopyrrole, and poly(3,4-ethylenedioxylthiophene) (PEDOT)] are not amenable to frequently-used polymerization strategies for nonconjugated polymers. Instead, techniques such as oxidative polymerization using a chemical agent or electrochemical polymerization have been commonly implemented for polythiophene-based CRPs; however, some oxidative impurities can be retained in final products.[45,48,49] To circumvent this issue, direct arylation polymerization (DArP) has been used to synthesize a TEMPO-Based CRP with little or no metallic residues.[51] In a similar manner, Stille coupling and Grignard metathesis (GRIM) polymerization methods have been applied to offer copolymers of CRPs that contain little or no residual impurities.[50] Importantly, versatile synthetic strategies have been developed for CRPs that should enable diverse CRP development to occur in a rapid manner.

Beyond the oft-used design paradigm of having a radical group attached at the pendant site of common conjugated polymers, low-bandgap, open-shell donor-acceptor conjugated polymers have recently arrived as a new means by which to generate CRPs, as demonstrated primarily by the Azoulay group (Figure 5b).[52–55] This type of radical polymer is realized by the Stille cross-coupling copolymerization of cyclopentadithiophene (the electron donor) and thiadiazoloquinoxaline (the electron acceptor) molecular building blocks. The donor-acceptor structure of these two moieties renders several unique features including: (i) that the singlet state (S=0) and the triplet state (S=1) are almost degenerate, resulting in an open-shell ground state; (ii) narrow optoelectronic; and (iii) the fact that the open-shell species are resonance stabilized by extended π-electron systems as well as steric hindrance. These properties make CRPs largely complementary to non-conjugated radical polymers and use cases can be envisioned where both might be used. Additionally, the diradical CRP ground state renders distinct electronic and spintronic properties that will be introduced in Sections 3 and 4. Although this class of material is still in its early stages, it is also expected to quickly develop since it can leverage mature synthetic approaches developed for donor-acceptor copolymers polymers.

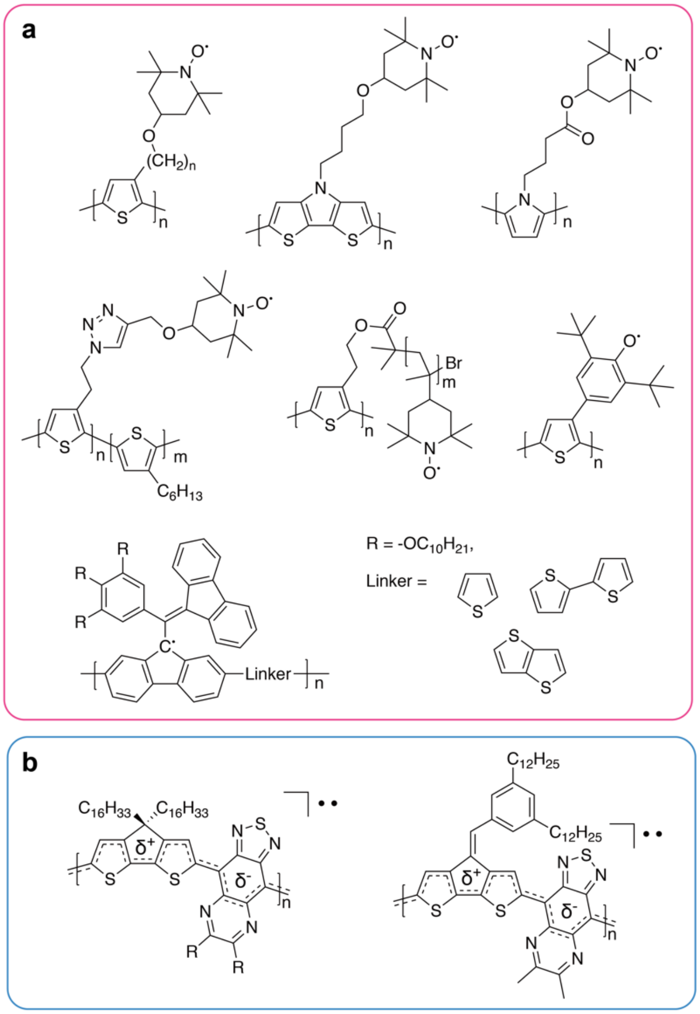

Figure 5. Two types of synthesized conjugated open-shell macromolecules. These are (a) conjugated radical polymers composed of polythiophene, polypyrrole, polydithienopyrrole, polyacetylene, and poly(3,4-ethylenedioxylthiophene) (PEDOT) backbones with pendant open-shell groups present, and (b) low bandgap, open-shell donor-acceptor conjugated polymers that have diradical character associated with them.

2.3 Polyradicals

Polyradicals are polymers composed of open-shell repeat units that lack distinct backbone and open-shell components. They are distinguished from the previous macromolecular classes in that they often display large degrees of radical delocalization; however, it should be stressed that there is no clear delineation between polyradicals and conjugated radical polymers. Thus, there is some overlap between these classes as defined in this effort. With this caveat in place, and following the Rajca classification system,[56] there are two primary types of polyradicals (Figure 6). Class I comprises polyradicals with open-shell moieties recurring along the main backbone of the polymer (Figure 6a),[56–63] and Class II comprises polyradicals with open-shell moieties that are associated with the pendant groups of the macromolecules *and* where these open-shell groups are linked to the conjugated backbone through a series of conjugated bonds (Figure 6b).[64,65] These advanced architectures led to a high density of and strong interaction among the radical sites in polyradicals. In turn, this design motif typically results in these materials exhibiting a high-spin ground-state and long-range magnetic ordering.

Due to the synthetic challenges of generating these materials, the number of polyradical reports is limited relative to those seen for the nonconjugated and conjugated radical polymers described above.[56–63] In the case of Class I polyradicals, their building blocks are usually interconnected "triphenylmethyl" radicals that function as ferromagnetic coupling units (fCUs), which are formed by a controlled oxidation of the corresponding carbanions utilizing s-bock metals. These fCUs support the dominant interactions between neighboring radical sites through π-orbital facilitated coupling. Dendritic and star-branched structures built on the fCU units have been developed to increase the number of electron spins; however, these spin systems are weak when defects are presented. Impressively, the Rajca group has adopted several strategies to minimize the defect impact, including a cyclic structure design to provide two pathways for spin interactions, and an organic spin cluster framework to minimize spin loss caused by out-of-plane twisting. On the other hand, Class II polyradicals are less studied, and they are often based on phenoxyl-bearing systems with an eye towards their spin properties (*vide infra*). On the whole, however, it is clear that the initial synthetic difficulties of polyradicals have been overcome by excellent polymer chemists, and the future development will point to design of polyradicals with ambient stability and applications in organic magnets (Section 4.4).

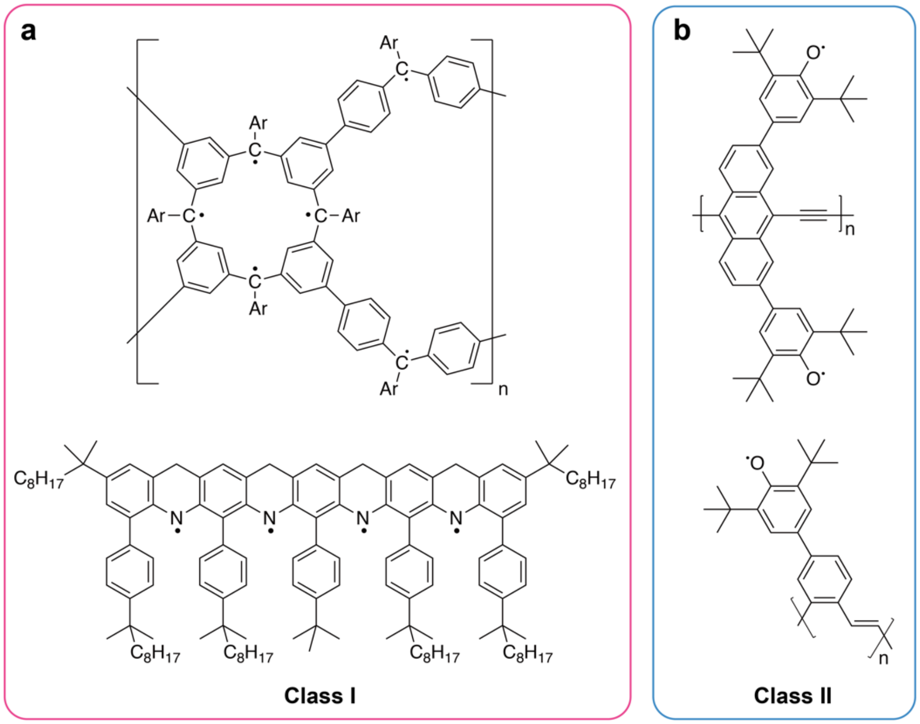

Figure 6. Representative polyradical chemical structures that are either (a) Class I or (b) Class II according to the Rajca nomenclature system (see main text for description).

In summary, through the combination of emerging radical chemistries and advanced polymerization techniques, three different categories of open-shell macromolecules with different radical types, degrees of delocalization, and macromolecular architectures have been produced. The optimization and advancement of these material systems have allowed for the elucidation of structure-functional relationship and transport mechanism within these macromolecules. Moving forward, we anticipate that even more advanced materials design avenues will be developed to spur future technological advances as well.

3. Charge and Mass Transport in Open-Shell Macromolecules

Open-shell macromolecules transport charge via self-exchange reactions provided that the radicals are present at such a degree that they exhibit significant electronic coupling and/or if the segmental motion of the polymer is large enough to increase the interaction radii of the radicals. Furthermore, these mechanisms are strongly impacted by processing and application details, including whether the polymer is dry or swelled by an electrolyte, the degree of radical delocalization, and whether mass transport is coupled with charge transport. All of these factors are also related to the polymer morphology, which can significantly vary within and across the distinct open-shell macromolecular classes described in the previous section. We have organized the discussion of these factors into distinct sections on charge transport (Section 3.1) and mass transport (Section 3.2), while recognizing that, in many cases, these properties are coupled.

