# Chapter 2
# Syntheses of Radical Polymers

## 2.1 Expectations and Synthetic Limitations: Optimizing the Design of Radical Polymers

What forms, follows functions; however, even the best of intentions can only be realized if and only if a successful formation (i.e., synthesis) of the targeted material can be achieved. Thus, a discussion of the viable and facile synthetic routes for the formation of the desired radical polymers is itself an important field of research. This is because one needs to understand and contain the reactivity of the pendant radical units [1]. Ambient stable radicals can be, and often are, reactive towards various chemical species including other radicals [2]. For instance, radical polymerizations of radical-containing stable monomers may not be a viable approach for the synthesis of radical polymers due to their reactivity. Thus, the choice of polymerization and the associated choice of monomer units are crucial in design and formation of any given radical polymer or polyradical (Fig. 2.1).

## 2.2 Different Strategies in the Syntheses of Radical Polymers

In order to appreciate the abovementioned challenges of such syntheses in full, an example of the classic and the most investigated radical polymers, poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA), will be used (Fig. 2.2). PTMA can be regarded as one of the simplest systems among all the different classes of radical polymers. However, the conventional approach in the polymerization of nitroxide-containing methacrylate groups using standard free (or controlled) radical polymerization methodologies does not result in the formation of PTMA. Thus, a different polymerization is required if the radical-containing monomer is polymerized, or post-polymerization modification of other closely related, closed-shell monomer and polymer architectures is required in order to form PTMA. In their seminal 1972 report,
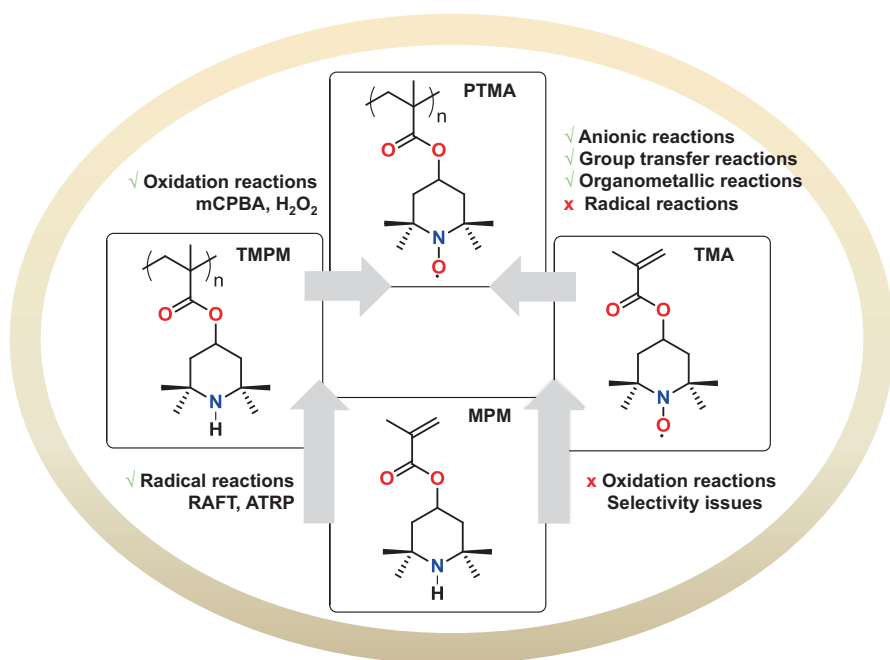
**Fig. 2.1** A brief overview of the strategies involved in the synthetic methodologies for a model radical polymer, PTMA. While the synthetic strategies all vary with respect to their ease and type of final product, they all lead to the same general type of PTMA macromolecule, although important macromolecular architecture changes can take place using certain reaction conditions

Okawara and coworkers demonstrated [3] the synthesis of PTMA from the controlled room temperature oxidation of poly(2,2,6,6-tetramethylpiperidine methacrylate) (PTMPM) using $H_2O_2$ and $Na_2WO_4$ in the presence of ethylenediaminetetraacetic-acid (EDTA) in methanol. Today, this is a relatively straightforward synthetic scheme as PTMPM can be easily synthesized from its precursor methacrylate monomer using radical polymerization with AIBN; however, this deep insight by the Okawara team was the first demonstration of this fascinating class of materials known as radical polymers. To have this insight at such an early time, and before any clear application for these materials was present, was visionary in many regards.

In order to improve upon (i.e., lower) the dispersity (Đ) of radical polymers like PTMA, more than four decades later, our team utilized the reversible addition-fragmentation chain transfer (RAFT) polymerization method in the synthesis of PTMA [4]. Here, the use of the RAFT polymerization method affords a product polymer with low dispersity (Đ < 1.2); however, its direct oxidation to PTMA using mCPBA resulted in an insoluble (presumably cross-linked) product, which is most likely ascribed to the presence of the terminal sulfur-containing unit in the chain transfer group at the terminus of the polymer chain. On the other hand, the removal of the RAFT terminus using excess azobisisobutyronitrile (AIBN) provides a methyl-terminated PTMPM, which can be readily oxidized to PTMA (e.g., using
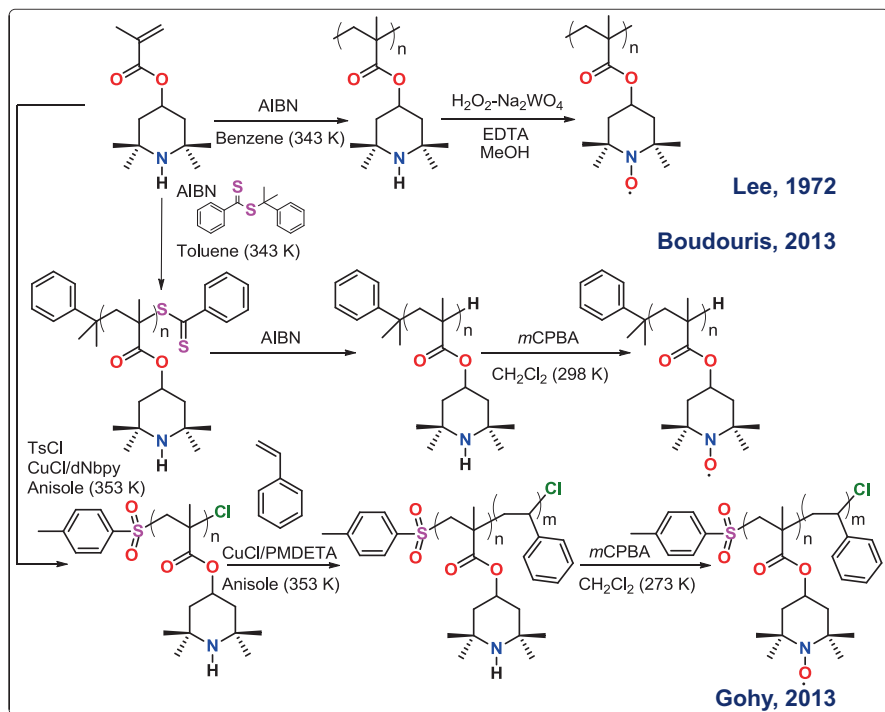
**Fig. 2.2** Radical polymerization methods include free radical and controlled radical (e.g., RAFT polymerization and ATRP) polymerization methods for the synthesis of PTMA and related random or block polymer structures. One of the key advantages of radical polymers relative to most conjugated polymers is the relative ease of synthesis in making these organic electronic materials using well-known polymerization schemes

