

Versatility of radical coupling in construction of topological polymers

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The development of various polymerization mechanisms has paved the way for the construction of well-defined polymers with complicated structures. However, a single polymerization mechanism or a simple combination of several mechanisms often cannot meet the requirements. Thus, some efficient coupling reactions would play an important role in polymer science. In this review, we focused on the application of radical coupling in the construction of topological polymers. The atom transfer radical coupling (ATRC) reaction and agent (such as styrene, nitrene or diene) assisted radical coupling proceeded in a homocoupling style and polymers with symmetrical structures were obtained. As a more versatile method, nitroxide radical coupling (NRC) was also discussed, which proceeded in a heterocoupling style and polymers with various asymmetrical structures could be designed. Finally, the prospects of radical based coupling reactions in polymer science were also suggested.

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1 Introduction

In the past several years, “living”/controlled polymerization mechanisms, such as living anionic polymerization,^{1–10} nitroxide mediated radical polymerization (NMRP),^{11–14} atom-transfer radical polymerization (ATRP),^{15–20} reversible addition fragmentation transfer polymerization (RAFT),^{21–29} single electron transfer living radical polymerization (SETLRP),^{30–36} ring-opening polymerization (ROP)^{37–43} and ring-opening metathesis

polymerization (ROMP),^{44–49} have been developed and widely used in polymer science. Usually, a certain polymer with complicated topological structure or composition could not be obtained by adopting a single polymerization mechanism or a simple combination of several mechanisms. In most cases, efficient and versatile coupling methods should also be considered for modification of polymers and connection of different polymeric segments,^{50–57} such as the classical reaction between carbon anionic and chlorosilane agent, carboxyl or acyl and hydroxyl or amino groups, and the recently developed thiol–bromide reaction,^{58,59} thiol–ene addition (Scheme 1)^{60–64} and thiol–yne addition (Scheme 2),^{65–70} copper-catalyzed azide–alkyne click (CuAAC) chemistry and Diels–Alder (DA) [4 + 2]

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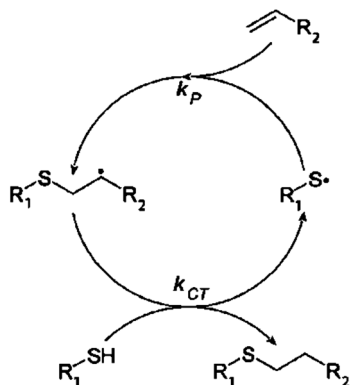
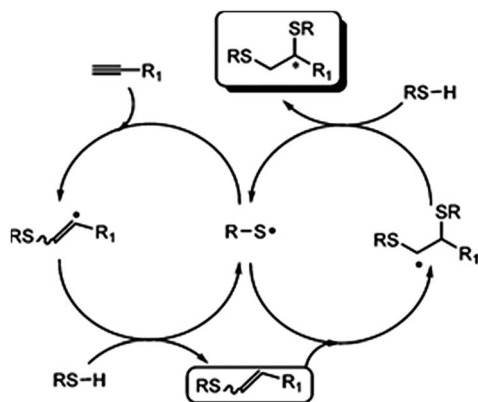


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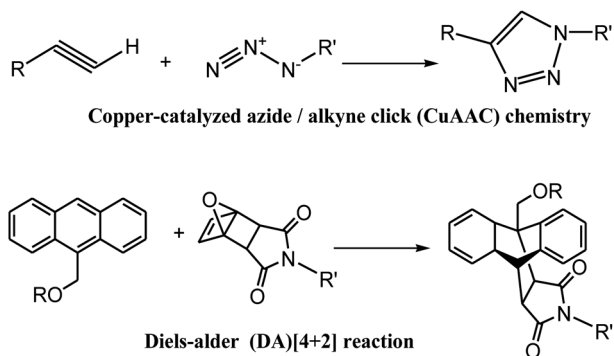
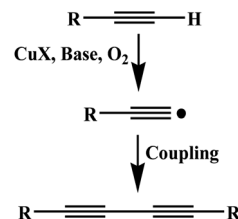


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Scheme 1 The mechanism for thiol-ene reaction.⁶³Scheme 2 The mechanism for thiol-yne reaction.⁶³

reaction (Scheme 3),^{54,71–75} and alkyne-alkyne reaction (also known as Glaser coupling) (Scheme 4).^{76–80} Actually, the coupling methods were perfectly complementary to the polymerization mechanisms. Up to now, the above mechanisms and coupling methods have been well combined and used to synthesize various polymers with complicated structures, including graft,^{81,82} hyperbranched,⁸³ cyclic,⁸⁴ dendrimer^{85–87} and star-shaped copolymers.⁸⁸ However, with increasing requirements from different researches, more and more polymers with well-defined topological structures and compositions

Scheme 3 The mechanism for CuAAC and DA [4 + 2] reactions.⁷¹Scheme 4 The mechanism for Glaser coupling.⁷⁷

should be designed and synthesized. Because of the regulated topological structures and compositions, these polymers are usually used as model copolymers for studies on structure-property relationships, as well as for some special applications.

It was well known that each mechanism was only suitable for some special monomers and catalytic systems, as well as certain operational conditions. Also, each coupling method was also limited by certain functional groups and applicable conditions. For example, in the thiol-bromide, thiol-ene and thiol-yne addition reactions, the introduction of the usually unstable thiol group onto a required polymer was not easy to do, and these three coupling methods were mainly used for the post-modification of polymers by small molecules containing a thiol group.^{58–70} As for the widely used click chemistry, including the typical CuAAC chemistry and DA [4 + 2] reaction, the introduction of photosensitive azide groups, bulky maleimide or anthracene groups onto a functionalized polymer generally required multi-step synthesis and purification procedures.^{71–75} In the Glaser coupling reaction, the high activity and difficult introduction procedure of alkyne groups were also key points to limit its application.^{76–80} Thus, the enrichment and optimization of the coupling methods are always important tasks in polymer science.

On the other hand, the “living”/controlled radical polymerization mechanisms of ATRP, SETLRP, RAFT and NMRP were all presented according to the principle of transforming the major radicals into dormant ones and decreasing the concentration of radicals for minimizing irreversible termination reactions (such as bimolecular combination, disproportionation or chain transfer reactions, and so on). Differently, the radicals in ATRP, SETLRP, RAFT and NMRP mechanisms were generated by M(i)X/ligand/R-X, M(0)/ligand/R-X, transfer agent (such as Z-C(=S)-S- groups) and nitroxide radicals (such as the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) group or its derivatives), respectively. Under certain conditions, the radicals generated by the atom transfer procedure tended to terminate by bimolecular combination in the absence of vinyl monomers, and this reaction was termed as atom transfer radical coupling (ATRC).⁸⁹ However, in some cases, the coupling efficiency of the ATRC reaction was rather low because of the disproportionation, chain transfer reaction and other side reactions happening to the generated radicals. Some strategies were presented and adopted to change the activity of the corresponding radicals to increase the coupling efficiency of the ATRC reaction, such as the styrene (St) assisted radical coupling reaction,⁹⁰ and the later nitrone⁹¹ and diene^{92,93} assisted radical coupling reactions. All these radical based coupling reactions proceeded in a

homocoupling manner, and the obtained polymers showed rather symmetrical structures and compositions.