3.1 Charge Transport in Radical Polymers

Open-shell chemistries can be classified as p-type (preferentially oxidized), n-type (preferentially reduced), and ambipolar (capable of being either oxidized or reduced in a relatively facile manner).[33] In all three scenarios, charge transfer occurs between a radical unit and its (neighboring) ionized analogue in a low-dielectric, and typically amorphous, medium. Due to the significant structural disorder, the relatively localized charge carriers, and the weak electronic coupling between radicals,[66] charge transport has been modeled based on several activated hopping mechanisms.[67–72] That is, with respect to solid-state conduction, charge transport in radical polymers is expected to be similar to that observed in conjugated polymers, with the main difference consisting in the degree of charge localization in radical polymers. For instance, TEMPO-based radicals are strongly localized to a pair of nitrogen-oxygen atoms and would likely be better approximated as a small polaron. On the other hand, resonance stabilized open-shell units can exhibit polaron dimensions akin to conjugated organics. In either case, the hopping mechanism includes an elementary hopping event where a charge moves between two adjacent sites. The hopping charge transfer rates can be calculated using Marcus theory to account for the polaron reorganization energy, as shown below.

$$k_{\mathrm{CT}} = \frac{2\pi}{\hbar}(H_{\mathrm{AB}})^2 \frac{1}{\sqrt{4\pi\lambda k_{\mathrm{B}}T}} \exp\left(-\frac{(\Delta G_0+\lambda)^2}{4\lambda k_{\mathrm{B}}T}\right) \qquad \text{Equation 1}$$

Here, H_{AB} is the electronic coupling proportional to the overlap integrals between the two hopping sites, λ is the reorganization energy of charge transfer, and ΔG_0 is Gibbs energy difference between sites. All of these quantities are, in principle, obtainable from density functional theory (DFT) calculations, with the caveats that the common approximation for the external contribution to the reorganization energy is crude[73] and that no inexpensive methods currently exist for performing configurational averaging of these quantities. For example, we recently demonstrated the importance of configurational averaging for the various quantities in Equation 1 by showing that the calculated charge transfer rates at a fixed nearest-neighbor separation could vary by several orders of magnitude depending on the molecular orientation and whether Boltzmann-averaging (i.e., weighting the probability of a configuration by its energetic likelihood) was used. This study confirmed the weak-coupling limit of the charge transfer for several prospective p-type, n-type, and ambipolar open-shell chemistries while also revealing the strong orientational dependence of transfer rates and the high-variability of reorganization energies across the species.

Energetic disorder is another important factor for charge transport that is indirectly included in Equation 1 through the ΔG_0 term. For a self-exchange reaction, ΔG_0 would ordinarily be zero because the reactants and products correspond to the same species; however, distinct electrostatic environments around each species can break this equivalence and lead to energy broadening and charge trapping. For a solid-state polymer thin film, the source of this broadening might be caused by structural defects associated with the amorphous morphology, while for electrolyte-swelled polymers heterogeneous dielectric environments may contribute to the broadening. For both scenarios, the current reliance on open-shell chemistries that exhibit large dipole moments is likely detrimental to charge transfer. Although exceptions exist, large dipole moments are conducive to trap formation and have typically been avoided by the organic semiconductor community. Similarly, Kemper et al. recently reported that an average energetic disorder of ~230 meV and the occurrence of deep energetic traps in the PTMA radical polymer due to large electrostatic fluctuations.[67] These factors suggest that moving towards symmetric and lower dipole moment radical motifs may be a relatively facile means of improving charge transport by reducing trap formation in the next generation of open-shell macromolecules.

On the other hand, relatively little has been established regarding how polymer morphology affects charge transport in radical polymers and the degree to which non-ideal morphologies are currently a limitation to charge transport. From a computational perspective, the absence of validated force fields for this class of materials is a major impediment to performing the molecular dynamics (MD) studies that could address these questions. For example, Larsen and co-workers have performed one of the few MD investigations on the interplay between internal polymer packing and solid-state charge transport in PTMA by supplementing the Amber force-field with TEMPO terms.[68] This study predicted the magnitude of inter-radical packing at a separation of 6-7Å (Figure 7a). Additionally, this work introduced an inter-site radial distribution function (RDF) weighted by squared-electronic-coupling, and it concluded that interchain charge transport dominated (i.e., it accounted for 84% of the charge transfer events) relative to intrachain radical-radical charge transfer.

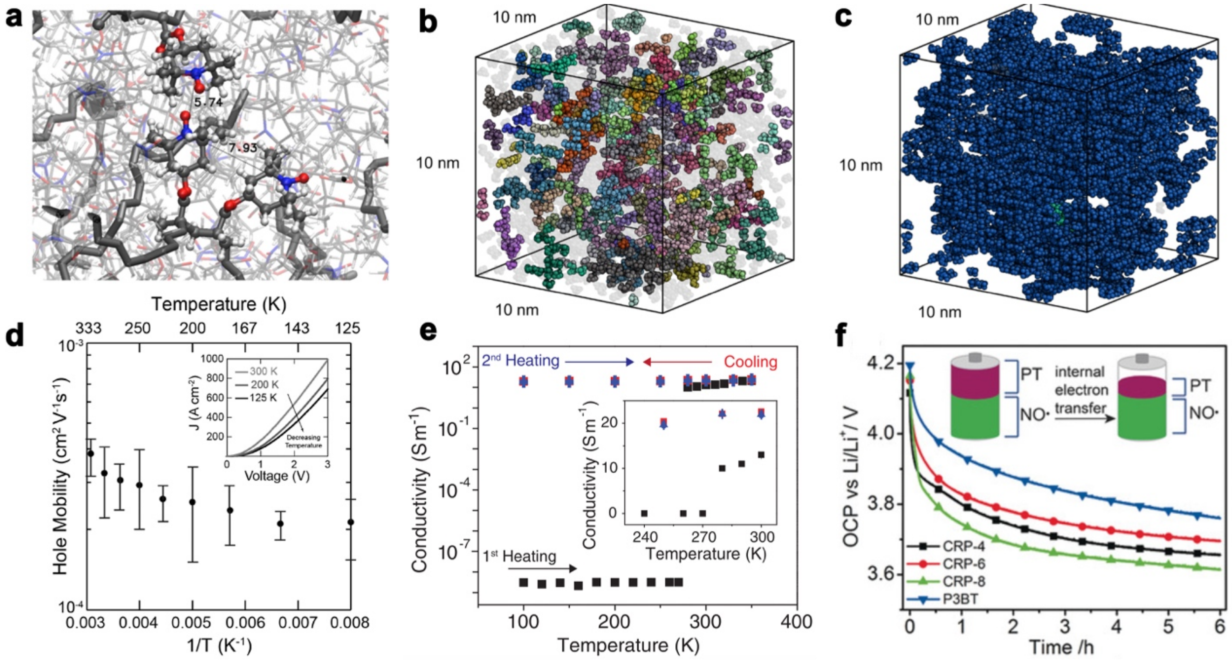

Figure 7. (a) PTMA morphology snapshot calculated by classical MD simulations. Atom representations. C – gray; H – white; O – red; N – blue. Monte Carlo configurations for (b) unannealed and (c) annealed PTEO films. Independent networks composed of less than five molecules are colored as gray and transparent in (b). The continuous, percolating network for charge transport is colored navy blue in (c). (d) A weak temperature dependence of the PTMA hole mobility measured in space charge-limited current device is observed in experiments. (e) Real-time annealing and electrical conductivity measurement of a PTEO film across a range of temperatures. (f) The open circuit potential as a function of time demonstrates the internal charge transfer in a CRP. Image (a) is reproduced with permission from ref 68. Copyright 2014 American Chemical Society. Image (b) (c) (e) are reproduced with permission from ref 74. Copyright 2018 AAAS. Image (d) is reproduced with permission from ref 72. Copyright 2014 AIP Publishing. Image (f) is reproduced with permission from ref 47. Copyright 2017 Wiley-VCH.

A morphology change has also been hypothesized to occur in the champion solid-state radical conductor, PTEO, after thermal annealing above the glass transition temperature.[74] In this case, annealing is concomitant with a permanent increase in conductivity by more than ten orders of magnitude. This large of a jump is more consistent with the annealing causing a percolation transition than with a mean increase in local charge transfer rates. Lattice-based Monte Carlo simulations were used to demonstrate how PTEO fails to form spontaneously percolating radical networks at typical TEMPO loadings (Figure 7b), while marginal radical reorganization from thermal annealing leads to percolation over larger scales (Figure 7c). Additional evidence for a change in the percolation lengthscale being responsible for this jump in conductivity was that the high conductivities post-annealing remained limited to relatively small channel lengths (~0.5 μm), suggesting that the percolation lengthscale was on this order after annealing.

Quantifying the effects of charge carrier densities and carrier mobility on the solid-state conductivity of nonconjugated radical polymers has proven challenging. That is, increasing the radical concentration yields more charge carrier sites and also alters the polymer morphology and radical packing, which in turn, alters the expected mobility of the system. By comparing the Kuhn length and the polymer contour length , Martin et al. concluded that an increased radical content will lead to a more rigid PTMA polymer, and a closer intermolecular radical proximity.[75] Furthermore, Bobela et al. implemented electron paramagnetic resonance spectroscopy to investigate the radical packing in PTMA-based copolymers that also contained poly(methyl methacrylate) (PMMA). These copolymers contained 20%, 60%, and 100% radical content, from which they observed that when the radical loading is > 60% of the number of repeat units, the radical-radical exchange coupling reaches a maximum.[76] Computational simulations of PGMS, an n-type radical polymer based on the galvinoxyl radical, also suggested that the intrachain coupling between radicals can saturate at concentrations as low as 50% when the radicals have a strong propensity to aggregate, while still requiring high loadings for effective inter-chain transport.[44] Thus, while it is difficult to separate the distinct factors that accompany increased charge carrier density, the evidence suggests that higher radical loadings are generally favorable and that exceeding a threshold level that is specific to each polymer-radical combination is necessary for obtaining significant charge transport.

Even within the restricted scope of a polaron hopping mechanism, a variety of macroscopic behaviors are still potentially possible (e.g., distinct temperature, electric field, and magnetic field dependencies) as is consistent with variable-range hopping and Gaussian disorder models. For example, a persistent mystery for these systems is that charge transport is typically weakly temperature independent for solid-state radical conductors, whereas hopping models predict a strong temperature dependence. This has been observed for the conductivity measurements of PTMA, PTNB, and PGSt, as well as the mobility measurement of PTMA ($\sim 10^{-4}$ cm^2 V^{-1}s^{-1} using a space charge-limited current (SCLC) model)[72] in several distinct device configurations (Figure 7d), which is more consistent with tunneling transport. Significantly, even the conductivity of the record-setting conductive polymer, PTEO, exhibits a no temperature dependence over a 180 K window, demonstrating that the phenomenon is not limited to low conductivity materials (Figure 7e). In contrast, for electrolyte swelled polymers (Section 3.2), charge transport appears to be more strongly coupled to polymer segmental motion and exhibits consistent exponential temperature dependence. We stress that, at present, this tension has yet to be resolved, and establishing the foundational principles behind this observation would be a major advance for the field.

Charge transport in conjugated radical polymers is dominated by the inter- and intra-charge transfer along and between the conjugated backbone. In addition, internal charge transfer between conjugated units with radical sites also contribute (Figure 7f).[47] This has been confirmed by the rapid initial drop of the open-circuit potential (OCP) during in situ spectroelectrochemical measurements a series of TEMPO-based CRPs, which is an indicator of internal electron transfer. The poorly matched redox potentials between the conjugated backbone and the radical species lead to spontaneous doping and de-doping, which is undesirable. Such systems remain fundamentally interesting but have yet to achieve high conductivity values. Among the design challenges is the need for a non-conducting spacer that links the open-shell species to the conjugated backbone which impacts the polymer packing and conductivity. For low bandgap open-shell donor-acceptor conjugated polymers, on the other hand, high conductivity (8.18 S cm^{-1}) has been reported. The origin of this high conductivity is the result of effective electronic communications among delocalized open-shell sites in electronic communication along the long-range ordered rigid backbone conformations.