oxidizing agents like mCPBA) without any observed cross-linking. The versatility of this method opens the opportunity for controlled and facile synthesis of bulk amounts of PTMA of relatively low dispersity and highly targeted molecular weights. Moreover, this method can be efficiently used for the syntheses of block polymers containing TEMPO groups, although using the RAFT-mediated scheme for generating radical polymer-based block polymers has not been yet discussed in the literature.

Prior to the RAFT-mediated work and using an independent path, Gohy and coworkers demonstrated that well-defined PTMA could be synthesized also using the controlled radical polymerization technique of the atom transfer radical polymerization (ATRP) method, which initially produced the PTMPM backbone that could be oxidized to form a PTMA backbone according to previous reports. Moreover, they were also able to utilize this controlled polymerization technique to generate radical-containing block polymers [5]. The utilization of ATRP chemistry in the synthesis of well-defined radical polymer materials, especially PTMA, has become a common technique at this point in time. As such, it is one of the most

popular means by which to generate high-quality homopolymers and block polymers in the literature. However, the limitation of generating any PTMA-based block polymer using a controlled radical polymerization scheme remains in the fact that the other block of the copolymer must be stable towards oxidizing agents (e.g., mCPBA or $H_2O_2$), although there is a clear means by which to circumvent this issue using other controlled polymerization techniques (vide infra). However, using similar methods as described above, several random copolymers containing TEMPO functionalities have been developed and reported in the recent literature [6, 7]. On the other hand, the synthetic methodologies for radical polymers are not restricted to only classical radical polymerization methods. Modern synthetic techniques allow a significant number of independent routes to achieve the common objective, even compatible with stable radicals present during the reactions.

Although radical polymerization of nitroxide-containing monomer units can be problematic, these issues can be readily circumvented by using an anionic polymerization route as the stable radical groups are not greatly impacted by the propagating anionic chain terminus (Fig. 2.3). Very recently, Nishide and coworkers first demonstrated a successful anionic polymerization of 4-methacryloyloxy-TEMPO using a methyl methacrylate-capped 1,1-diphenylhexyllithium (DPHLi/MMA) [8]. The nucleophilicity of this reagent can be regarded as moderate enough to suppress side reactions between the carbanion and the radical sites. With this method, the authors were able to produce PTMA of considerably low dispersity (Đ < 1.2) with very high yields (i.e., ~95%). However, in the absence of the DPHLi/MMA initiating species, the authors observed evidence of side reactions, which were ascribed to the formation of tertiary carbon radicals and propagating anions. Later in 2014, the authors used a similar strategy to grow PTMA brushes around a polynorbornene backbone, achieving bottlebrush polymeric structures for the first time in the realm of radical polymers [9]. In 2016, using anionic polymerization techniques, the Ober group demonstrated the assembly of radical-containing block copolymers on macroscopically patterned substrates [10]. With proper substrate modifications and detailed annealing techniques, the authors were able to obtain highly ordered hexagonally packed nanoscale cylinders. Furthermore, the compatibility issues of the radicals with the polymerization methods also can be avoided in a completely different manner. In this approach, the formation of radical-containing block copolymers and random copolymers can be also achieved from substitution reactions of activated ester containing polymers [11], which is currently considered as a quite versatile strategy for post-synthetic modification of polymer chains and avoids all the activity issues of nitroxide groups towards any reagent, which may appear during a considerably long synthetic scheme. Apart from these advanced techniques, polymerization of 4-methacryloyloxy-TEMPO had been also realized earlier through group transfer polymerization techniques, which used 1-methoxy-2-methyl-1--trimethylsilyloxypropane as a reagent [12]. However, these techniques are comparatively inefficient due to their rather uncontrolled nature, which results in radical polymers with relatively high distributions of molecular weights. However, GTP methods are promising with respect to their ability to control the tacticity of the
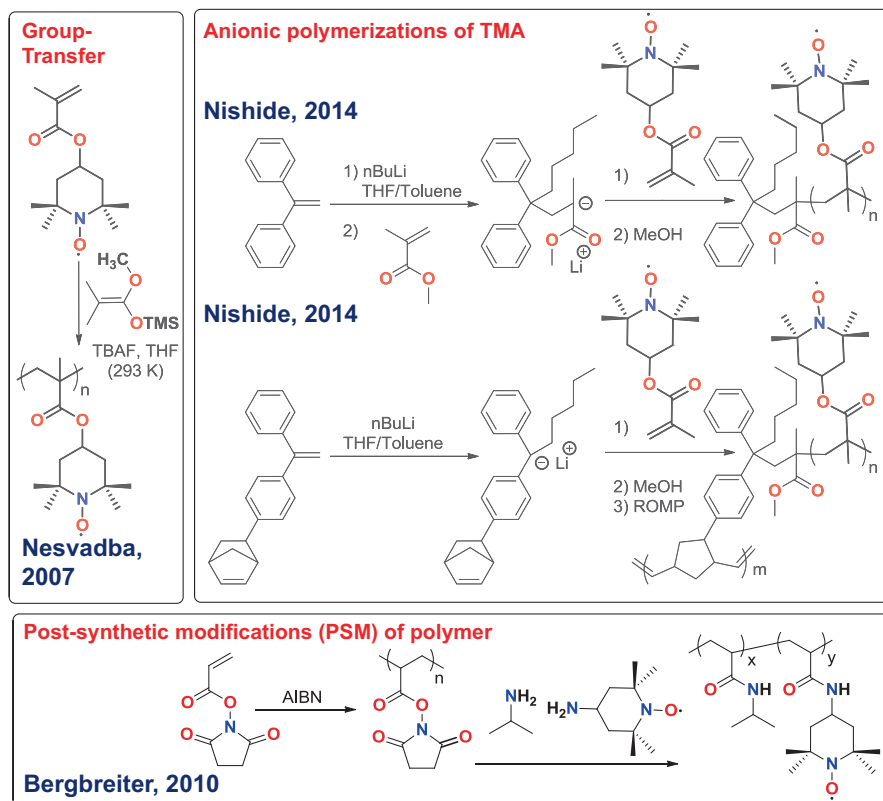
**Fig. 2.3** Group transfer and anionic polymerization methods for the synthesis of PTMA (*top*). Post-synthetic modification of activated ester backbones for the preparation of TEMPO-containing polymeric structures (*bottom*)