Alternatively, when the generated radicals in atom transfer procedures were captured by stable nitroxide radicals (such as TEMPO or its derivatives) in the absence of vinyl monomers, this reaction was termed as atom transfer nitroxide radical coupling (ATNRC).^{94,95} Later, according to the SETLRP mechanism, the radicals generated by single electron transfer (SET) procedures could also be captured by stable nitroxide radicals, and this reaction was termed as the single electron transfer nitroxide radical coupling (SETNRC) reaction.⁹⁶ Also, these two kinds of reactions could be simplified as NRC reactions. Different from the above ATRC reaction or agent (including styrene, nitrene or diene) assisted radical coupling reaction, precursors for generation of radicals and those containing stable nitroxide radicals with controlled molecular weight and low polydispersity indices (PDIs) could be performed by different polymerization mechanisms. Thus, the NRC reaction could proceed in a heterocoupling manner, and polymers with asymmetrical structures or compositions could be achieved.

In some previous reviews, radical based coupling reactions were discussed by concentrating on their mechanisms and the preliminary applications.^{97–103} Herein, we focused on the introduction and comparison of the above radical based coupling reactions according to their history from the development of the initial ATRC reaction to its enhanced version, the NRC reaction. The first section is about the introduction and applications of ATRC reaction. The second section concerns the agent (including nitrene and diene) assisted radical coupling reactions. The third section is about the progress of NRC reactions. The applications of the ATRC homocoupling reaction and its enhanced version the NRC heterocoupling reaction in the construction of topological polymers are the key features. These radical based coupling reactions would show their versatility in the design and synthesis of telechelic, block, H-shaped, star-shaped, macrocyclic, cross-linked, dendrimer polymers and so on.

2 The atom transfer radical coupling (ATRC) reaction

2.1 The mechanism of ATRC reaction

Based on the atom transfer radical addition (ATRA) mechanism,^{104,105} the ATRP mechanism was developed by Wang and Matyjaszewski,^{106–108} and Sawamoto.^{109,110} The key point of the ATRP process was the equilibrium ($K_{\text{ATRP}} = k_{\text{act}}/k_{\text{deact}}$) between the active (Pn^{\bullet}) and dormant species (PnX) via a reversible redox reaction. Typically, the dormant species formed a radical (Pn^{\bullet}) and the metal halide in a higher oxidation state (XMt_{n+1}/L) (k_{act}), and the propagating radical reacted reversibly with the metal halide to regenerate the lower oxidation state transition metal and a polymer with a halogen end group (k_{deact}). In such an ATRP system, because the concentration of radicals was rather low, the termination reactions (k_{tc} , k_{td} , or k_{trs}) could often be neglected.^{16,18–20} Obviously, the higher oxidation state XMt_{n+1} served as the deactivator in the reaction medium and played an important role in the ATRP mechanism.

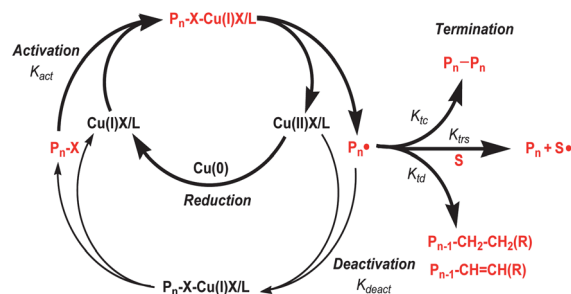
Thus, one could envision, once the quantity of deactivator was decreased or the activator was increased, the equilibrium was shifted and the concentration of radicals would increase. In this case, if excess monomers existed, the ATRP procedure proceeded quickly in an uncontrolled manner. If no monomers existed, the termination by disproportionation (k_{td}) and bimolecular combination (k_{tc}), chain transfer reaction (k_{trs}) or other side reactions would be enhanced.¹¹¹ Under certain conditions, if the termination by disproportionation and chain transfer reaction were hugely or completely suppressed, only termination by bimolecular combination would facilitate the ATRC reaction (Scheme 5).⁸⁹

Typically, the ATRC process relied on the *in situ* formation of macroradicals by an atom transfer radical equilibrium. In order to improve the ATRC reaction, zerovalent copper ($\text{Cu}(0)$) was usually used as a reducing agent, which helped the reduction of deactivator Cu^{2+} species into activator Cu^+ species, and the latter was necessary to achieve activation of the carbon-halide bond. Thus, the equilibrium was strongly shifted toward the formation of active macroradicals whose higher concentration favored irreversible termination reaction by ATRC reaction. Besides the $\text{Cu}(0)$, zerovalent iron ($\text{Fe}(0)$), tin octanoate (SnOct_2), tin ethyl hexanoate ($\text{Sn}(\text{EH})_2$), and ascorbic acid could also be used as reducing agents. Similar to the factors affecting the ATRP mechanism, the ATRC reaction was also strongly influenced by the nature of the ligand, the molecular structure connected to the halogen, the nature of the polymer, the solvent, the reaction temperature and so on.^{112–127} Especially, the molecular structure connected to the halogen was a key factor for the ATRC reaction.

The homocoupling was a typical characteristic of the ATRC reaction, which resulted in polymers with symmetrical structures and compositions. For example, telechelic, multiblock, H-shaped and macrocyclic polymers could be successfully designed and synthesized by the ATRC reaction. Also, the ATRC reaction could be cooperated into step-growth polymerization. These applications of the ATRC reaction in polymer science will be discussed in detail in the following sections.

2.2 The applications of ATRC reaction in polymer science

2.2.1 The synthesis of α,ω -telechelic polymers by ATRC reaction. α,ω -Telechelic polymers are macromolecules that contain two reactive end groups at each end of a linear polymer.

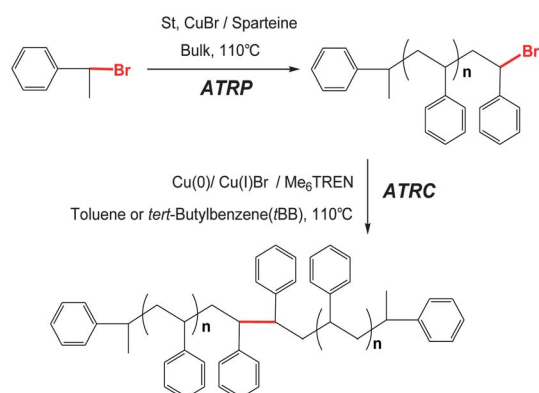


Scheme 5 The scheme for copper-mediated atom transfer radical coupling (ATRC) reaction (Pn : polymer chain, L : ligand, S : chain transfer agent).

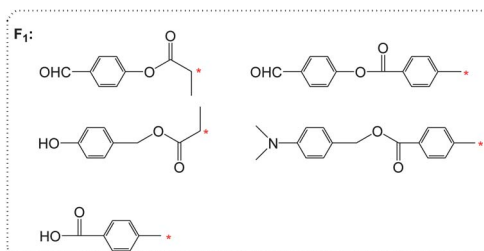
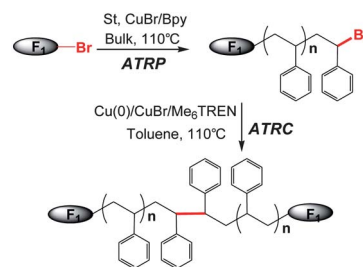
These polymers are usually used as crosslinkers, chain extenders, and important building blocks for various macromolecular structures.¹²⁸ Usually, α,ω -telechelic polymers can be obtained by living anionic polymerization, ATRP, NMRP, SETLRP, RAFT and ROMP mechanisms and so on. Indeed, in order to obtain α,ω -telechelic polymers with high functionalities, an efficient coupling reaction would be a preferable choice.