3.2 Mass Transport in Electrochemical Systems

In electrolyte-support systems, the timescale of physical diffusion and charge diffusion are comparable; thus, the influence of mass transport on charge transport is not negligible as in the solid-state transport scenario described above. A diffusion-cooperative model has been proposed that is specific to radical polymers (Figure 8a).[70] This model quantitatively explains the ~10^3 fold decrease in the charge transfer rates of bimolecular and heterogeneous for the first time (Figure 8b). It also validates that the physical diffusion is much faster than electron diffusion in a solution-based system.

Moreover, mixed conduction persists in systems where charge transport is strongly coupled with ion transport.[77–81] To computationally investigate PTMA as a cathode material, for instance, Larsen and co-workers have introduced solvent and ions to molecular dynamic simulations, and the change of state of charge (SOC) reflects different charged state of a battery.[82] The simulations suggest that the counterion in solvent strongly binds to the TEMPO cation (i.e., binding energy greater than $2k_BT$), thereby hardly altering the radical packing. Real-time dual ion transport in PTMA has been reported by Wang et al. for the first time, via in situ electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) during cyclic voltammetry, which pointed out that dual modes including lithium ion expulsion and anion uptake dominate the redox process (Figure 8a and c).[77] These electro-chemical studies strongly suggest the coupled features of charge, ion and mass transport in open-shell macromolecules. In the future, further efforts in developing novel modeling and experimental means are encouraged in the community to elucidate the different transport phenomenon in dry solid-state devices and electrolyte-supported systems.

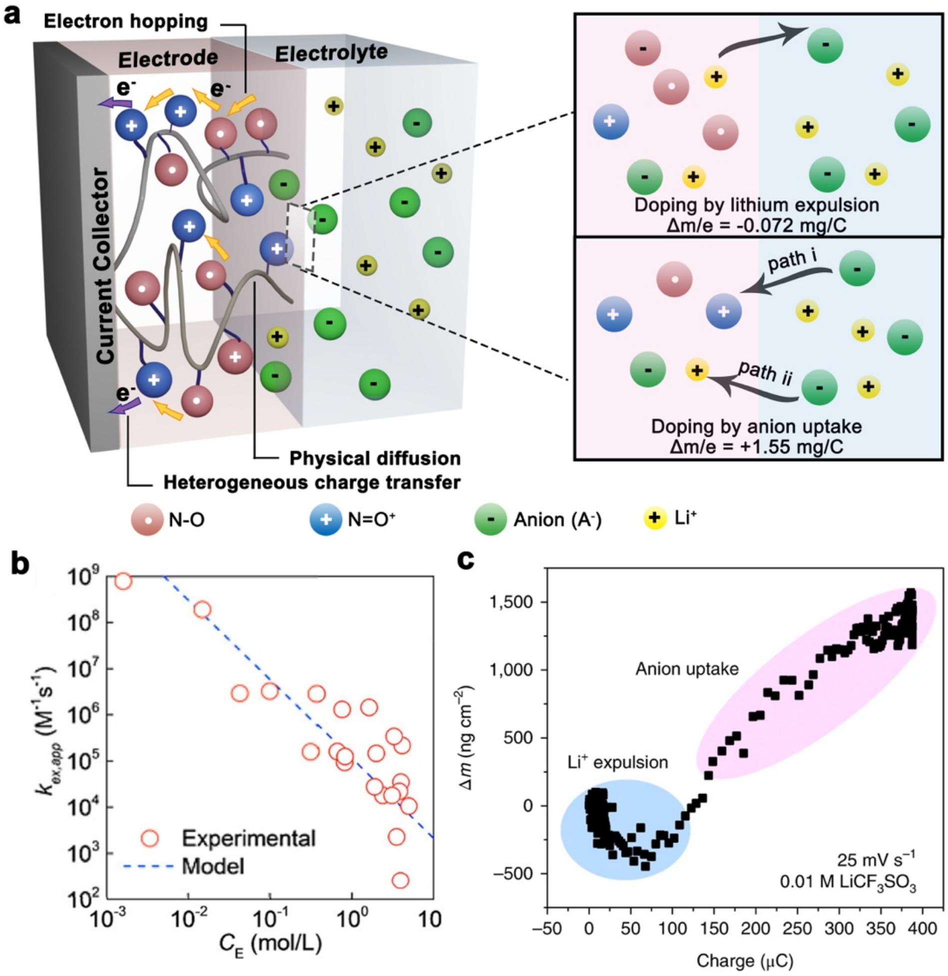

Figure 8. (a) An illustration of electron hopping, and heterogeneous charge transfer ($k_{ex,\ app}$) in a nonconjugated radical polymer in the electrode in the left side. The ion doping process (lithium expulsion and anion uptake) between electrode and electrolyte in the right side. The mass change per electron charge transferred (Δm/e) data is provided from ref 77. (b) The diffusive-cooperative model exhibits good agreement with experimental measurement in terms of the $k_{ex,\ app}$ - redox concentration (C_E) relationship. (c) The electrode mass change versus charge passed during a PTMA oxidation process mearured by EQCM-D. Image (b) is reproduced with permission from ref 70. Copyright 2018 American Chemical Society. Image (c) is reproduced with permission from ref 77. Copyright 2019 Springer Nature.

4. Applications in Electronic and Spintronic Devices

The unique electronic structure of radical-containing polymer makes them appealing for use in a variety of organic electronic and spintronic devices. For example, manipulating the redox chemistry allows new applications in batteries and energy storage devices. Controlling the charge transport enables applications in memory devices. The doublet excited state of the radial-containing species provides a new possibility to circumvent the triplet state energy lost in organic light-emitting diodes (OLEDs). Furthermore, studying the spin transport allows for spintronic applications. While many potential comments could be made with respect to these end-use applications, we will focus on how the molecular design of open-shell macromolecules impacts their governing physical chemistry, and thus, the desired application properties.

4.1 Batteries

Due to the scarcity of metals that are commonly used in rechargeable batteries (e.g., Li and Co) and the continuation of the trend to move towards flexible electronic applications, many research efforts were had with respect to organic materials in batteries.[83–85] Organic radical batteries (ORBs) are a subclass of organic batteries where one (metal-ORB) or both (all-ORB) electrodes are replaced by an organic, radical-containing material (Figure 9a), and these batteries have many attractive features.[85] First, many stable radicals have redox potentials that allow for high plateau voltages to be had. Second, the single redox potential ensures a stable voltage compared to π-conjugated polymers where the redox potential changes with doping level.[84] Third, radical polymers have remarkably short charging time (> 100 C, zC = fully charged in z^{-1} hours).[83] Due to their significant promise, ORBs are the most well-studied application of radical polymers, and this application space has driven the syntheses of many new materials.

The first metal-ORB was published first by Hasegawa,[86] and a subsequent effort was published by Nishide[87] where the cathode of a lithium-ion battery was replaced by a radical polymer-based (i.e., PTMA) composite. These systems have a high voltage of ~3.6 V vs. Li/Li$^+$, resulting in the specific capacity of 77 A h kg^{-1}, which is a good fraction of the theoretical limit of

111 A h kg^{-1}. Moreover, the battery demonstrated good stability over > 1,000 cycles and the capability of being fully charged within 5 minutes due to the fast electron-transfer rate (> 10^{-2} cm s^{-1}). Since then, PTMA has become the most prevalent material incorporated into ORBs, and the theoretical maximum capacity of PTMA was reached by optimizing cell geometries.[88–90] Despite the fact that PTMA has led the charge, many additional efforts have been made to develop new materials with a higher theoretical capacity. This includes the development of the 6-oxoverdazyl, nitronyl nitroxide (PTIO),[91,92] phenoxyl,[26] and PROXYL[23] radical species as the pedant groups in a variety of macromolecules for ORB applications. Replacing the polymer backbone was also attempted, such as in the case of PTVE (Figure 1b), which has a higher theoretical specific capacity of 131 A h kg^{-1} relative to PTMA.[93] Another way to improve the theoretical capacity is utilizing both TEMPO oxidation (i.e., to form the oxoammonium cation) and reduction (i.e., to form the aminoxy anion) reactions together. In the past, reduction reaction is usually not employed because the it is irreversible. However, if reversible TEMPO reduction can be realized, the theoretical specific capacity of PTMA would be doubled (up to 222 A h kg^{-1}).[94,95] These efforts in improving specific capacity manifested the structure-properties relationship of radical polymers and motivated the development of many new radical polymers.

Despite the progress in specific capacity, a major drawback of these organic radical polymers as electrode materials is their low electrical conductivity, and therefore, highly conductive additives (~50%) and binders (~10%) are usually needed, which decreases the overall capacity of the battery. Although the electrodes can be optimized by engineering the composites, such as wrapping PTMA on the SWCNT,[97–99] the low conductivity problem of radical polymers has not been resolved in full.[40,85] Conjugated radical polymers (section 2.2) were developed with the aim of improving the conductivity of nonconjugated radical polymers, yet they showed poorer conductivity and specific capacity when used as active material due to the internal charge transfer.[15,47,48] As such, the intrinsically conductive non-conjugated radical polymers (e.g., PTEO) may be more promising.[74]