radical polymer chain, which might be of interest in certain cases where substituent side chain location is of prime import.

The chemical grafting of radical polymers on different substrates and nanoparticle surfaces has been also realized (Fig. 2.4). In 2011, the Lee group reported the growth of PTMA brushes on flexible conducting substrates by using a surface-initiated ATRP method and microcontact printing [13]. Following the patterning of octadecyltrichlorosilane (OTS) on an ITO surface (that had been coated on a flexible substrate), the substrate was placed in an initiator solution of 4-(trichlorosilyl) butyl 2-bromo-2-methylpropanoate. After this attachment of the initiator on the ITO surface, PTMPM brushes were grown on the material, which were finally oxidized to produce the grafted PTMA brushes. This method has been extended in very recent reports where similar brushes have been grown from $Fe_3O_4@SiO_2$ core-shell nanoparticles [14]. In 2013, the Nishide group reported a comparable strategy to grow PTMA polymer on the surface of silica particles [15]. However, in this case, a
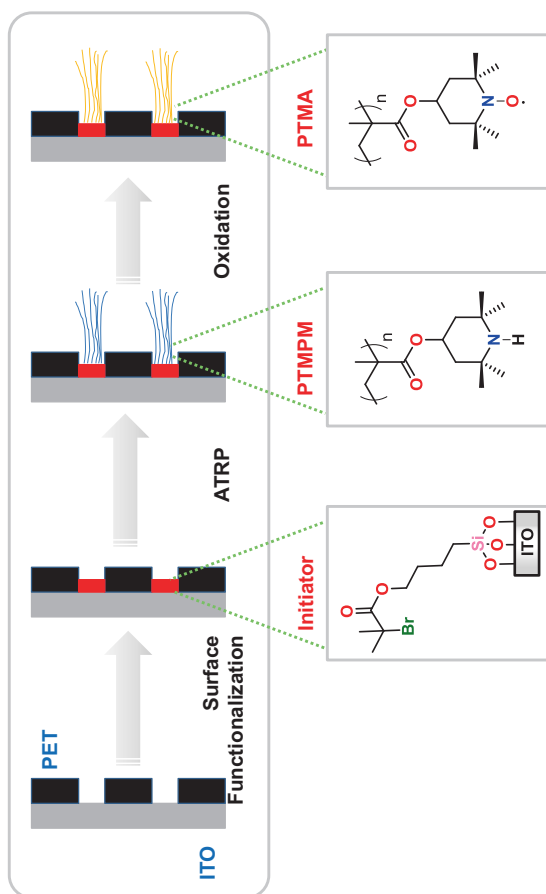
**Fig. 2.4** Surface functionalization strategy from common substrates (e.g., tin–doped indium oxide), which can be patterned using a polymer photoresist. The growth of PTMPM brushes on the ITO surface is followed by an oxidation step to achieve PTMA brushes on the substrate
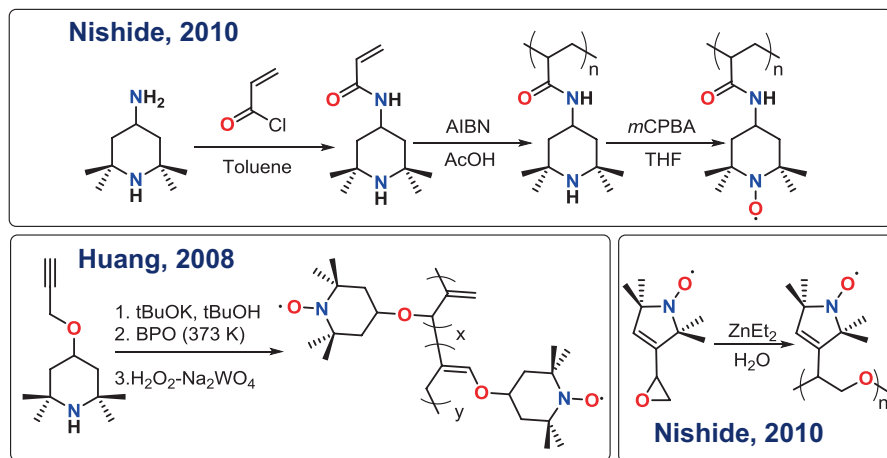
**Fig. 2.5** A few examples of related polymeric materials consisting of stable radical units as the building block. The use of acrylamide units, alkynes, and epoxides has been investigated in order to fine-tune the physical properties of stable radical containing polymers

RAFT initiator and synthetic route was followed to build the PTMPM structure on silica.

Structures that are closely related to PTMA also have been developed in recent years, although their applications have been limited. For example, poly(2,2,6,6-tetramethylpiperidinyloxy-acrylamide) (PTMa) is a structural sibling of PTMA, and its synthesis has been reported by Nishide and coworkers (Fig. 2.5) [16]. Similarly, polymers like PTVE (poly-TEMPO-vinyl ether), which are inherently hydrophilic in nature, have been developed for specialized applications [17]. Other polymers with TEMPO groups as repeat units have been also developed to a limited extent (Fig. 2.5). These investigations have demonstrated the versatile chemical landscape of radical polymers. Also, the use of different monomer units allows formation of libraries of polymers with tuneable physical and chemical properties [18]. Due to this decoupling of the polymer backbone from the pendant group chemistry, there is a great opportunity to further develop nitroxide-based materials.