Originally, in 2002, the ATRC reaction was firstly presented by Fukuda *et al.* using a bromide functionalized polystyrene (PS-Br) precursor with the catalytic system of CuBr/Cu(0)/tris[2-(dimethylamino)ethyl]amine (Me₆TREN) at 110 °C (Scheme 6).⁸⁹ In their work, for the ideal ATRC reaction, the produced PS radicals were modulated and reached a high concentration (about 6.0×10^{-8} mol L⁻¹). The addition of Cu(0) could increase the concentration of PS radicals by a factor of about 30, and hence the coupling reaction by a factor of about 30^2 to 10^3 .^{129,130} Also, they confirmed that the solvent *tert*-butylbenzene (*t*BB) could give a somewhat smaller transfer constant than that by toluene, the ligand Me₆TREN could give a much larger equilibrium constant than that by 4,4'-di(*n*-heptyl)-2,2'-bipyridine (dHBipy).¹³¹ The maximum coupling efficiency could reach to 91% in a short time (<10 min) and there was some fraction of ($7 \pm 4\%$) chains terminated by disproportionation. This preliminary work showed that the ATRC reaction could actually be used in polymer science, however, this ATRC reaction might be affected by several factors, such as the solvent, ligand, and so on.

Later, using the above ATRC reaction, Yagci *et al.* firstly prepared α,ω -telechelic PS bearing different functional groups, such as aldehyde, aromatic hydroxyl, cyano, carboxylic acid and dimethylamino groups, using CuBr/Cu(0)/Me₆TREN as the catalytic system at 110 °C. In their work, the PS-Br precursor was obtained by ATRP (Scheme 7)^{132,133} or by reverse atom transfer radical polymerization (RATRP) (Scheme 8)¹³⁴ of styrene monomers using different initiators containing the corresponding functional groups. For the PS-Br precursor from the copper-mediated ATRP or RATRP mechanism, the ATRC reactions were efficient and a maximum coupling efficiency of 99% could be obtained. However, relatively low coupling efficiency was achieved when the iron-mediated RATRP system was used

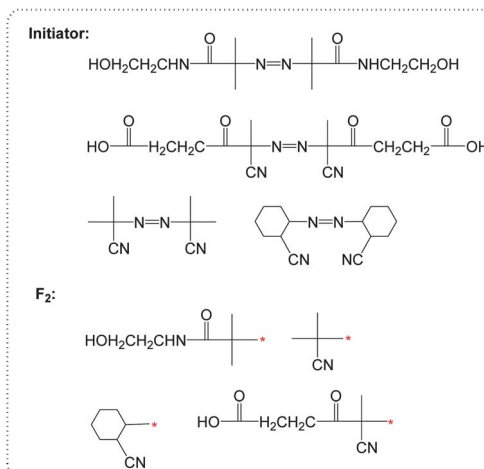
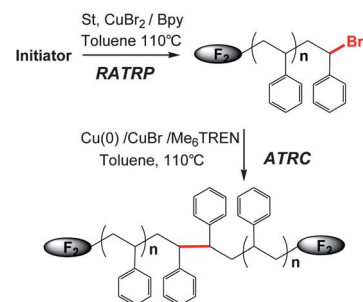


Scheme 6 The synthesis of PS by ATRP mechanism and ATRC reaction.⁸⁹



Scheme 7 The synthesis of α,ω -telechelic PS containing functionalities by ATRP mechanism and ATRC reaction.¹³²

for PS-Br, because the residual ferric salt could not be removed by conventional purification procedures and would interrupt the following redox reactions. Similarly, Boutevin *et al.* also prepared several hydroxyl, acid, or ester group functionalized α,ω -telechelic PS by ATRP mechanism and the following ATRC reaction using Cu(0)/Bpy as the catalytic system and anisole as

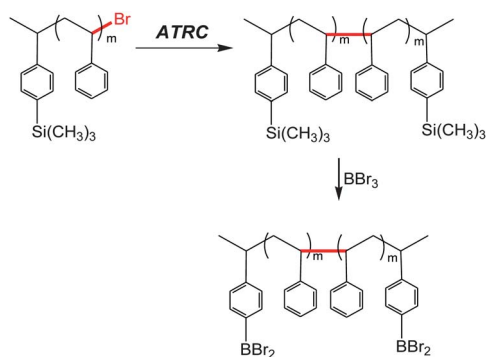


Scheme 8 The synthesis of α,ω -telechelic PS containing functionalities by RATRP mechanism and ATRC reaction.¹³⁴

the solvent.¹³⁵ The coupling efficiency was between 79 and 100%, which depended on the structures of the initiators.

Simultaneously, Matyjaszewski *et al.* also studied the ATRC reaction of PS-Br in detail.¹¹⁸ Their work showed that nanosize Cu(0), Fe(0), SnOct₂ and ascorbic acid could all be used as reducing agents. Also, they further synthesized functional HO-PS-Br precursors by ATRP mechanism using a hydroxyl functionalized initiator, and the following ATRC reaction was operated for α,ω -telechelic HO-PS-OH using CuBr/Cu(0)/PMDETA as the catalytic system and toluene as the solvent.⁹⁰ Interestingly, Matyjaszewski *et al.* discriminated the purity of the obtained α,ω -telechelic HO-PS-OH using Gradient Polymer Elution Chromatography (GPEC), which could sufficiently separate polymers with similar molecular weights but different hydroxyl functionalities.¹³⁶ The measurement showed that the α,ω -telechelic HO-PS-OH obtained from the ATRC reaction gave quantitative information about the termination by bimolecular combination. However, the chain-end functionality of α,ω -telechelic HO-PS-OH from post-modification of α,ω -telechelic Br-PS-Br by nucleophilic substitution and subsequent click reactions contained less hydroxyl groups. Thus, their work further confirmed the high coupling efficiency of the ATRC reaction.

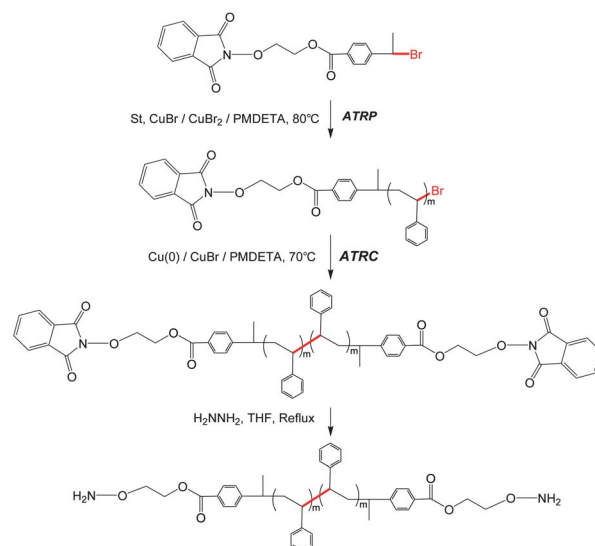
Later, based on the above progress in ATRC reaction, a library of α,ω -telechelic polymers were successfully realized by several groups and applied in various fields. For example, Jakle *et al.* designed and synthesized a novel α,ω -bis(borane)-functionalized PS by ATRC reaction of the trimethylsilyl-functionalized PS-Br and the following exchange with boron tribromide (BBr₃) and subsequent reaction with nucleophiles (Scheme 9).¹³⁷ The obtained α,ω -bis(borane)-functionalized PS showed some special self-assembly behavior in solutions. Monge *et al.* prepared α,ω -bis(trimethylammonium)-functionalized PS by ATRC reaction of (*N*-Boc-propylamino)-functionalized PS-Br and subsequent removal of the *tert*-butyloxycarbonyl group and permethylation reactions.¹³⁸ The obtained α,ω -telechelic PS could be used in liquid crystals for their special aggregation behavior. Similarly, by combination of the ATRP mechanism with the ATRC reaction, Maynard *et al.* synthesized α,ω -bis(aminooxy)-functionalized PS, in which the precursor was obtained by the ATRP mechanism using 1-bromoethylphenyl possessing an *N*-hydroxyphthalimide