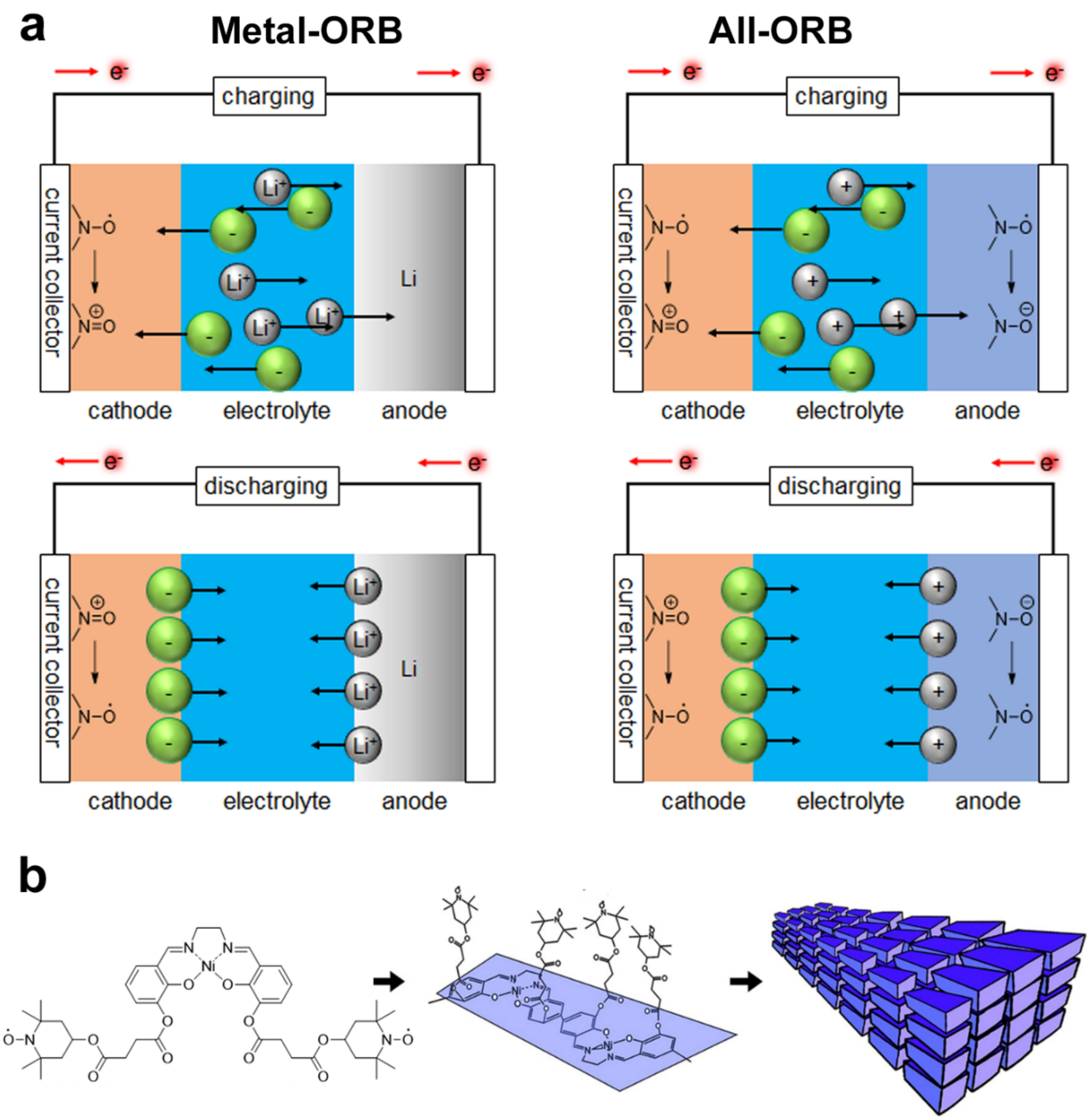

Figure 9. (a) Schematics of metal-ORB and all-ORB during charging and discharging. The nitroxide is taken as an example for the cathodes. Li is taken as an example for the anode for metal-ORB and the nitroxide reduction is used for the all-ORB. (b) Formation process of highly conductive p-DiTS cathode. Image (b) adapted with permission from ref 96. Copyright 2020 Wiley-VCH GmbH.

In fact, Guo et. al showed that, by using the PTEO, only 30% of conductive agents was required to achieve power density of more than 500 W h kg^{-1}.[100] More recently, a different team demonstrated that it is possible to grow highly conductive (> 100 S cm^{-1}) polymeric bis(salicylideniminato) nickel ((NiSalen) bearing TEMPO pendent groups directly on a metal electrode (p-DiTS) (Figure 9b). The p-DiTS serves simultaneously as current collector and active material, resulting in 83 A h kg^{-1} at 60C to 800C without additives.[96] Eventually, improving the conductivity aligns with the overarching goal of studying charge and mass transport within radical polymers.

Another key issue is self-discharge, in which the radical polymers slowly dissolve in the electrolyte solution, forming a redox shuttle that discharges the battery.[88] Efforts have been made to address this issue, including: modulating the polymer backbones and electrolyte composition to tune the solubility,[101,102] crosslinking,[103] grafting the polymer on the collector,[104] and encapsulation.[105] If the electrolyte solvates the active material adequately without dissolving it, high ionic conductivity can be achieved. For example, the poly(acrylamide) with TEMPO pedant groups (PTAm) had good solvation in aqueous electrolyte while remained undissolved, and the resulting conductive agent-free film showed capacity proportional to the thickness, indicating good conductivity.[101] These recent progresses in electrical conductivity of radical polymers provide a clear path toward higher energy-density ORBs.

All-ORBs, in which both electrodes are replaced by organic radicals, allow for the realization of recyclable plastic batteries that are cost-effective and environmentally benign. In fact, certain efforts have achieved this goal by using an n-type anodic material that is paired with TEMPO-based p-type cathodic materials. The first All-ORB was realized using PGSt (Figure 2b) as the n-type material and PTNB (Figure 2e) as the cathode. The resulting cell showed a plateau voltage at 0.66 V,[107] which is relatively low for practical applications. This low voltage was due to the rather close redox potential between the cathode and anode. Thus, using redox pairs with higher potential difference is extremely promising.

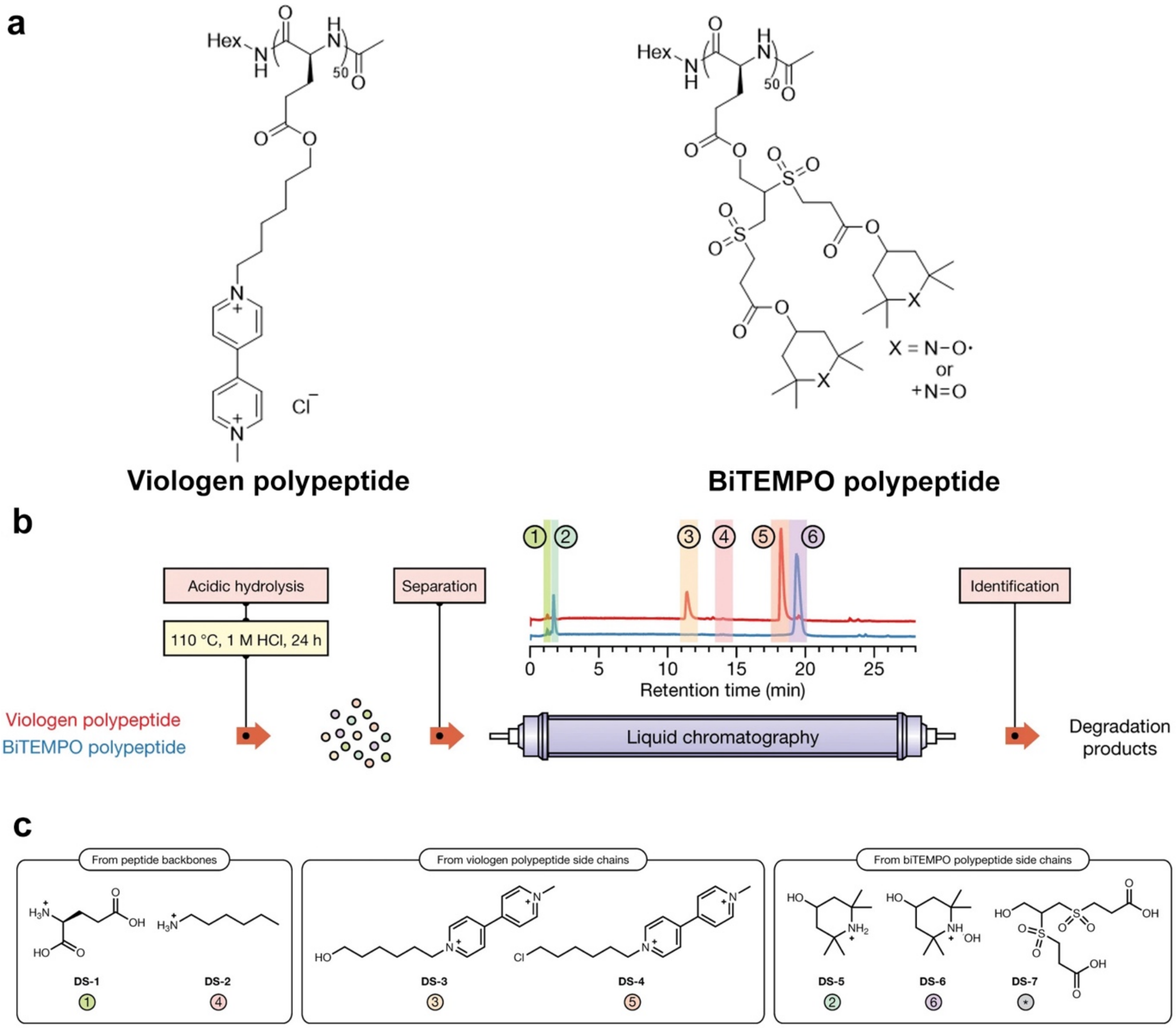

Figure 10. (a) Chemical structure of the BiTEMPO polypeptide and the viologen polypeptide. (b) On-demand decomposition of the polypeptide cell in 1 M $HCl_{(aq)}$.at 110 °C and (c) the corresponding products. Images (b), (c) reproduced with permission from ref 106. Copyright 2021 Springer Nature.

For example, a PTAm (cathode) and polyviologen derivative PV10 (anode) cell showed a high plateau voltage of 1.2 V.[101] In another work, an ambipolar PTIO radical-based radical polymer, poly[4-(nitronylnitroxyl)styrene], was employed on both electrodes of an ORB, forming a "poleless" battery, which can be charged/discharge in both directions and showed a plateau voltage of 1.3 V.[108] Recently, an innovative effort developed a new recyclable all-ORB with radical-containing polypeptides (Figure 10a). The all-ORB was composed of biTEMPO polypeptide (cathode), and viologen polypeptide (anode) had two plateau voltages at 1.1 V and 1.6 V with a specific capacity of 37.8 A h kg^{-1} (theoretically 44.5 A h kg^{-1}). Interestingly, the cell featured on-demand degradation. By placing the cell in 1M or 6M HCl at 110 °C, the polypeptide backbones hydrolyzed into recyclable products that can be used as raw materials of the cell(Figure 10b, c).[106] This work has proven that, with the incorporation of bioinspired chemistry, ORBs can be truly "green".

To integrate the intermittent power generation from renewable energy into the power grid, large-scale energy storage is required, and redox flow batteries (RFBs) are a safe and scalable option (Figure 11a).[109] Because the redox-active materials are dissolved in solution, the solutions containing them are called the catholyte and the anolyte in a manner that corresponds to the cathode and anode in lithium-ion batteries. During operation, these solutions circulate through the redox chamber, undergo oxidation and reduction processes, and a membrane prevents the intermixing of active materials while allowing for counterion exchange. While most RFBs utilize vanadium-based systems as the active materials, the scarcity of vanadium and the expensive ion-exchange membrane that must be used to prevent crossover results in high cost.[109] For these reasons, organic RFBs are being studied as means to replace the anolyte, catholyte, and/or both. Contrary to ORBs, where the organic radicals need to be polymerized to prevent dissolution, RFBs require high solubility of the active materials for a high specific capacity. As such, small molecules are usually more advantageous than polymers and several examples of TEMPO and viologen based RFBs have been published.[110–113] Nevertheless, molecular RFBs are susceptible to cross-contamination (i.e., interdiffusion of anolyte and catholyte across the membrane) that deteriorates the long-term capacity. Using ambipolar species as both the catholyte and anolyte is a possible solution for non-aqueous RFBs.[114–116] For aqueous RFBs, typical ambipolar radicals exhibit redox couples that exceed the water voltage window (i.e., at voltages < 1.2 V) and are not suitable. One workaround has been to form bipolar species by covalently attaching a suitable catholyte and analyte such that a symmetric RFB with a voltage of ~1.2V can be obtained.[117,118]