Apart from six-membered nitroxide-containing rings like TEMPO, smaller ring systems like proxyl moieties have been incorporated into the pendant groups of radical polymers [19]. Being a ring structure with fewer carbons relative to TEMPO, proxyl moieties can provide comparatively greater radical density in polymers. For example, the Nishide team has reported proxyl-containing poly(ethylene oxide)-like (PEO-like) systems in order to achieve high radical density in polymers as the proxyl moieties have lower repeat unit molecular weight compared to previously discussed examples (Fig. 2.5) [20]. Later, the Rajca group independently developed peripherally spirocyclohexyl-proxyl group decorated dendritic structures as MRI contrast agents as well [21]. However, the relative hardship of the synthetic procedures has kept these materials much less explored compared to TEMPO-containing polymers.
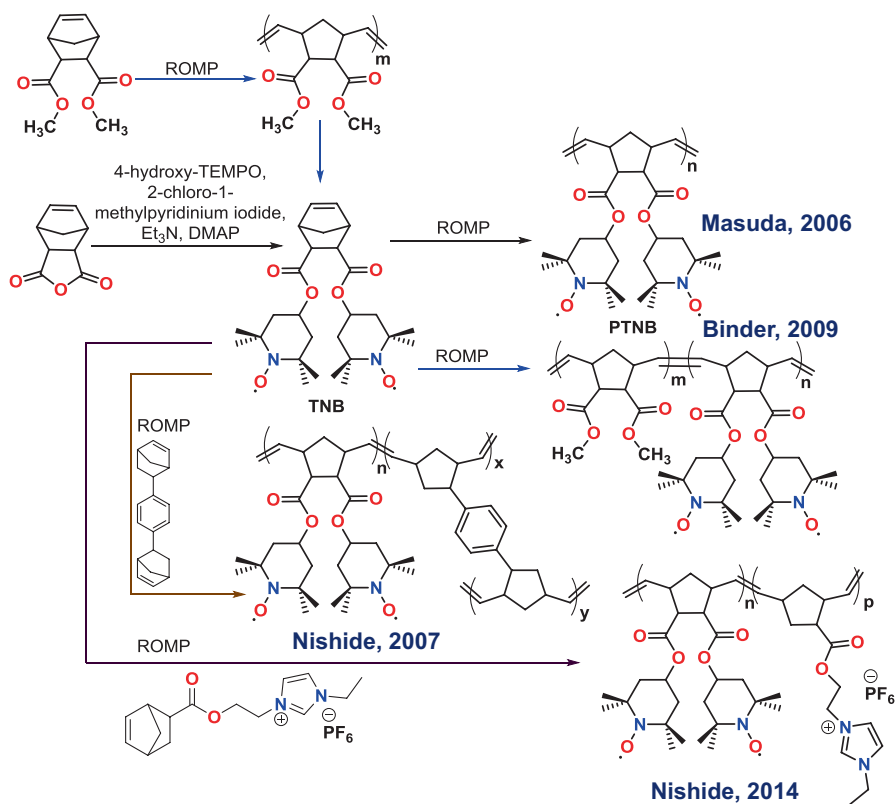
**Fig. 2.6** Opportunities for the ROMP methodology in the synthesis of various radical polymer structures, including random and block copolymers and cross-linked materials

The TEMPO-containing radical polymers have also benefited from the progress of modern synthetic chemistry. In particular, ring-opening metathesis polymerization-based (ROMP-based) methods have drawn significant attention in the development of different and versatile classes of radical polymers (Fig. 2.6). In 2006, Masuda and coworkers developed a facile synthetic route to easily accessible TEMPO-functionalized polynorbornene derivatives [22]. It should be noted that the commercial availability of TEMPO molecules with groups that are capable of being functionalized is mostly restricted to their hydroxy-, carboxy-, and amine- derivatives, which are used as the starting points in most synthetic methods. The team showed that the hydroxyl- and carboxy-containing TEMPO molecules can be coupled with a norbornene backbone to form TEMPO-containing norbornene monomers. Norbornene-based molecular systems provide great opportunities as the formation of high molecular weight and narrow molecular distribution polymers is possible with various metal-catalyzed reactions [23]. This versatility, in turn, has made these types of syntheses of great interest. Thus, TEMPO-containing norbornene monomers can be easily polymerized using Grubbs' catalyst to form TEMPO-containing poly(norbornene)s in large scales. The versatility of this method

also allows for the formation of random copolymers and block polymers. For instance, the Nishide team further used this synthetic strategy to incorporate photo-crosslinkable units in poly-bis(2,2,6,6-tetramethylpiperidinyloxy-4-yl) bicy-clo[2.2.1]hept-5-ene-2,3-dicarboxylate (PTNB), which can be activated after polymerization to induce cross-linking in the material [24]. Polymerizations of bis(2,2,6,6-tetramethylpiperidinyloxy-4-yl)                     bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (TNB) in presence of suitably designed cross-linking agents can also directly form insoluble cross-linked PTNB [25]. This ROMP-based polymerization method has been also utilized in the development of TNB-containing block copolymers. Most of the work along these lines has been reported by Binder and coworkers [26, 27]. In 2009, they studied the formation of block polymers, of which several contained PTNB as one of the blocks, via mass spectrometric techniques [26]. Later, the researchers also demonstrated the synthesis of a series of TNB-containing block copolymers and evaluated the role of catalysts and reaction conditions related to this reaction [27]. Although these reports can be regarded as "proof-of-concept" experiments in the development of radical-containing block polymers via the ROMP method, these critical initial studies offer the promise that will allow for a vast opportunity of future discovery.

Apart from cyclic nitroxides, aromatic nitroxide-based radical polymers also have been synthesized previously [28]. Well-designed protecting groups on *N-tert*-butyl-*N*-oxyl-styrene groups can be directly polymerized using conventional radical polymerization procedures (Fig. 2.7). Following this step, the deprotection of the nitroxyl moiety (i.e., using $Bu_4N^+F^-$ and $Ag_2O$) occurs. The presence of the aromatic groups provides a great opportunity for functionalization and electronic fine-tuning in these polymers. For instance, the polymer with no other substituents on the aryl rings (R═H) is a material that is more easily oxidized due to its low oxidation potential. However, inclusion of an electron-withdrawing trifluoromethyl group (R═$CF_3$) in the aromatic backbone completely alters the electronic preference of the system and lowers its reduction potential, providing a material that is more likely to be reduced. However, the multistep synthesis and relative lower stability of these materials have resulted in only limited exploration of these polymers.