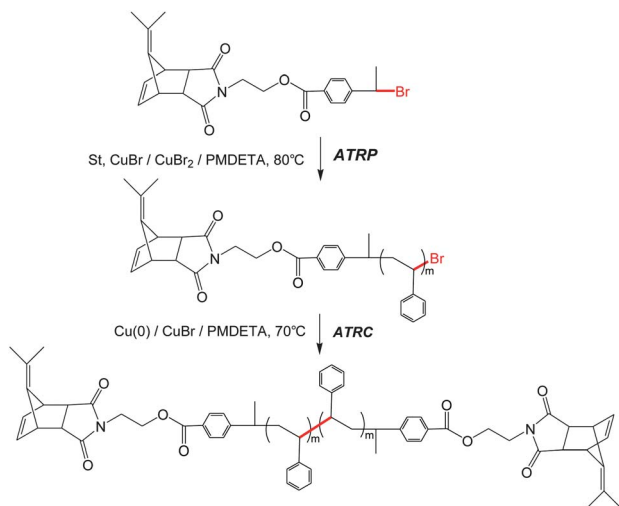
Scheme 9 The synthesis of α,ω -bis(borane)-functionalized PS by ATRP mechanism, ATRC reaction and the subsequent silicon–boron exchange.¹³⁷

group as initiator (Scheme 10).¹³⁹ Also, they synthesized a series of thiol-reactive α,ω -telechelic PS by ATRC reaction, and the precursor was synthesized by the ATRP mechanism from a dimethylfulvene-protected maleimide-functionalized initiator (Scheme 11).¹⁴⁰ These two α,ω -telechelic PS synthesized by Maynard *et al.* could be used for conjugation of proteins and applied in biotechnology and nanotechnology. Anthamatten *et al.* synthesized α,ω -bis(ureidopyrimidinone)-functionalized PS by a combination of the ATRP mechanism with the ATRC reaction (Scheme 12).¹⁴¹ The end-group aggregation or stacking behavior induced by hydrogen bonding greatly lowered their miscibility in blends, which would endow this polymer with some special applications.

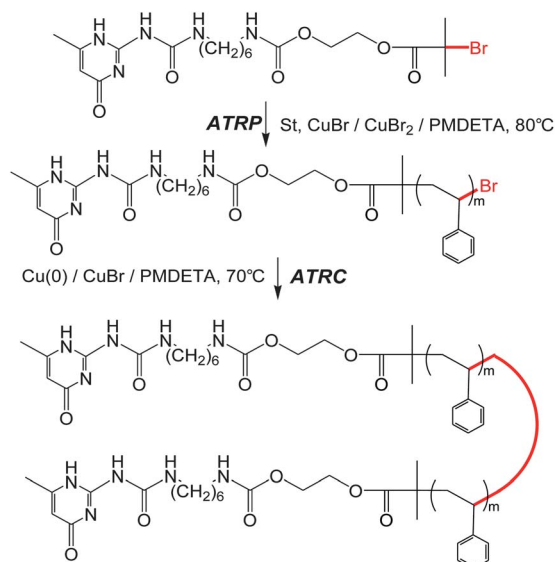
However, one should note that the precursors used in the above ATRC reaction were mainly composed of PS chains and high (almost quantitative) coupling efficiency could be reached. Some researchers also tried to extend the sort of polymers adapted to the ATRC reaction. For example, Matyjaszewski *et al.*⁹⁰ synthesized hydroxyl-terminated poly(methyl acrylate) (HO-PMA-Br) by ATRP mechanism using a hydroxyl functionalized initiator, and the ATRC reaction was also investigated for α,ω -telechelic HO-PMA-OH (Scheme 13). Compared with the ATRC reaction for the above HO-PS-Br precursor, under similar ATRC reaction conditions, the coupling reaction of HO-PMA-Br was slow since the ATRP equilibrium constant of HO-PMA-Br was approximately 100 times lower than that of HO-PS-Br, and consequently the radical concentration of HO-PMA radicals was about 4 orders of magnitude lower than that of HO-PS-Br. Later, the low coupling efficiency of poly(methyl methacrylate) (PMMA) was also confirmed by Anthamatten's work, and only 66% efficiency of ATRC reaction was achieved when ureidopyrimidinone-functionalized PMMA-Br was used as precursors.¹⁴¹ Alternatively, Matyjaszewski *et al.* reported that, when a small quantity of St monomers were introduced into the ATRC reaction system of HO-PMA-Br, the HO-PMA radicals



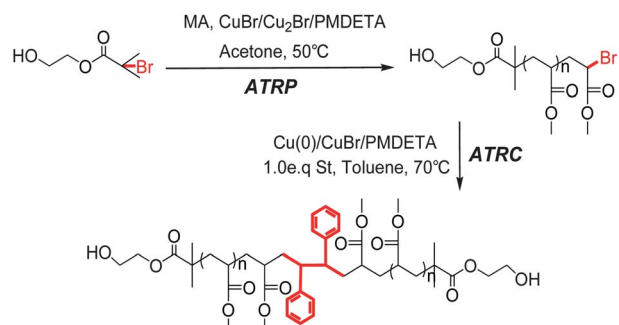
Scheme 10 The synthesis of α,ω -bis(aminooxy)-functionalized PS by ATRP mechanism and ATRC reaction.¹³⁹



Scheme 11 The synthesis of thiol-reactive α,ω -telechelic PS by ATRP mechanism and ATRC reaction.¹⁴⁰



Scheme 12 The synthesis of α,ω -bis(ureidopyrimidinone)-functionalized by ATRP mechanism and ATRC reaction.¹⁴¹

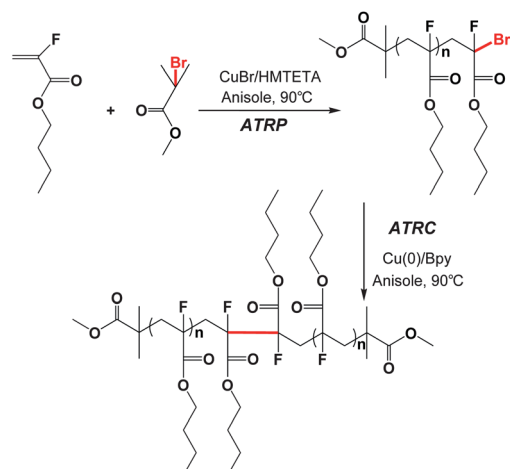


Scheme 13 The synthesis of HO-PMA-OH by ATRP mechanism and ATRC reaction.⁹⁰

generated during the activation step would first react with the styrene monomers and produce styrene-terminated HO-PMA-St radicals, which were combined at rates similar to that of PS chains.⁹⁰ Later, a similar styrene assisted ATRC strategy was also developed and confirmed by Yagci *et al.*¹³³ As a systematic work, Boutevin *et al.* investigated a library of ATRC reactions of polyacrylate precursors prepared by ATRP mechanism, and Cu(0)/Bpy was used as the catalytic system in the ATRC reaction.¹⁴² Their results showed that the coupling efficiencies were mainly determined by and depended on the nature of the monomers for ATRP. Using a styrene assisted ATRC reaction similar to that of Matyjaszewski, the primary functionalization of the brominated polyacrylate chain end with styrene might greatly increase the coupling efficiency. They also prepared bromide functionalized poly(butyl α -fluoroacrylate) [Poly(FABu)-Br] by ATRP of butyl α -fluoroacrylate monomers, and the subsequent ATRC reaction was performed and investigated (Scheme 14).¹⁴³ For this Poly(FABu)-Br precursor, the coupling efficiency by bimolecular combination was 80%, however, about 20% was ascribed to disproportionation termination. Interestingly, the coupling efficiency for Poly(FABu)-Br was higher than its hydrogenated homologue (approximately 60%).