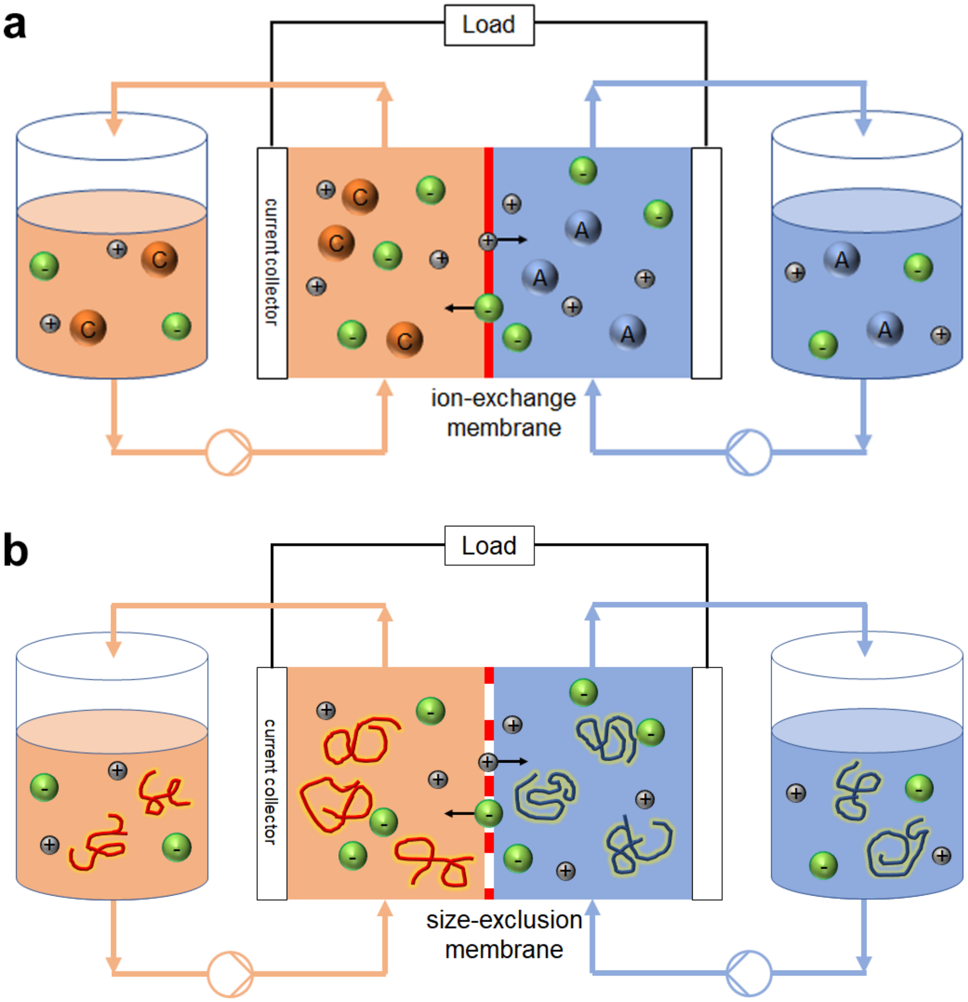

Figure 11. (a) Schematic of RFB. Spheres with "C" and "A" labels represent the catholyte and anolyte, respectively. For metal ion or small molecule active materials, an ion exchange membrane is required. (b) All-organic RFB with polymeric active materials (represented by self-crossing lines). Due to the large hydrodynamic radius of polymers, cost-effective size-exclusion membrane can be used.

Polymeric RFBs are especially powerful in terms of preventing cross-contamination because of the large hydrodynamic radii associated with macromolecular species relative to small molecule radical derivatives. In turn, this allows for the use of inexpensive size-exclusion membrane separators in the RFBs (Figure 11b). However, the high viscosity nature of linear polymeric solution is problematic.[109] As such, non-linear polymers or micelles are more favorable for having large hydrodynamic radius while contributing relatively little to the solution viscosity. An example is PTMA that had a polynorbornene derivative grafted to it (PNB-*g*-PTMA), of which the hydrodynamic radius can be controlled by molecular weight (i.e., from 3 nm to 20 nm in tetrahydrofuran) while maintaining a low viscosity.[119] Similarly, the Schubert team demonstrated an RFB that contained a radical polymer that was synthesized by copolymerizing MMA monomers with TEMPO and trimethyl ammonium chloride pedants (P(TMA-*co*-METAC) to form the catholyte. Then, styrene monomers were copolymerized with methyl viologen and trimethyl ammonium chloride to create the anolyte macromolecule. The resulting solutions had low viscosity values and a Newtonian response. This resulted in an aqueous RFB that achieved 10 A h L^{-1} in capacity and high current density of 100 mA cm^{-2}.[120] Similar attempts were made with small molecule MV[121] or $Zn(ClO_4)_2$ anolyte.[122] Forming micelles in the solution serves a similar purpose. For example, a PTMA-*b*-PS block polymer formed a PS core and TEMPO corona in carbonate electrolytes, which allowed for 93% material utilization in terms of electrochemical activity.[123] The solubility was further improved by making the copolymer zwitterionic. More specifically, poly(TMA-co-[(2-(methacryloxy)-ethyl)dimethyl-(3-sulfopropyl)]ammonium hydroxide) exhibited high degree of utilization and solubility in NaCl aqueous electrolyte, and catholyte capacity over 20 A h L^{-1}.[124] By carefully choosing the functional groups and electrolyte compositions, radical polymer RFBs have overcame the solubility issues while wisely avoiding cross-contamination as well.

4.2 Memory Devices

Memory devices are essential building blocks for the microelectronics industry, and they come in distinct flavors. For instance, volatile memory devices, which often take the form of random access memory (RAM), need to be refreshed in a short period of time; thus, they require an external power source. Nonvolatile memory devices, on the other hand, can retain the data without refreshing. Based on the nature of how they are reprogrammed, nonvolatile memory devices can be further categorized into write-once-read-many (WORM) memories and data-erasable flash memories. No matter the memory type, these devices need to have different electrical resistance states. Thus, a good material for memory applications needs to have different conductivity states that can be triggered easily. Due to the reversible oxidative state change, stable organic radicals were studied as active materials for nonvolatile memories, especially in the form of resistive memories (i.e., as memristors).

The first radical polymer flash memory was introduced in 2007, and the device was composed of ITO/PTMA/PVDF/PGSt/Al. Here, the radical polymers served as charge injectors while the PVDF provides charge accumulation sites and prevents the recombination events (Figure 12a).[20] The high conductance ON state of the device was triggered by applying a negative bias of –7 V, where charges accumulate at the PTMA/PVDF and PVDF/PGSt interfaces. This lowers the charge injection barriers at the metal-organic interfaces, resulting in easier trap-assisted transport to PVDF layer. Similarly, it was returned to low conductance OFF state by applying a positive voltage of +5 V to remove the accumulated charge (Figure 12b). This resulted in 4 orders of magnitude change in the current ON/OFF ratio when it was read at and applied read voltage of +1 V, and it can undergo write-read-erase-read process (WRER) of > 10^3 cycles.[20]

The memristors mentioned above required both p-type and n-type materials and metal contacts with work functions that matched the SOMO levels of the radical with which they are in contact. However, the device structure can be simplified by using an ambipolar radical polymer that can inject both holes and electrons. In fact, Lee et. al. realized a flash memristor with Au/radical/Au simple device structure using the nitronyl nitroxide radical derivative, 2-(3'-*tert*-butyl-4',5'-dimethoxymethoxybi-phenyl-4-yl)-4,4,5,5-tetramethylimidazolidine-1-oxyl-3-oxide (NN-Ph-CarMOM). The resulting device behaved symmetrically against applied bias and showed stability for ~10^3 WRER cycles and retention for ~700 s.[125] Memristors employing ambipolar radicals can be further optimized through careful evaluation of the neutral SOMO level and the corresponding change in SOMO level due to the change in oxidative states (i.e., the Hubbard interaction energy). To this point, an ambipolar oxoverdazyl-based polymer, P6OV (Figure 1e), was utilized in memristor devices with structure of metal/polymer/metal (Figure 12c). The cathode was composed of Al/Ca due to the work function of Ca (3.1 eV) aligning well with the SOMO level of the reduced oxoverdazyl radical (i.e., the corresponding anion). By changing the negative electrode materials (ITO, few-layer graphene (FLG), Al and Ca/Al), the authors thoroughly studied the transport mechanism of the device and found that using ITO as negative electrode was the optimal for ITO work function matches well with the SOMO level of oxidized oxoverdazyl radical, promoting the hole injection. At the same time, the SOMO level of neutral oxoverdazyl molecule lies near the middle of Ca/Al and ITO, making the OFF state very resistive, resulting in on-off ratio ~ 10^2 to 10^3.[126]

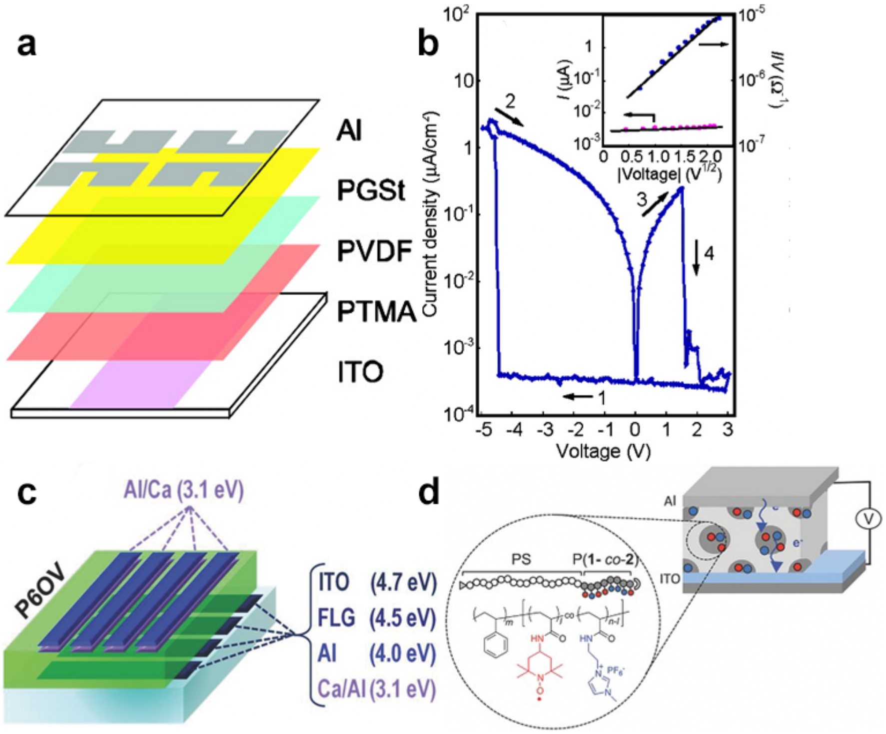

Figure 12. (a) The first memristor based on organic radical polymer and the (b) corresponding I-V behavior. (c) The P6OV memristor device using different bottom contact materials. (d) Schematic of the memristor based on block copolymer incorporating TEMPO (red circle) and imidazole (blue circle) on the same block in sphere morphology (radical/imidazole ratio: 0.70/0.27). Image (a), (b) reproduced with permission from ref 20. Copyright 2007 American Chemical Society. Image (c), (d) adapted with permission from ref 126. and ref 127. Copyright 2016 and 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In addition, the memory characteristics of the ambipolar radical polymers can be modulated by the presence of other species. As discussed above, TEMPO is ambipolar when an ionic liquid is present. As such, it was not surprising to observe hysteretic behavior in the poly(oxoammonium cation) derivative when it was mixed with PF_6 anion.[128] Base on this result, the Nishide group developed a TEMPO-grafted BMIM PF_6 ionic liquid. Mixing it with a block polymer of polystyrene and poly(ethylene oxide) (PS-*b*-PEO), the ITO/polymer/Al devices showed morphology-dependent memristor behavior. They further synthesized a PTNB-*b*-poly(ionic liquid) (PIL) with ROMP, and the resulting ITO/PTNB-*b*-PIL/Al devices showed WORM-like response.[129] Inspired by these works, flash behavior was achieved by synthesizing a block polymer containing poly(pentafluorophenyl acrylate) (PPFPA). Specifically, PS-*b*-PPFPA was synthesized using a RAFT polymerization mechanism followed by a click amidation to functionalize the PFPA block randomly with imidazolium and TEMPO (Figure 12d). With a spherical nanostructure the ITO/polymer/Al device showed flash behavior, an on-off ratio of $10^3$and a retention time of 15 hours with a radical/ion ratio of 0.70/0.27 were achieved.[127] The radical memristors not only provide a unique approach toward organic memories, but also demonstrate the importance of SOMO level alignment with electrodes work functions.