On the other hand, closely-related nitronyl-nitroxides have also found interest as building blocks of radical polymers (Fig. 2.7). In 2011, Nishide and coworkers demonstrated the successful development of poly[(4-nitronylnitroxyl)styrene] (PNNS) [29]. Similar to other related nitroxides, post-synthetic modification of a silicon-protected imidazolidine polymer leads to the formation of the desired polymer. The cleavage of the O-Si bond followed by controlled oxidation of the 1,3-bis(silyloxy) imidazolidine systems was essential for the formation of the oxygen-centered radical species. The symmetric structure of the system, coupled with the available conjugation with the aryl moiety, stabilized the radical system in the polymer structure. Interestingly, these types of macromolecules are ambipolar (i.e., can be oxidized and reduced with relatively equal ease) in nature, as the cationic and anionic counterparts of this radical structure are both comparatively stable. In a following report, Nishide and coworkers further demonstrated that, similar to TNB, nitronylnitroxide containing norbornene monomers can be also directly polymerized via ROMP methods [30]. Such steps further decrease the synthetic burden for the formation of
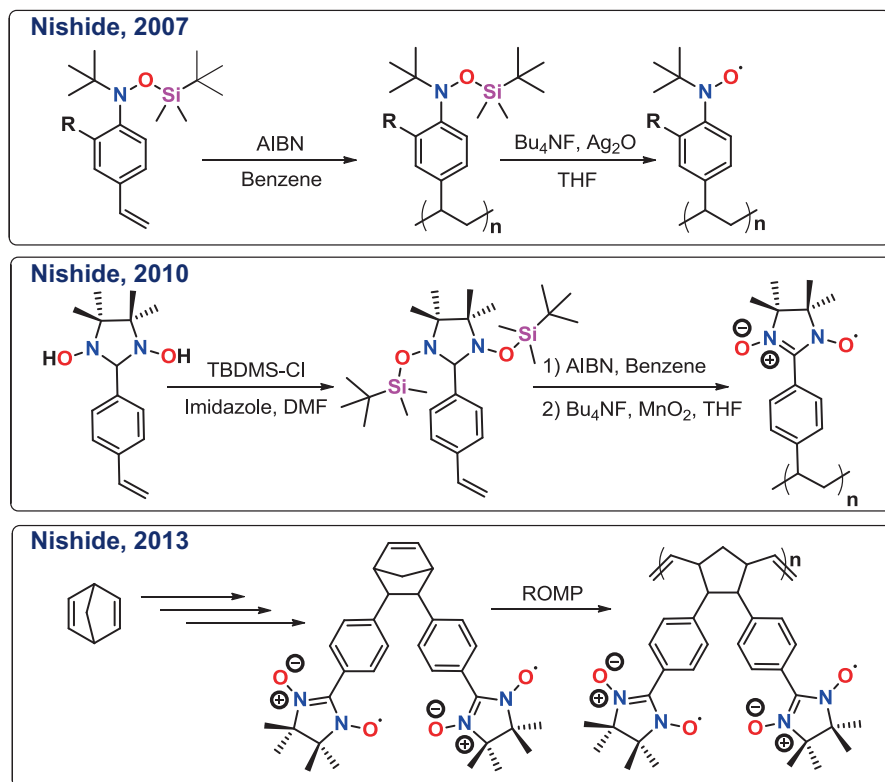
**Fig. 2.7** Synthetic strategies for poly(N-*tert*-butyl-N-oxyl-styrenes) and other polymeric structures containing "nitronylnitroxyl" radical species. The syntheses of these materials are important because of the tuneable properties of the polymers. In the example at *top*, if R=H, the synthesized material is an n-type polymer. On the other hand, if R=CF$_3$, n-type behavior is observed. For the other examples with "nitronylnitroxyl" moieties, the polymers are ambipolar in nature because they can reversibly undergo either oxidation or reduction forming corresponding cationic and anionic species

nitronylnitroxide containing polymers, opening versatile opportunities for future developments.

Until now, the discussions have focused on p-type radical polymers as the nitroxyl moieties often prefer to be oxidized to stable cationic species and do not prefer to be reduced to the comparatively weakly stable anion. However, compounds like PNNS are capable of showing ambipolar characteristics as the stability of the anion is also considerably higher in this case. Compared to p-type radical polymers, n-type materials have been quite limitedly discussed in the literature. In order to obtain a suitable n-type material, one needs to ensure the stability of the corresponding anionic species. In this regard, phenoxyl systems have drawn the most attention compared to any other class of materials (Fig. 2.8). Owing to the available conjugation with the pendant aromatic systems, phenoxyl anions are quite stable and often
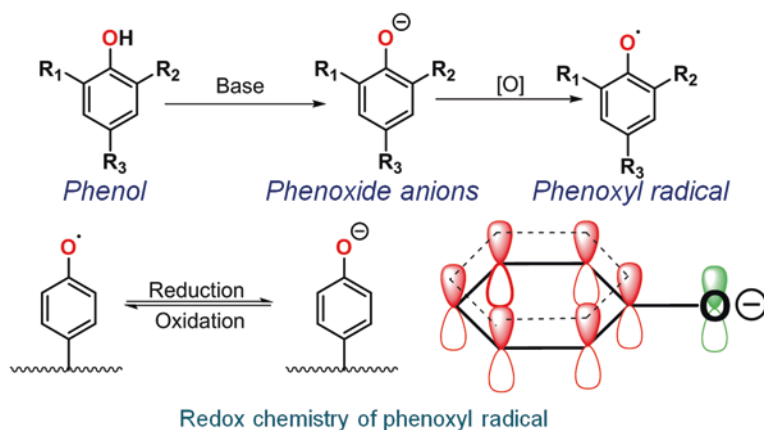
**Fig. 2.8** A design strategy towards the development of stable phenoxyl radicals is shown (*top*). The reversible reduction of phenoxyl radicals is stabilized via conjugation in the molecular (or polymeric) backbone
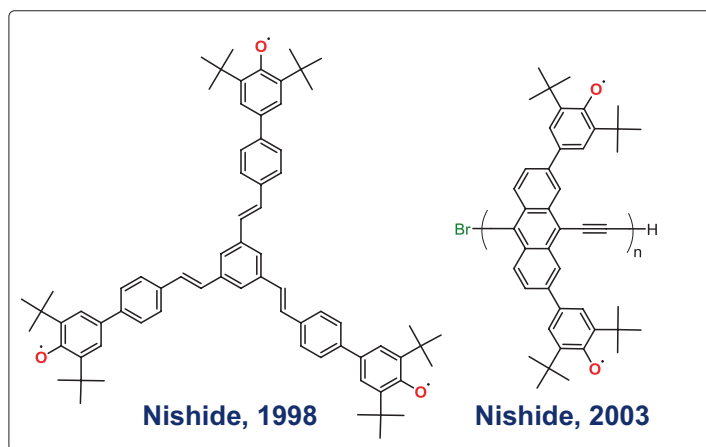