Obviously, the above works solidly confirmed that the structures connected to the halogen had an important effect on the activity of generated radicals. The PS radicals preferred bimolecular combination, however, the poly(methyl)acrylate radicals preferred disproportionation termination. Thus, in general, the latter was not suitable for the ATRC reaction.

Besides the above styrene assisted ATRC reaction, alternatively, some other strategies were also developed to increase the coupling efficiency of the ATRC reaction for poly(methyl)acrylate precursors. The first strategy, the replacement of usually a bromine group with an iodine group at the chain end would help the ATRC reaction for poly(methyl)acrylate precursors because of the weaker bond energy of the carbon-iodine bond compared to that of the carbon-bromine bond, which should favor the active radical species formation (Table 1).¹¹⁷ In order to



Scheme 14 The synthesis of Poly(FABu) by ATRP mechanism and ATRC reaction.¹⁴³

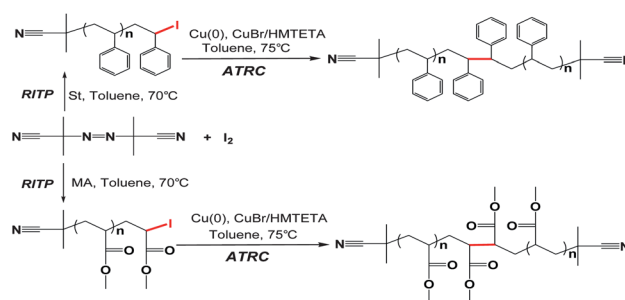
confirm this hypothesis, Boutevin *et al.* synthesized PS-I and PMA-I by reverse iodine transfer polymerization (RITP) mechanism, and the resulted polymers were coupled by ATRC reaction (Scheme 15). Fortunately, a quantitative coupling efficiency (100%) for the first time was obtained for PMA-I with CuBr/Cu(0)/1,1',4,7,10,10'-hexamethyltriethylenetetramine (HMTETA) as the catalytic system, which opened a facile and efficient route to α,ω -telechelic poly(methyl)acrylate polymers. The second strategy, enlightened by the SETLRP mechanism and the above ATRC reaction, Huang *et al.* reported that the radicals generated by the single electron transfer (SET) procedure could also be terminated by bimolecular combination, and this was termed as single electron transfer radical coupling (SETRC). This SETRC was carried out at room temperature using alkyne-PMMA-Br as precursor and nanosize Cu(0)/PMDETA as catalytic system, and the coupling efficiency could exceed 90% in 24 h (Scheme 16).¹⁴⁴ The lower temperature would largely depress the possible disproportionation termination and increase the expected bimolecular combination. Thus, this work also provides a promising strategy for preparing well defined α,ω -telechelic polymers with various functional groups, especially for poly(methyl)acrylate based structures.

Additionally, using PS-Cl or PS-Br as precursors, the activators generated by electron transfer (AGET) procedure was also integrated into ATRC reaction systems and termed as AGET ATRC by Tillman *et al.*¹⁴⁵ In place of nanosize Cu(0), "greener" reducing agents Sn(EH)₂, ascorbic acid, or glucose were used. Specially, the AGET ATRC was able to successfully carry out and use the oxidatively more stable Cu(II) as the initial state of the redox-active metal catalysts, which were later reduced to activators of Cu(I) *in situ*. The coupling efficiency of the AGET ATRC reaction was similar to that of typical ATRC systems, but only 10–25% of the copper metal was used. Actually, in the case of the ATRC reaction, an excess of metal (copper salt and so on) was used to alter an unfavorable equilibrium and create a buildup of the polymer radicals, which was essential for the bimolecular combination reaction to proceed at a suitable rate yet otherwise unfavorable in the preparation of polymeric materials. Thus, the AGET ATRC reaction might be endowed with many potential applications in the future.

As an alternative strategy, activation by silane radicals did not require the addition of any metals to the reaction mixture, which was termed as silane radical atom abstraction (SRAA) and could be incorporated into the radical coupling reaction.¹⁴⁶ In fact, the bromophilicity of silane radicals has been exploited in reactions involving alkyl bromides, generating carbon-based radicals that can be trapped by persistent, oxygen-based

Table 1 Bond energies and bond lengths for carbon–halide bonds (C sp³)¹¹⁷

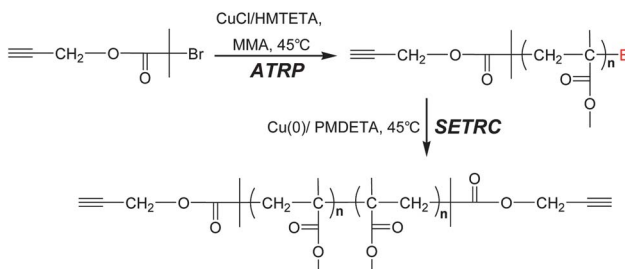
Bond type	Bond energy (kJ mol ⁻¹)	Bond length (Å)
C–Cl	330	1.79
C–Br	275	1.97
C–I	220	2.16



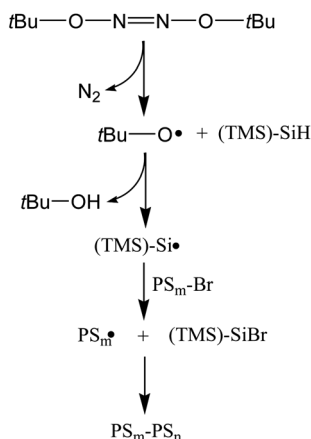
Scheme 15 The synthesis of α,ω -telechelic PMA and PS by RITP mechanism and ATRC reaction.¹¹⁷

radicals to produce a variety of alkoxyamines. Using the SRAA method, Tillman *et al.* showed that the radicals generated from 9-bromoanthracene or 9-chloroanthracene could be combined with TEMPO and modulate the NMRP mechanism.¹⁴⁷ Similarly, the macroradical generated from PS-Br was also coupled to TEMPO and used to mediate the NMRP mechanism for chain extension.¹⁴⁸ Very recently, using the SRAA mechanism, they also showed that the polymer radicals generated from mono-brominated PS-Br precursors with controllable molecular weight and low PDI could be used for radical coupling (Scheme 17).¹⁴⁹ The author claimed that these results compared favorably to literature reports of ATRC reactions run under similar conditions.^{118,132} Thus, these results preliminarily showed that the SRAA method might also have some applications in polymer science. However, there were some challenges which should be solved and more applications of the SRAA method should be extended in polymer science to confirm the versatility of this strategy.

Obviously, the synthesis of α,ω -telechelic polymers was the major application of the ATRC reaction. Because the atom transfer procedure in the ATRC reaction was derived from the ATRP mechanism, there were many common characteristics between the ATRC reaction and the ATRP mechanism. Thus, the established theory on the ATRP mechanism could also be applied to the ATRC reaction. Predicted as progress on the ATRP mechanism, the different activities between PS and poly(methyl)acrylate radicals would lead to distinguished differences for the coupling efficiencies of the ATRC reaction. However, the styrene assisted ATRC reaction, ATRC from RITP produced precursors, SETRC reaction, as well as the AGET ATRC reaction and SRAA based radical coupling reaction might be representative and potential strategies, which featured high



Scheme 16 The synthesis of α,ω -telechelic PMMA by ATRP mechanism and SETRC reaction.¹⁴⁴