4.3 Organic Light-Emitting Diodes (OLEDs)

OLEDs play an important role in commercialized organic electronics today. In conventional close-shell organic emitters, the internal quantum efficiency (IQE) is limited to ≤ 25% because the other 75% of injected carriers become triplet excitons, which are normally not emissive. When this is combined with the ~20% of outcoupling efficiency, the external quantum efficiency (EQE) of traditional fluorescent OLEDs is often limited to 5%.[130,131] This can be overcome by incorporating heavy metal species into the molecular design as these elements aid in promoting triplet phosphorescence.[132] Alternatively, the fluorescent singlet state population can be increased by employing materials that have thermally activated delayed fluorescence (TADF),[133] or triplet-triplet annihilation.[134] While these methods effectively overcome the issue, the resulting complexity in synthesis can be directly circumvented with the open-shell species that have doublet ground and excited states in nature (Figure 13a). Unlike the close-shell species, upon excitation, organic radicals only generate doublet excited states, of which the charge transfer is spin-allowed, resulting in theoretically 100% of IQE.

The field of doublet fluorescent in organic radicals has centered on chlorinated triphenylmethyl radicals, including tris-2,4,6-trichlorophneylmethyl radical (TTM) derivatives, [135–137] perchlorotriphenylmethyl (PTM) derivatives,[138–140] and (3,5-dichloro-4-pyridyl)-bis(2,4,6-trichlorophenyl)methyl radical (PyBTM) derivatives.[141,142] Despite the promising properties of these organic radicals, extra care should be taken when they are applied to OLED systems. That is, it is important to ensure that the electrons and holes are not injected into the SOMO level simultaneously, or the recombination eliminates the charges without exerting photon. Secondly, these radicals usually need to be dispersed in host materials to prevent aggregation-induced quenching.[143] To date, OLEDs based on organic radicals have primarily focused on red luminescent TTM derivatives. For example, red OLEDs based on TTM-1Cz doped CBP exhibited an EQE of 4.3%.[144,145] The donor-acceptor structure of TTM-1Cz allowed intermolecular charge transfer between the carbazole donor HOMO and the TTM acceptor SOMO, allowing for it to have better performance than the unfunctionalized TTM version (EQE 2.8%).[146] On the other hand, incorporating the acceptor benzimidazole allowed the material to achieve an EQE of 5.4% and doublet formation ratio of 69% with blue shifted radiation.[147] The performance of TTM-donor emitter was further improved with TTM-DACz to a maximum EQE of 10.6%,[148] with TTM-NCz to a maximum EQE of 27%.[149] Li and colleagues elaborate on the design rules of the donor-acceptor type TTM emitter to be non-alternant hydrocarbon and must have substantial orbital amplitudes on the atoms to join the radical SOMO and donor HOMO.[150] Although the maximum EQE of the devices have been improved significantly in the past few years, the devices still suffer from large efficiency roll-off and poor stability.

Radical-containing polymers may provide a promising solution for improving the stability of these OLED devices. For instance, TTM-1Cz was attached to a polystyrene backbone to create PS-CzTTM (Figure 13b), and this macromolecule showed a photoluminescent quantum efficiency (PLQY) of 37.6% in solution and 24.4% in the solid state without host materials. Indeed, it had improved photostability compared with the small molecles.[19] Despite holding the potential of host-free geometry, the EQE of a host-free OLED based upon PS-CzTTM was only 0.9%, while with TPBi, the EQE was 3.0% (Figure 13c). This is due to the higher bandgap TPBi assisted the charge transport and provided pathway to charge trapping on the PS-CzTTM emitter. Nevertheless, the PS-TTMCz allows solution processibility and much higher current density at 8.1 mA cm^{-2}.[151] Despite radical-based OLEDs are still at the infancy, their initial efficiency values have demonstrated their potential. We expect the chemical design of radical moiety as well as the macromolecule backbone can further improve the performance of radical-based doublet OLEDs.

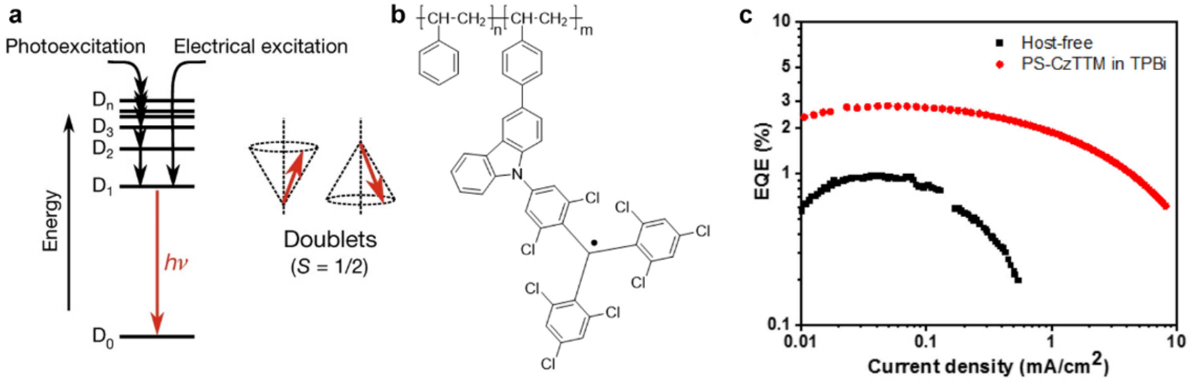

Figure 13. (a) Doublet emission following photo- and electrical excitation and the illustration on the electron spin vector representation for doublets. (b) The chemical structure of PS-CzTTM. (c) EQE-current density curve for PS-CzTTM with (red) and without (black) host TPBi. Image (a) adapted with permission ref. 149. Copyright 2018 Springer Nature. Image (c) reproduced with permission ref 19. Copyright 2020 American Chemical Society.

4.4 Spintronic Applications

The field of spintronic materials and devices has attracted burgeoning attention over the last two decades due to the potential for this arena to address the pressing issue of increased power-dissipation in nanoelectronic circuits.[152,153] Excessive heat generation increases electron scattering, and thus affects charge transport. Conversely, spintronic devices use the electron spin degree of freedom to process and store information, which does not result in heat production. However, the field is still in its developmental stage due to materials design and device fabrication challenges.

That is, state-of-the-art inorganic semiconductors do not meet the proper requirements for spintronic technology because of their extremely short spin relaxation times (~10 ns).[154] Spin relaxation time is an essential component because it characterizes how fast a non-equilibrium spin population decays, thereby determining if the material is suitable for spintronic systems.[153,154] As such, organic materials are promising candidates as these materials possess weak spin-orbit couplings, higher spin-relaxation times (~10 μs), and long spin-diffusion lengths (~100 nm), which are important components for efficient spintronics device to achieve the spin-conserved transport.[155,156] Spin-orbit coupling in organic small molecules and polymers is low because of the absence of nuclear spin in lightweight elements that compose most organic materials. Furthermore, organic electronic molecules are often designed to have a great deal of π-conjugation, and the orbital wavefunction of these charge carriers leads to weak hyperfine interactions.[157] This makes the spin relaxation time in organic molecules longer than that of inorganic materials.[158–160] In fact, the presence of these long spin relaxation times initially motivated the use of organic materials in the spintronics device.[161] Since the discovery of the first organic spintronics device,[161,162] a tremendous amount of effort has been performed on the spin transport properties of small molecules and π-conjugated polymers. Many of these materials have shown interesting results, and we point to an excellent review paper that discusses these results and their foundational mechanism in detail.[163] However, these materials have not shown much success in the spintronics as compared to their success in organic electronics because of their diamagnetic nature, where the spins oppose the applied magnetic field. That is, in π-conjugated polymers, the frontier electrons occupy full orbitals and there are no unpaired spins to interact with the electron spins injected from the ferromagnetic contact. This mostly leads to a loss of spin polarization, resulting in less effective spin devices. Thus, there is a critical need to discover new organic materials that possess a coexistence of conductivity and magnetism to solve the current challenges in organic spintronics devices. This coexistence of conductivity and magnetism for spintronics has been pointed out in many previous reports,[164–168] and radical-containing polymers offer a fresh perspective on this front in terms of a molecular design approach.

The most widely studied organic spintronic device is a spin-valve[162] in which the organic material is sandwiched between two ferromagnetic electrodes. These ferromagnetic electrodes respond to an externally applied magnetic field because of a non-equilibrium state between spin-up and spin-down electrons, and the electrons with majority spin are injected into the organic layer. When the direction of the magnetic field is parallel to the magnetic moment of the ferromagnetic electrode, spin-polarized injection of electrons is easier, resulting in low device resistance, while an antiparallel configuration leads to high resistance.[169] This change in resistance between the parallel and antiparallel configurations is called magnetoresistance (MR). There are three primary requirements for high magnetoresistance values in spintronic device. These are: (i) efficient injection of spin polarized carriers from the ferromagnet electrode to the organic semiconductor; (ii) spin-conserved transport through the organic layer; and (iii) successful detection of spin carriers by the other ferromagnetic electrode.[169,170] Efficient spin injection and detection can be increased by properly engineering the spin interface between the ferromagnetic electrode and organic material as smooth layers reduce the electron scattering events.[171–173] Moreover, the conductivity mismatch[174] between the ferromagnet electrode and the organic material can be addressed by employing conductive organic magnetic materials, which can aid successful spin injection, leading to high magnetoresistance response.