**Fig. 2.9** Some of the first examples of phenoxyl-moiety containing polyradicals, as developed by the pioneering work of the Nishide group

encountered as ligands in coordination chemistry [31]. Suitably designed phenoxyl systems can be also obtained as neutral radicals [32]. However, the formation of detectable phenoxyl cation is quite unknown due to the expected instability of the system, arising from the high electronegativity of oxygen atom. Thus, these systems are of interest if the goal is to develop a preferably n-type radical polymer.

Initial challenges regarding the syntheses of these compounds had restricted the studies of phenoxyl radical-based monomeric and oligomeric systems. However, in 1998, the Nishide team reported the synthesis of terminal phenoxyl-bearing poly(1,2-phenylenevinylene) systems as high-spin organic polymers (Fig. 2.9) [33].
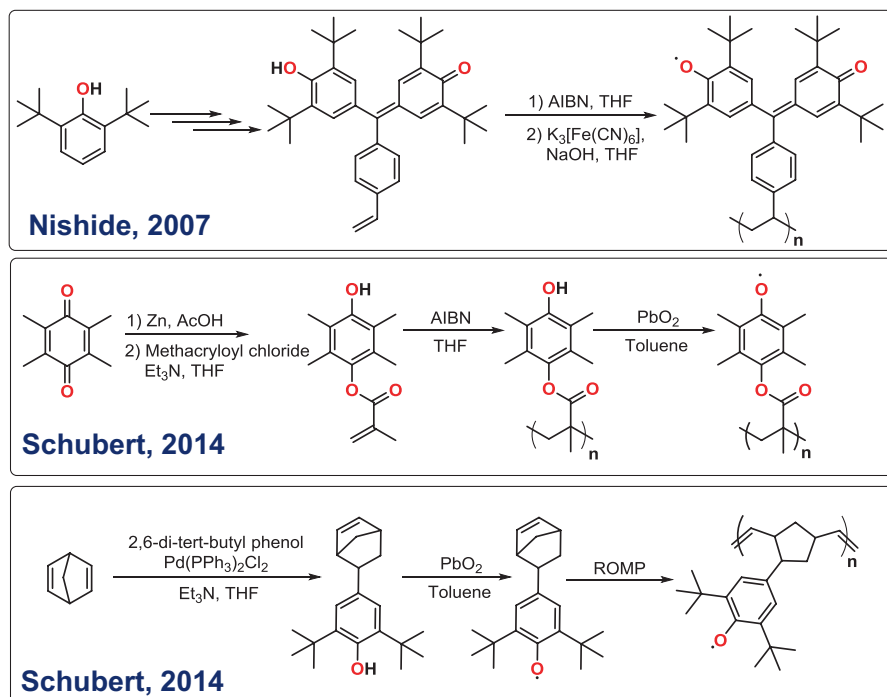
**Fig. 2.10** Synthetic strategies for the polymerization of PGSt (*top*) and other related stable phenoxyl containing radical polymers using classical radical polymerization method (*middle*) and ROMP (*bottom*). The use of ROMP method can be followed directly for stable radical containing molecules

The reactivity of phenolic compound was maneuvered using protecting groups on the oxygen atoms throughout the synthesis, following deprotection to obtain the corresponding phenol analogues. Five years later, the same group further demonstrated spin coupling of radical sites on a polyradical where the phenoxyl radicals were situated on the edges of the anthracenyl moieties. Here, the polymer is generated through the connectivities of the 9 and 10 positions of the anthracenyl units (Fig. 2.10) [34]. Thus, this polyradical can be described as a linear conjugated polymer peripherally decorated with radical entities, which can participate in conjugation throughout the polymer backbone.

However, the successful synthesis of a polymer containing galvinoxyl units as the building block was demonstrated only quite recently [35]. Galvinoxyl is a phenoxyl-based radical species, which is quite stable under ambient conditions [36]. The extended conjugation, coupled with the steric protection of the alkyl substituents, provides a measure of thermodynamic and a great extent of kinetic stability to the system. The Nishide group demonstrated that the synthesis of the poly(galvinoxyl styrene) (PGSt) can be accessed in a quite facile manner using radical polymerization of the phenolic monomer, which can be also readily achieved from commer-

cially available components (Fig. 2.10). The phenolic polymer can be easily oxidized using $K_3Fe(CN)_6$ to form PGSt in large scales. The ease of this method allowed for the formation of random copolymers upon the polymerization of this species with other acrylate monomers. In turn, this opened opportunities to form different classes of materials including cross-linked PGSt. Following its successful formation, PGSt also found significant interest in various applications which were also mostly pioneered by Nishide and coworkers [37]. Later in 2014, Schubert and coworkers demonstrated the development of several different phenoxyl-based polyacrylates and polynorbornenes, opening versatile new opportunities for n-type radical polymers (Fig. 2.10). The ROMP method does not interfere with organic radicals, and it can be versatile in developing a shorter and more cost effective synthetic route [38]. Similar to TEMPO-based materials, polyacrylates containing phenoxyl moieties cannot be directly obtained using radical polymerization and require post-synthetic modifications of the precursor phenolic polymer. However, this restriction is lifted for ROMP-based synthesis of polynorbornenes and the radical-containing norbornene monomer can be directly polymerized in a one-step reaction.