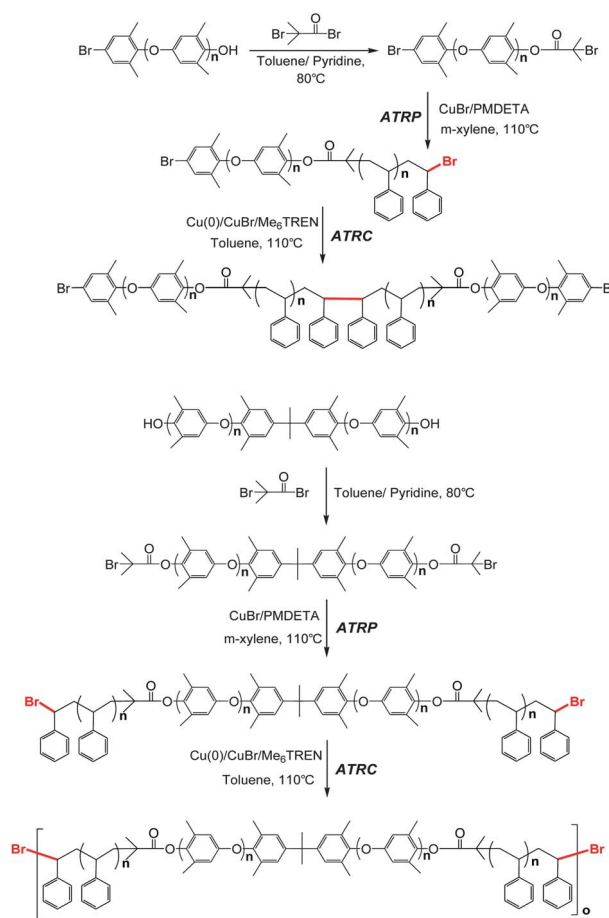


Scheme 17 The proposed mechanism of SRAA to generate PS radicals.¹⁴⁹

coupling efficiencies and are universal to both PS and poly(methyl)acrylate precursors.

2.2.2 The synthesis of multiblock polymers by ATRC reaction. Based on the above studies on the ATRC reaction, one could suggest that if the precursors for telechelic polymers were changed from a homopolymer to a block polymer with end halogen groups, multiblock polymers could be obtained. The block polymers were usually prepared *via* ATRP mechanism using various macroinitiators. For example, in 2004, Hocker *et al.* synthesized several PS-*b*-poly(bisphenol A carbonate)-*b*-PS (PS-*b*-PC-*b*-PS) and PMMA-*b*-PC-*b*-PMMA triblock polymers by ATRP of St or MMA monomers using a bifunctional macroinitiator, which was obtained by esterification of bishydroxyl telechelic PC with α -chlorophenylacetyl chloride.¹⁵⁰ Similarly, they also synthesized some poly(phenylene oxide) (PPO)-*b*-PS and PS-*b*-PPO-*b*-PS polymers by ATRP of St monomers using monofunctional and bifunctional macroinitiators, which were derived from mono- and bishydroxyl telechelic PPO esterified with 2-bromoisobutyryl bromide.¹⁵¹ Using the above obtained diblock or triblock polymers as precursors, the ATRC reaction was performed for multiblock polymers using Cu(0)/CuBr/ligand or Cu(0)/ligand as catalytic systems (Scheme 18).¹⁵² However, significant degradation of the PC segment was observed under ATRC conditions, which confirmed that the block polymers with PC segments were not suitable for ATRC reactions. The coupling efficiency of ATRC reaction for block polymers containing PS and PPO segments was lower than that in the case of low molecular weight ($M_n < 5000 \text{ g mol}^{-1}$) PS homopolymers because of the smaller concentration of reactive end groups compared to the concentration of repeating units. Also, the side reactions of hydrogen transfer from the $-\text{CH}_3$ groups of the PPO repeating units to an active chain end might be another reason for the lower coupling efficiency.

Similarly, Sawaguchi *et al.* prepared isotactic polypropylene (iPP)-PS ($M_n = 25\,000 \text{ g mol}^{-1}$ and PDI = 4.1) and iPP-PMMA ($M_n = 39\,000 \text{ g mol}^{-1}$ and PDI = 2.8) by ATRC reaction of PS-*b*-iPP-*b*-PS ($M_n = 8900 \text{ g mol}^{-1}$ and PDI = 1.3) and PMMA-*b*-iPP-*b*-PMMA ($M_n = 13\,000 \text{ g mol}^{-1}$ and PDI = 1.4) triblock polymers, respectively. All of the precursors of triblock polymers were

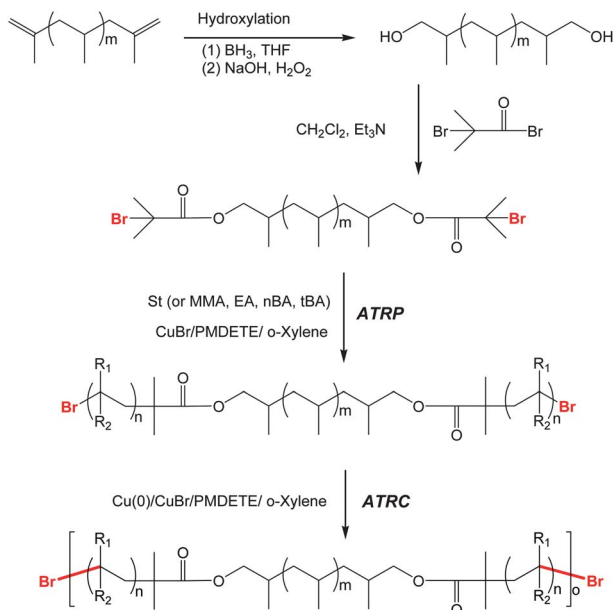


Scheme 18 The synthesis of multiblock polymers containing PS and PPO segments by ATRP mechanism and ATRC reaction.¹⁵²

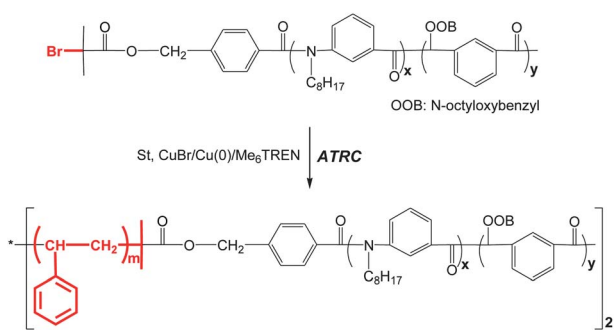
obtained by ATRP of St and MMA monomers using Br-iPP-Br as a bifunctional macroinitiator (Scheme 19).¹⁵³ Alternatively, the ATRC reaction of high molecular weight AB-type diblock copolymer, 2-bromoisobutyryl-terminated poly(*N*-octyloxybenzyl-*m*-benzamide)-*b*-poly(*N*-octyl-*m*-benzamide) ($M_n = 9300 \text{ g mol}^{-1}$, PDI = 1.09), was conducted to yield ABA-type triblock polybenzamides ($M_n = 18\,000 \text{ g mol}^{-1}$, PDI < 1.18) with a high coupling efficiency of 94% by Yokozawa *et al.* (Scheme 20).¹⁵⁴ Furthermore, the selective removal of the octyloxybenzyl groups would result in a poly(*N*-H-*m*-benzamide) segment.

Obviously, it was different from the synthesis of telechelic polymers by ATRC reaction, the coupling efficiencies in the synthesis of multiblock polymers were greatly decreased due to the hindrance brought by the increasing molecular weight of multiblock polymers.