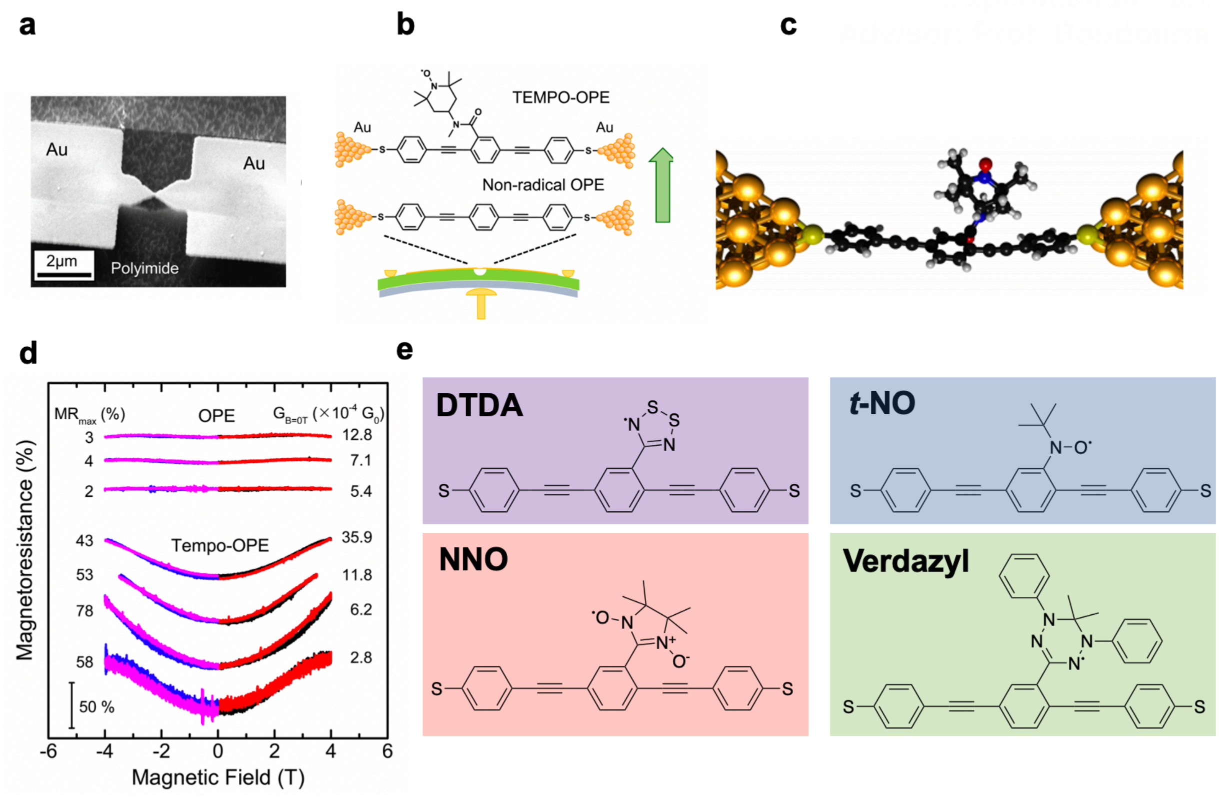

Figure 14. (a) The SEM image of single molecule junction. (b) TEMPO-OPE compared to a non-radical OPE with an applied magnetic field. (c) The framework for incorporating radicals between gold electrodes. (d) Large MR behavior due to the presence of the radical group showing that TEMPO is a promising chemistry for spintronic applications. (e) Possibility of different incorporation of radicals in the OPE backbone and study the spin-transport behavior. Image (a), (b) and (d) reproduced with permission from ref 175. Copyright 2016 American Chemical Society. Image (c) is reproduced and (e) is adapted with permission from ref 176. Copyright 2021 American Chemical Society.

Here, we stress the need to evaluate a different class of organic materials with unpaired electrons that are tailored for spintronics applications. That is, the spin of the unpaired electrons in radicals gives rise to magnetism, and this spin degree of freedom can find its best use in spintronic device applications.[177] For instance, many stable open-shell chemistries, such as the TEMPO, verdazyl, and nitronyl-nitroxide radicals, have been studied for their suitable magnetic properties.[178,179] For the bulk magnetic properties of the radicals, it is important for the unpaired electron to be delocalized over the large part of the atomic skeleton, and these bulk magnetic properties of these radicals have been discussed and summarized well in recent review article.[179]

Besides magnetism, these stable radicals have also shown promising spin transport behavior when employed in single molecule junction devices. In one of the reports, TEMPO-based single molecule junction demonstrated the encouraging nature of open-shell radicals for spintronic device.[175] The spin was only delocalized on the radical unit, and the conjugated oligo(*p*-phenyleneethynylene) (OPE) backbone provided the system with conduction electrons (Figure 14). When the TEMPO radical was oriented towards the thiol group (covalent bond between OPE and Au electrode), the unpaired electron could interfere with the conduction electrons in the presence of a magnetic field, thereby affecting charge transport. This brought forward the large that magnetoresistance when the TEMPO radical was present compared to no magnetoresistance being observed when the TEMPO radical was absent (Figure 14d). This result suggested that radical interferes with the π-orbitals of the conduction electrons, and thus, affects charge transport. The authors also mentioned the possibility of incorporating the other stable radicals, as shown in Figure 14e, into the similar backbone.[176] Sugano et al.[180] reported the first organic molecule in which TEMPO was connected to a π-donor unit through an imide linkage. The idea was to provide the conduction electrons through the π-donor unit, which could interact with the localized spin on TEMPO. Besides TEMPO, other radical groups, such as the nitronyl nitroxide radical, are also promising stable radicals for spintronic applications.[181]

Several groups synthesized open-shell molecules with π-donor units bearing stable organic radicals of nitronyl-nitroxide.[182] The charge transfer complexes, and ion radical salts derived from these π-donor radicals showed the coexistence of both semiconducting and paramagnetic properties which are indispensable for spintronic devices. In two reports, a monolayer of the (2-(diethyl 4-methylbenzylphosphonate)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) (NitPOR$_2$) radical was grown on the magnetic electrode using common wet-chemistry-based strategies to design an organic spin valve (Figure 15).[173,183] The high positive magnetoresistance (~ +7%) was observed at low temperatures (i.e., 3 K), as shown in Figure 15c.

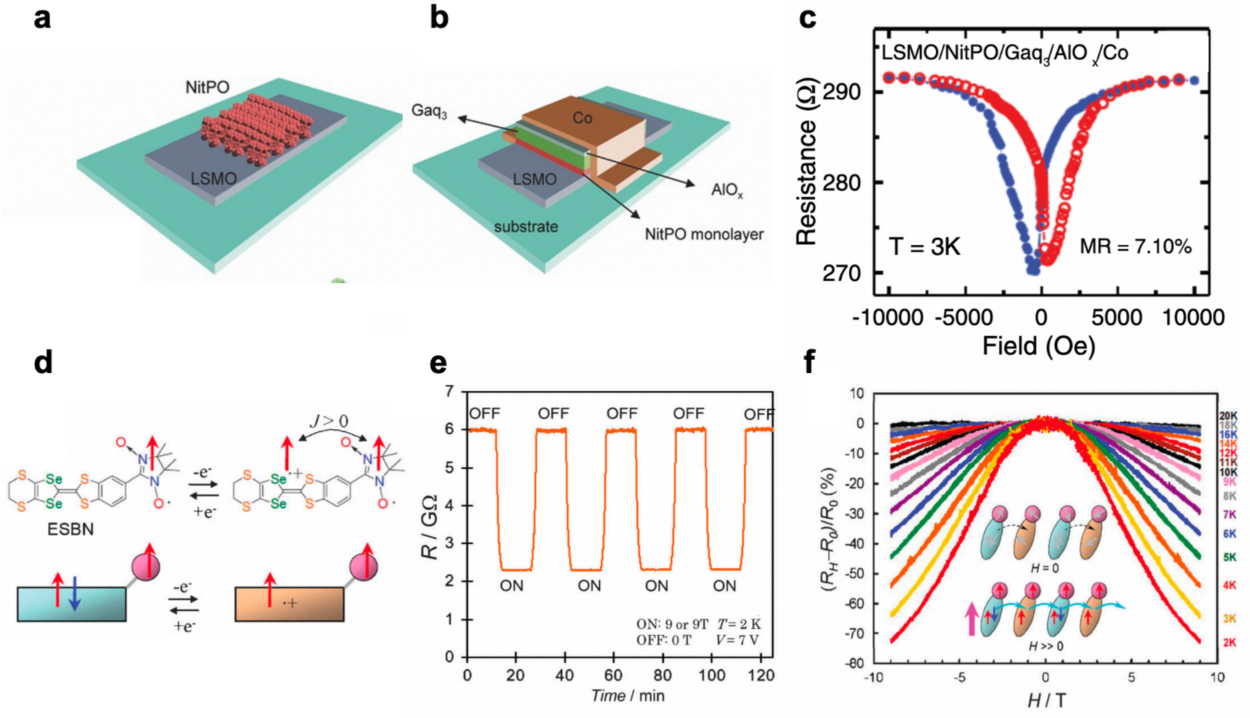

Figure 15. (a) The use of NitPO as a self -assembled monolayer on the bottom ferromagnetic electrode to improve spin injection. (b) A schematic of a spin valve fabricated using NitPO monolayer with ferromagnetic electrodes. (c) Magnetoresistance behavior of spin valve in (b), showing the promising nature of the nitronyl-nitroxide radical to improve spin-injection. (d) ESBN attached to the nitronyl-nitroxide radical. (e) Change in resistance with respect to time at applied field of 9T at 2k for schematics in (d). (f) Temperature-dependent magnetoresistance of (d). Image (a), (b) and (c) are reproduced with permission from ref 183. Copyright 2016 Wiley-VCH Verlag GmbH and Co. KGaH. Image (d), (e) and (f) are reproduced with permission from 184. Copyright 2008 American Physical Society.

Moreover, in two other reports, an ion-radical salt, (ESBN)CLO_4, with a nitronyl nitroxide group as the radical unit exhibited giant negative magnetoresistance of –70% at a temperature of 2 K with the applied magnetic field of 9 T (Figure 15d).[184] In this system, the tetrathiafulvalene (TTF) units are aligned parallel to each other, and there is a formation of half-filled conduction band due to the oxidation of these aligned TTF units. In the half-filled conduction band, the conduction electrons are magnetically coupled with the spin bearing radical unit. Thus, the observed negative magnetoresistance is attributed to the interaction between the conduction electrons and the spin of the localized radical site. In addition, more interesting properties were found for a benzo-TTF core bearing a nitronyl-nitroxide group as the BTBN radical. In this system, two bromine atoms are attached to the dithiol ring to increase the intermolecular interactions. As it is known that intermolecular interactions are important for the ordering of the spins a negative MR of –90% was detected at 2 K under the applied field of 2 T.[182] These results suggest that radicals can be beneficial for spintronics devices in multiple ways. The first studies on nitroxide radicals incorporated into conjugated backbones (i.e., conjugated radical polymers) can be used as an effective spin-transport channel in spin-valve devices. Other reports of nitronyl-nitroxide radicals grown as a self-assembled monolayer suggest that engineering the spin interface could be a successful strategy for improved charge injection. That is, engineering the spin interface for 100% charge injection is a huge hurdle in organic spintronics, and radicals grown as self-assembled monolayers offer a promising means by which to address this opportunity.