## 2.3   Conjugated Radical Polymers

Conjugated polymers with stable radical units as well as block polymers of conjugated polymers with radical polymers have been also demonstrated in literature (Fig. 2.11). Here, we will refer to these materials as conjugated radical polymers (CRPs) in order to draw a clear line between these macromolecules and polyradicals. In 2001, the Nishide group demonstrated the synthetic landscape of a series of radical-bearing polythiophenes where each of the building units contains a radical site [39]. As shown in Fig. 2.11, they demonstrated the incorporation of a series of n-type radical species on the polythiophene backbone. In 2011, the Wolf group reported the synthesis of TEMPO-decorated poly(3-alkylthiophene)s via post-synthetic modification of the polythiophenes using facile click chemistry (Fig. 2.11) [40]. The quantitative yield of the click method allows precise loading of the TEMPO units on the conjugated polymer chain. Following this, in 2012, the Lee group demonstrated the development of bottlebrush-like polymer structures where the core constitutes of a polythiophene chain and the brushes are similar to PTMA [41]. Using each individual thiophene unit as an ARTP initiation site, they were able to grow PTMA brushes around the polythiophene moiety. In recent years, overcoming the oxidative polymerization efforts discussed earlier, electropolymerization techniques have been used to obtain TEMPO-grafted polythiophenes. In 2015, Ma and coworkers demonstrated that the electrochemical polymerization of radical-bearing thiophenes can be quite useful to obtain conjugated polymers with radical substitutions on each individual repeat unit [42]. Later, the Lutkenhaus group also followed a similar procedure to obtain polythiophenes-bearing pendant nitroxide radicals [43]. Following this report, the Armand group also reported a similar strategy to develop a radical-containing PEDOT species [44]. These examples can be
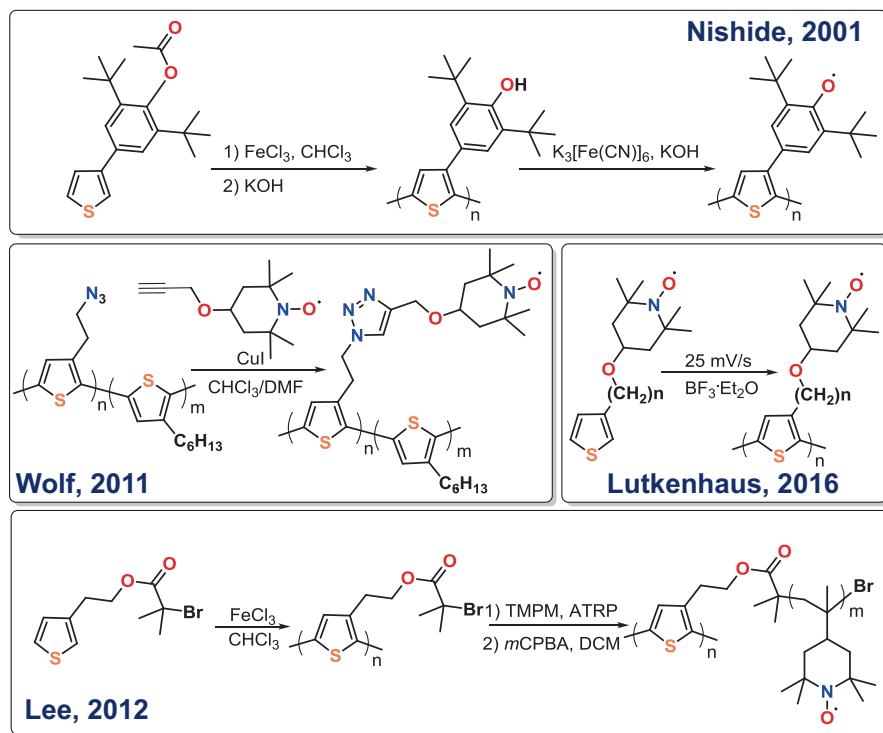
**Fig. 2.11** Different strategies to develop conjugated radical polymers (CRPs) containing pendant stable radical units are demonstrated. The use of oxidative polymerization can be performed in either a chemical or an electrochemical pathway even in presence of a stable radical. Moreover, post-synthetic modifications of conjugated polymers are also possible and allow for the formation of CRPs

summarized to state that versatile different synthetic routes have been developed in recent times to obtain different families of CRPs. Further versatile structures made from conjugated structure and radical sites form a large family of compounds known as polyradicals, which are discussed in the following section.

## 2.4  Polyradicals

The development of polyradicals requires much more rigorous synthetic method-ologies compared to the previously discussed radical polymers. Although a large amount of research has been performed in the field of polyradicals, the limited scope of this book can only briefly discuss this topic. As such, we direct the reader to excellent review articles in the open literature on this topic [45d, 46b]. In most cases, which were primarily developed by the Rajca group, polyradicals can be considered to be different variations of interconnected "triphenylmethyl" radicals

[45]. Based on the targeted entity, the reticular design of the monomeric units is essential to achieve the desired compounds. In most synthetic scenarios, the final step involves the formation of the radical sites. Thus, it is quite important that the last step is near quantitative in yields. The Rajca team has established that radicals can be quantitatively formed through the controlled oxidation of the corresponding carbanions. In most cases, such carbanions are formed by the reduction of the triaryl tertiary carbon sites using s-block metals (e.g., Li, or Na/K) in the presence of a suitable leaving group (i.e., with structures like -OMe) containing backbones [45, 46].