2.2.3 The synthesis of nonlinear polymers with complicated structures by ATRC reaction. As described before, homocoupling was the typical characteristic of the ATRC reaction. Thus, great limitations were found for the ATRC reaction in designing of polymers with complicated structures, and only a few examples were available. In 2009, Huang *et al.* firstly prepared ABC star-shaped precursors composed of PS (A), poly(ethylene oxide) (PEO) (B), and poly(*tert*-butyl acrylate) (PtBA) (C), and H-shaped ABCAB terpolymers were obtained by



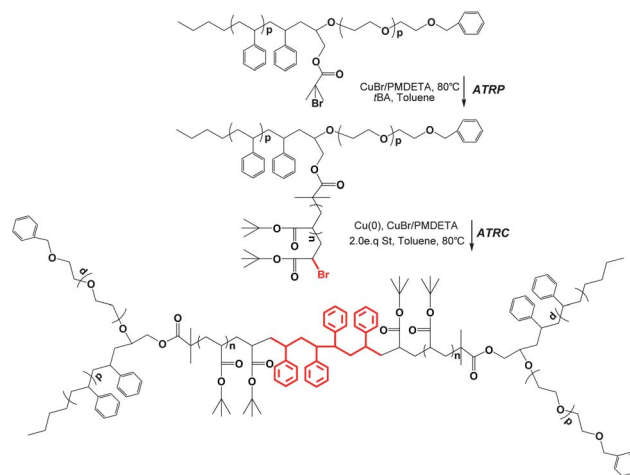
Scheme 19 The synthesis of multiblock polymers containing iPP, PS or PMMA segments by ATRP mechanism and ATRC reaction.¹⁵³



Scheme 20 The synthesis of ABA-type triblock polybenzamide by ATRC reaction.¹⁵⁴

ATRC reaction *via* the recombination of the *Pt*BA end (Scheme 21).¹⁵⁵ As discussed in the above, the tendency of *Pt*BA-Br to the disproportionation termination and the space hindrance brought by the huge star-shaped precursors might lower the coupling efficiency. Again, by means of the styrene assisted ATRC reaction, the H-shaped terpolymer could be successfully formed in the presence of a small quantity of styrene monomers, and $\text{CuBr}/\text{Cu}(0)/\text{PMDETE}$ was used as the catalytic system at 90 °C.

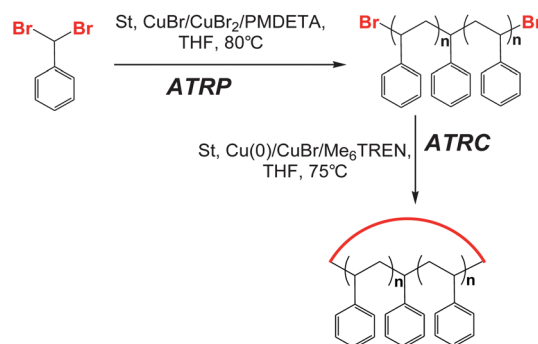
Recently, macrocyclic polymers were attracting more and more attention from researchers because of their special topological structures. However, looking for an efficient and simple strategy was always the key point for macrocyclic polymers.^{156–161} Without exception, the ATRC reaction was also used for the preparation of macrocyclic polymers by an intramolecular style. For example, Tillman *et al.* synthesized macrocyclic PS in high yields (>90%) by intramolecular ATRC reaction of the chain ends using $\text{CuBr}/\text{Cu}(0)/\text{Me}_6\text{TREN}$ as the catalytic system (Scheme 22).¹⁶² In their preparation procedure, the slow



Scheme 21 The synthesis of H-shaped ABCAB terpolymers by ATRC reaction.¹⁵⁵

addition of the dibrominated Br-PS-Br precursors into a refluxing tetrahydrofuran (THF) solution was the key step and must be performed cautiously. During the ATRC cyclization, the intramolecular ring closing reaction was also accompanied by some minor competition from intermolecular coupling observed from gel permeation chromatography (GPC) measurement, and the latter seemed to be unavoidable. Also, the ATRC reaction could be used to crosslink polymers. Chen *et al.* designed a multifunctional initiator with chemically labile disulfide and ester groups bearing four bromoisobutyryl groups by esterification of bis(2-hydroxyethyl) disulfide with 2,2-bis(2-bromoisobutyroyloxymethyl)propionic acid.¹⁶³ After the synthesis of some well-defined four-arm star PS by ATRP of St monomers using the above multifunctional initiator, a polymer nanogel was obtained by ATRC reaction. Interestingly, owing to the presence of the disulfide and the ester linkages in precisely controlled positions of the core inherited from the initiator, the polymer nanogel demonstrated interesting stepwise cleavage properties.

Thus, one could further conclude that, besides the above mentioned homocoupling characteristic the hindrance brought by the complicated nonlinear structures accompanied with the



Scheme 22 The synthesis of macrocyclic PS by ATRP mechanism and ATRC reaction.¹⁶²

increased molecular weight were also important reasons for the low coupling efficiency, and ultimately limited the application of the ATRC reaction in the synthesis of polymers with complicated structures.

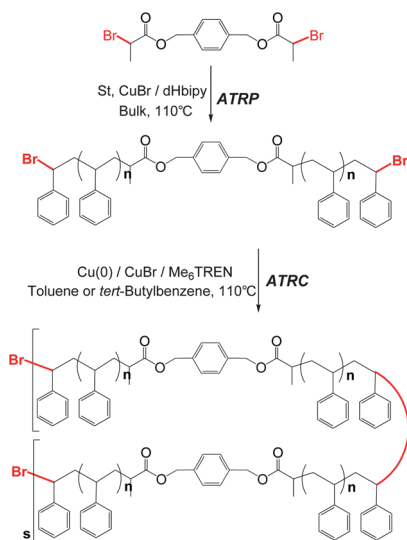
2.2.4 The application of ATRC reaction in step-growth polymerization. In principle, reactions between two active groups could all be used in step-growth polymerization, such as the reaction between carboxyl or acyl and hydroxyl or amino groups. Accordingly, the radical based ATRC reaction could also be used in step-growth polymerization. In fact, this radical coupling reaction was scarcely used in step-growth polymerization because radicals could undergo disproportionation, chain transfer reactions and so on, which made it impossible to produce polymers with high molecular weight. In recent years, however, there were some tentative works reported on step-growth polymerization by ATRC reaction.

Originally, using α,ω -dibromide functionalized polystyrene (Br-PS-Br) with the catalytic system CuBr/Cu(0)/Me₆TREN, Fukuda *et al.* completed the chain extension in a step-growth style by ATRC reaction (Scheme 23).⁸⁹ The coupling reaction produced polymers with a variety of chain lengths, whose distribution obeyed the theory of random coupling. Later, Matyjaszewski *et al.*¹¹⁸ also studied the ATRC reaction of Br-PS-Br, and their results also showed that the coupling of Br-PS-Br homologues gave high molecular weight products with high PDIs. As described before, during the synthesis of macrocyclic PS by ATRC reaction from dibrominated Br-PS-Br precursors, Tillman *et al.* also found the product of chain extension from intermolecular coupling in the CuBr/Me₆TREN/Cu(0) catalytic system.¹⁶² Recently, Narain *et al.* performed the ATRC reaction of α,ω -dibromide functionalized poly(γ -caprolactone) (Br-PCL-Br) using CuCl/Me₆TREN as the catalytic system in the absence of nanosize Cu(0) reducing agent (Scheme 24).¹⁶⁴ The precursor HO-PCL-OH was synthesized with an excess of 2-bromoisobutyryl bromide, leading to above 99% esterification. Their work showed that the main reaction was bimolecular

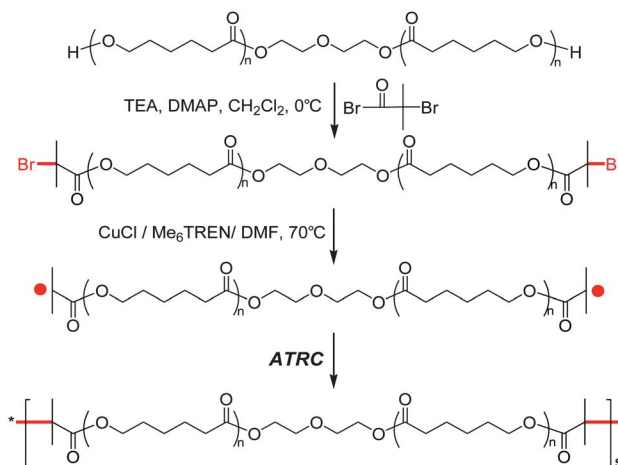
coupling ($\sim 80\%$), while a shoulder at molecular weights about 6–7 times that of the macroinitiator was also observed, attributed to multimolecular coupling. Thus, one could observe that, during the step-growth polymerization by ATRC reaction of polymeric precursors, the possible occurrence of side reactions such as disproportionation might hinder further radical coupling of the free chain ends, especially for the precursors with high molecular weight.