Moreover, nonconjugated radical polymers with stable radical open-shell sites and conjugated donor-acceptor[52,55,185] radical polymers also offer a promising future in spintronic devices due to their stability and high conductivity[55] as well as their interesting magnetic properties.[53] In a recent publication, the Azoulay group showed that these low bandgap donor-acceptor polymers possess high conductivity[55] and demonstrate paramagnetic behavior (Figure 16).[53,185] Moreover, a large spin lattice relaxation time of about 1 μs was reported, which suggests that these materials could result in better magnetoresistance response because more spins are conserved.[185] This interplay between high conductivity, magnetism, and higher spin relaxation time is indeed a promising feature for spin-based electronics. Thus, if the magnetization axis of radicals is fixed by the external magnetic field, and spin-flip scattering processes are minor, spins have longer residences time while passing through these materials. In addition to spin valve functionality, the paramagnetic or ferromagnetic interactions within these radicals enables them to be used as effective spin filters, as depicted by recent theoretical investigations on small open-shell molecules.[186,187] The spin filter allows only spin with certain direction to pass through the material, and in this way, pure spin current decoupled from charge current can be generated at the actual device scale.

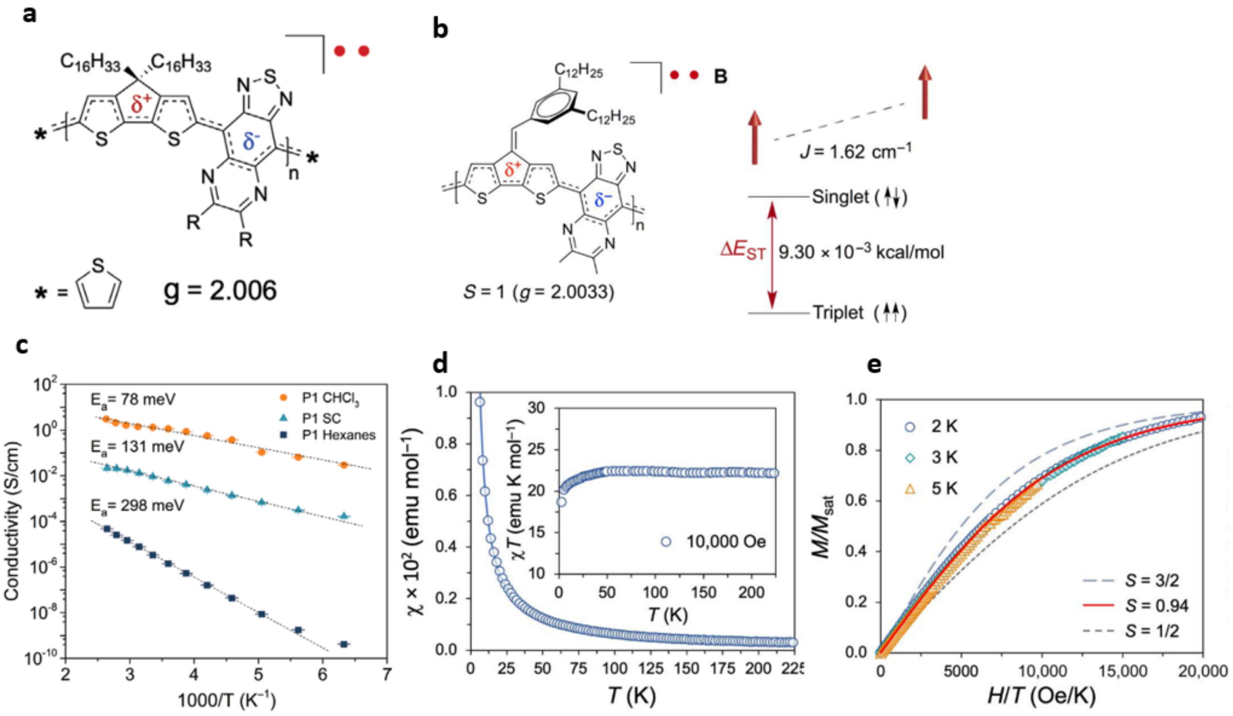

Figure 16. (a) An open-shell conjugated donor-acceptor polymer with diradical character. (b) Modified version of the polymer in (a) with diradical character and high-spin ground state. (c) High electrical conductivity of the polymer in (a) as a function of different processing methods and different solvent choice. (d) SQUID magnetometry data with the paramagnetic behavior of the polymer in (b) with a fit to the Curie Law. The inset shows the χT vs T behavior at 1 T applied field. (e) Fits to the Brillouin function, where the overall spin is 1, confirming the diradical character. Image (a) and (c) reproduced from ref 55. Copyright 2020 Wiley-VCH Verlag GmbH and Co. KGaH. Image (b), (d) and (e) is reproduced from ref 53. Copyright 2019 AAAS.

Open-shell materials possessing ferromagnetism at room temperature can also be used as ferromagnetic electrodes in spin valve devices. This would enable the fabrication of all organic-based spin valve devices and would eliminate the conductivity mismatch problem between the metallic ferromagnetic electrode and organic material layer. As such, tetracyanoethylene (TCNE), is one of the most important building blocks in organic-based magnets in spintronics research.[188–190] TCNE can accept electrons in its antibonding π-orbital, forming the corresponding anion. This electron gives the molecule an overall spin of ½, which is delocalized over the entire molecular ion. This material was utilized in a fully organic spin-valve, in which TCNE served as an organic ferromagnetic electrode to study spin transport in rubrene. It was the initial report demonstrating the fabrication of organic spin-valves with no metallic electrodes.[189] Moreover, extensive work was also conducted regarding the magnetic properties of TCNE.[191,192] As a result, this study has motivated the development of high spin organic molecules, with high radical density, and low energy gap between singlet and triplet states.

In particular, the Rajca group focused on synthesizing polyradicals as organic-based magnets.[56,193,194] Polyradicals as high spin organic macromolecules possess high paramagnetic properties that scale with S(S+1) factor, where S is the spin quantum number. The molecular design strategy is to ferromagnetically couple spin-bearing units (Section 2.3), generating a large energy gap between the high-spin ground state and low spin-excited state.[59,195] Polymers containing radicals can lead to high spin alignment between the pendant radicals and with conjugated polymer backbone (e.g., in the case of conjugated radical polymers). The early development of high-spin radicals was devoted to polycarbenes by Iwamura and coworkers with S = 5. However, these radicals were unstable, and the value of S was limited to S = 5 or less due to the presence of defects. The field of organic magnetism rapidly evolved during that time, with efforts focused on increasing the spin quantum number. There was a need to increase the number of spins bearing sites to obtain higher values of S, and several successful examples have been realized by the Rajca group, where the spin bearing sites were attached to give high spin states.

The highest spin state (reaching S = 5,000) was obtained for polyradicals derived from macrocyclic polyarylmethyl.[193] The magnetic behavior of the polymer with S = 5,000 was comparable to that of spin glass and super paramagnets.[59] Though high spin states were achieved in these polyradicals with ferromagnetic behavior, their stability and difficult synthesis at ambient conditions hampers their use in spin-electronic devices. If stability at ambient conditions is achieved, these materials could be used as organic magnetic electrodes in spintronics devices, thereby revolutionizing the field of all organic based spin-valve devices as promised by TCNE discussed above.

Radical-containing polymers have proven their capability and potential in device applications. Overall, batteries have driven the development of many novel radical polymers that have provided the foundation for charge transport and mix conduction mechanisms. Memristors, on the other hand, showcased the impact of SOMO level alignment on charge injection and the capability of open-shell groups to retain charge. Doublet-based OLEDs using radical polymers have improved the stability and current density comparing with the small molecule counterparts; however, there still exists much room for improvement in terms of the overall performance of the materials in devices. All these applications imply both material design, knowledge in transport and device physics are indispensable.

5. Conclusions and Future Outlook

Contemporary macromolecular design efforts of radical-containing polymers have been primarily driven by clear needs in end-use applications. This has allowed a relatively small community to impact multiple different solid-state and electrolyte-supported systems in a meaningful manner. In turn, this has given open-shell macromolecules a clear base from which to work and a solid foothold in terms of demonstrating their translational potential. Nevertheless, by adopting an application-driven focus, certain opportunities may have been missed in terms of developing robust structure-property-performance relationships, and these missed opportunities may be leading to slowed progress of the overarching field. This is especially true as open-shell macromolecules are proposed for next-generation device architectures as the true upper bounds of materials performance in these open-shell systems is not understood, or even reasonably estimated. Thus, we put forward that now is the ideal time to significantly grow the radical-containing polymer community with an eye towards impacting the fundamental nature of the materials systems. In turn, we anticipate that appropriate, multidisciplinary efforts on these fronts in the coming years will allow for a second wave of technological impact for open-shell macromolecules in the longer term. In this way, we continue to see an extremely bright future for open-shell polymers that will emerge from the excellent work that has been produced by the community to this point.

While many opportunities exist on the road ahead for radical-based polymers, we point out the following avenues as pressing needs in the field, and we stress that these opportunities may be best addressed by a diverse group of researchers with skillsets that are currently not included in the radical-containing polymer community. In particular, the breadth of open-shell chemistries that have been incorporated into polymeric architectures has been relatively limited. Moreover, most of the materials science aspects that connect molecular design to end-use properties have focused on nitroxide radicals. While there are good reasons for this paradigm (e.g., the stability of this open-shell group and the relatively straightforward nature of the syntheses of these molecules), it is not obvious that nitroxide-containing macromolecules are representative of the general class of materials. Additionally, it is not apparent where along the spectrum of ultimate end-use performance nitroxide radicals rank for many applications. Therefore, the relatively limited scope of radical group chemistries perhaps has placed artificial constraints on implementing these exciting macromolecules into certain practices. As such, there is an urgent need for synthetic chemists and polymer chemists to take up the open-shell macromolecule mantle to make significant macromolecular design breakthroughs in the near future. In a similar manner, the solid-state characterization of many types of radical-containing polymers has been limited, in part due to the (usually) amorphous nature of these materials. Thus, efforts to connect macromolecular design to nanoscale features has been hindered. Implementing advanced characterization techniques and expanding on the previous successes of efforts in this subfield will be critical in connecting design to structure in a complete manner. Computational modeling is also primed to play an important role in making these connections. Recent advances in simulation, including with respect to throughput and the ability to describe coupled mass and electron transport, have the potential to resolve the remaining details of transport in radical-containing polymers and place structure-function design rules on a stronger foundation. In addition, developments in machine learning, especially in the areas of force-field potentials and coarse-graining have the potential to accelerate the computational exploration of diverse radical-containing polymer chemistries at pivotal mesoscopic lengthscales. Finally, we note that there is a growing field of research on organic-inorganic hybrid materials that combines the bests from these two worlds. We believe open-shell chemistries provide a new exciting opportunity to this front. By combining the unique properties of the organic radicals with inorganic frameworks organically, new classes of materials with unprecedented functionalities and processabilities may be realized. As such, the urgent and apparent need for many different research communities to take up the mantle of open-shell macromolecules is clear, and we hope that this effort has provided the appropriate context and references to inspire growth in this field. In this way, we aim to allow radical-containing polymers to reach their full potential in terms of scientific breakthroughs, translational significance , and impact to the broader society.

Conflicts of Interest

The authors declare that there are no conflicts.

Acknowledgements

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