These methoxide-containing polyethers can be synthesized using aryl-lithium reagents to an ester, ketone, or acid-chloride [45, 46]. Divergent synthetic routes involving structurally related molecular units provide a rather generalizable synthetic approach towards the development of molecular siblings, as well as polymers (Fig. 2.12).
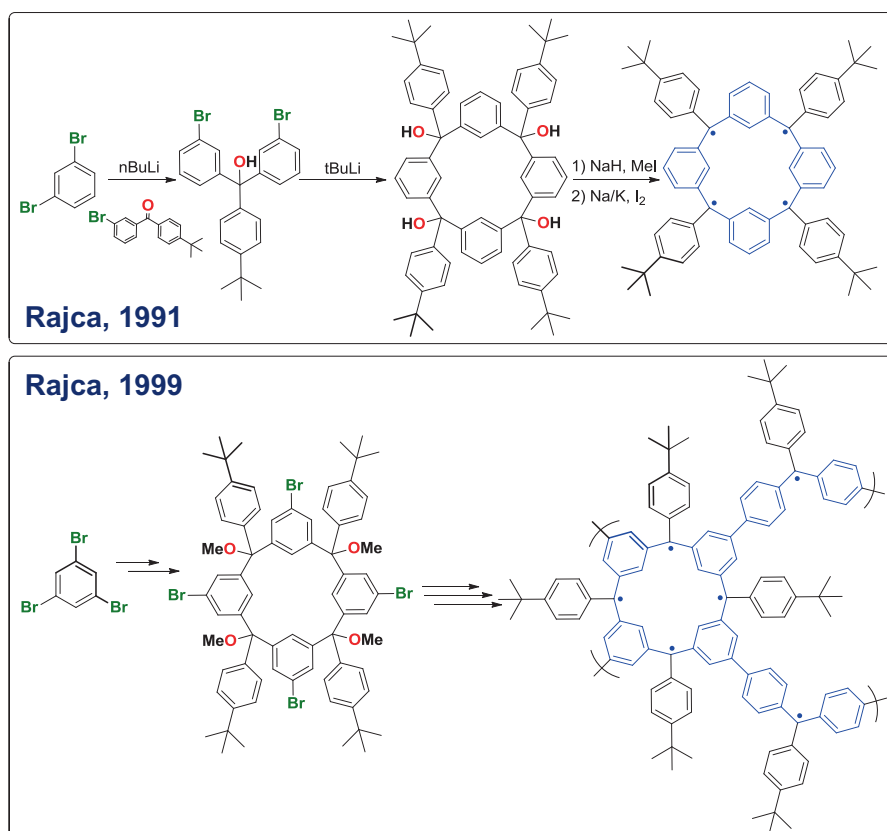


**Fig. 2.12** The design strategy behind the development of a cyclic polyradical and its conceptual extension to contain polymeric structures are depicted. These early results have been extended in recent years to generate remarkably high-spin structures of organic materials, and we refer the interested reader to the appropriate review materials for polyradical systems at the end of this chapter
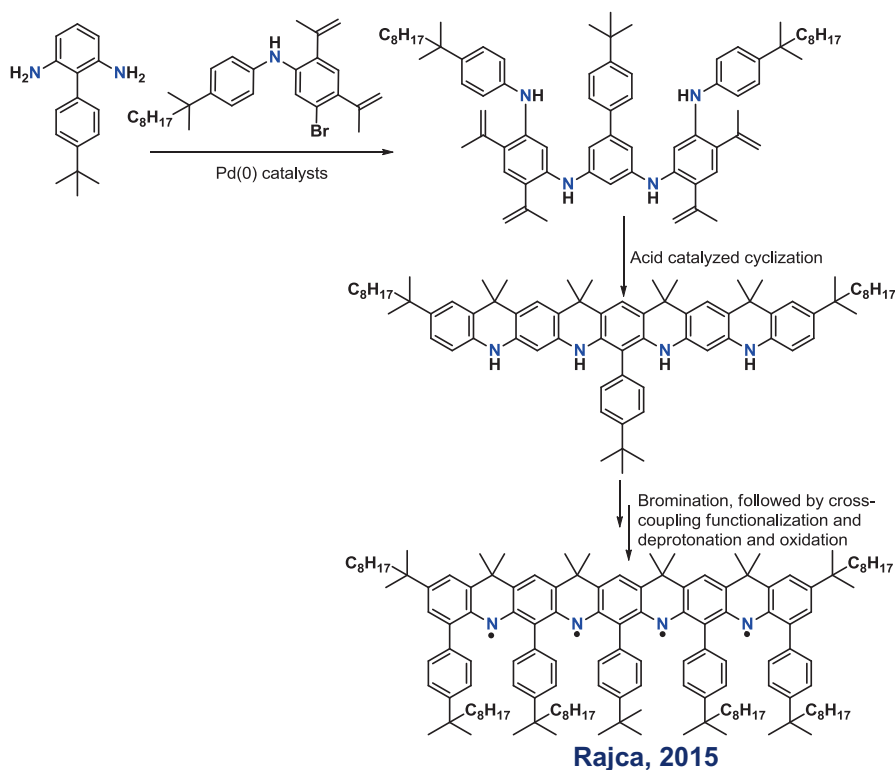
**Fig. 2.13** A typical synthetic methodology for the development of a tetraradical species. The formation of an interconnected conjugated structure is followed by a controlled oxidation process to obtain conjugated polyradical systems. The use of sterically bulky aromatic groups around the radical sites is intended to provide kinetic stability to the systems. Exclusion of these auxiliary aromatic units would allow the planar core to come in close contact with neighboring chemical species, which often compromise the stability of the radical systems

Polyradicals based on other related structures are relatively scarce due to their synthetic difficulties and limited stabilities. However, a number of efforts by the Rajca group have been targeted towards the developments of polyaminyl systems [47, 48]. The specific synthesis of these compounds is based on reactions like C-C and C-N bond formation (coupling reactions) and selected oxidation of the deprotonated bis-aryl-amines. Fig. 2.13 shows one of the representative schemes for the synthesis of a tetraradical [48]. However, the short half-lives of such compounds still pose a challenge to synthetic chemists. Nonetheless, the intriguing magnetic properties and related fundamental insights into the chemistry of organic spin systems inspire investigations of related systems.

In a few recent reports, a new post-synthetic modification (PSM) strategy has evolved in the synthesis of polyradicals from conjugated porous materials. For instance, in 2015, the Jiang group first demonstrated the use of this strategy to form a radical-enriched covalent organic frameworks (COFs) [49]. In a following report,

the Johnson group followed a similar strategy again in the synthesis of a series of radical enriched COFs [50]. Although fundamentally different from previously discussed polyradicals, these materials can be considered as radical enriched porous networks. Notably, such PSM strategies are exciting as they can be an effective tool for modification of any class of polymeric material in the near future.

## 2.5 Chapter Summary

In summary, the synthetic development of radical polymers and polyradicals has been steadily increasing, and the rate of this increase has amplified greatly in last two decades. With the aid of modern synthetic methodologies and characterization techniques, it is expected that the fundamental understanding and basic generalization of the synthetic methodologies are going to unveil uncharted avenues. The development of block polymer structures and patterned nanostructures is of fundamental interest in examining the opportunities of radical polymers in advanced electronic applications. Additionally, chemical fine-tuning of these materials also opens the opportunities to alter the minute physical properties of these materials which can be beneficial to the processing of these classes of compounds. Last but not least, the development of precise molecular structures (e.g., polyradicals) provides fundamental insights into the electronic structure and structure–property relationships of the compounds. Now, the text will move forward in the following chapters to using these unique structures towards the properties and functions of these functional materials.

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