Instead of the above ATRC reaction between dibromide functionalized precursors for polymers with high molecular weight,^{89,118} the ATRC reaction could also be applied in step-growth polymerization of small molecules. For example, a typical ATRP bifunctional initiator *p*-dibromoxylene was polymerized in ATRC conditions, yielding the insoluble poly(*p*-xylylene), by Yagci *et al.* (Scheme 25).¹⁶⁵ In order to confirm the success of the reaction, a more soluble product, PMMA-*b*-(*p*-phenylene-ethylene), was also synthesized by adding 5% PMMA with an activated bromine atom at the chain end in the feed. The results showed that the diblock polymer was formed. In a similar approach, a novel polyester was prepared by step-growth polymerization of 1,3-diyl-bis(2-chloro-2-phenylacetate) (DBCP) based on the ATRC reaction (Scheme 26).¹⁶⁶ Thus, the ATRC reaction might open a novel pathway for various functional polymers by using appropriate ATRP bifunctional (macro)initiators as monomers in ATRC conditions.

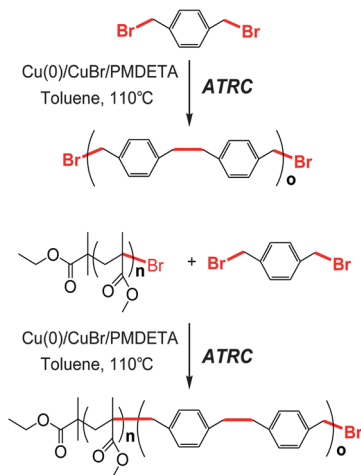
All in all, based on the homocoupling of radicals, the ATRC reaction had facilitated the construction of some polymers with well-defined symmetrical structures and compositions, such as α,ω -telechelic, multiblock, macrocyclic, crosslinked and H-shaped copolymers. For the homopolymer precursors, the preferred one was PS-Br, and the ATRC reaction for poly(methyl)acrylate precursor should be assisted by traces of styrene monomers or use of the precursor poly(methyl)acrylate preformed by the RITP mechanism, as well as adopting the similar SETRC method. Obviously, the application of ATRC reaction was mainly focused on the synthesis of α,ω -telechelic polymers, however, multiblock and nonlinear polymers with complicated structures were limited and rarely exemplified. Up to now, there



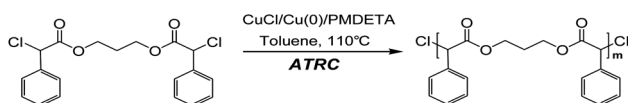
Scheme 23 The chain extension of Br-PS-Br by ATRC reaction.⁸⁹



Scheme 24 The chain extension of Br-PCL-Br by ATRC reaction.¹⁶⁴



Scheme 25 The synthesis of poly(*p*-xylylene) by ATRC based step-growth polymerization.¹⁶⁵



Scheme 26 The synthesis of polyesters by ATRC based step-growth polymerization.¹⁶⁶

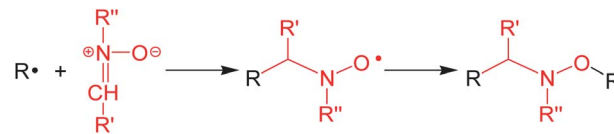
are still some difficulties for the synthesis of polymers with complicated structures and compositions by ATRC reaction, because the higher molecular weight ($M_n > 5000 \text{ g mol}^{-1}$) and branched topology of polymers would increase the space hindrance of radicals and induce some unavoidable side reactions (mainly by disproportionation) to the macroradicals. Later, the nitrone assisted radical coupling and diene assisted radical coupling reactions were developed to modify the above ATRC reaction.

3 The agent assisted radical coupling

3.1 The mechanism of nitrone assisted radical coupling

Alkoxyamines, as a characteristic unimolecular initiator for the NMRP mechanism, were usually prepared from the corresponding nitroxides and carbon-centered radicals.^{167,168} Also, alkoxyamines could be obtained by reactions between alkyl radicals and a nitrone compound.^{98,169–175} Typically, the *in situ* generated carbon-centered radical was reacted with a nitrone to form an intermediate nitroxide, and then, another radical was captured by the formed nitroxide immediately to produce the unimolecular alkoxyamine (Scheme 27). Obviously, one nitrone would react with two equivalents of carbon-centered radicals. Thus, the alkoxyamines obtained by this route have a symmetrical structure with the same groups attached to both the nitrogen and oxygen atoms by the double addition procedure.^{170–172,176,177}

Based on the reaction related to the nitrone used in small molecular alkoxyamines, the strategy for alkoxyamines was also firstly considered in polymer science by Barner-Kowollik *et al.* in



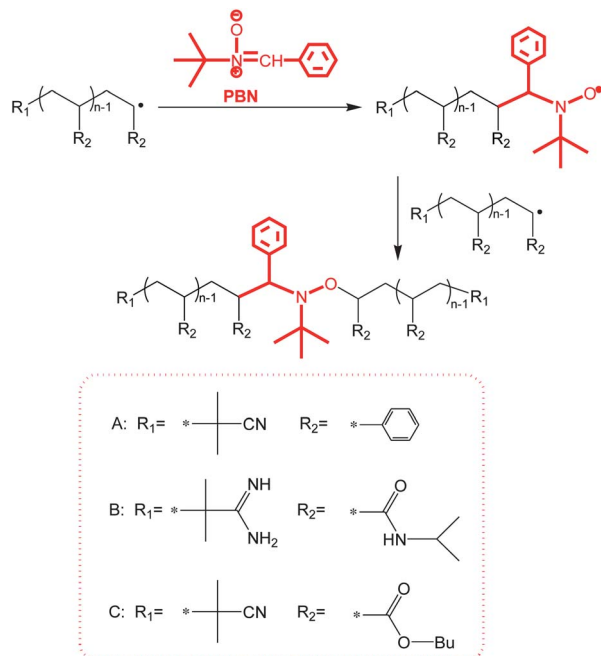
Scheme 27 The spin trapping reaction between radicals and a nitrone to form an alkoxyamine.⁹⁸

2008.^{91,178} Similar to the previously investigated styrene assisted ATRC reaction for increasing the coupling efficiency of poly-(methyl)acrylate polymers in Section 2.2.1,^{90,133} the nitrone could also be used to increase the efficiency of radical coupling according to the above synthesis procedure for alkoxyamine. This method was rather simple and efficient, which opened the door of the applications of nitrones in polymer science. Using nitrone assisted radical coupling, some midchain functionalized, star-shaped, dendrimer, crosslinked, macrocyclic and H-shaped polymers were prepared, and this strategy could also be used in step-growth polymerization to prepare some functional polymers.

3.2 The application of nitrone assisted radical coupling in polymer science

3.2.1 The synthesis of linear midchain functionalized polymer by nitrone assisted radical coupling. In classical radical polymerization, the nitrone agent was usually used as a terminating agent to modulate the molecular weight of polymers by adding some nitrones directly into the polymerization system. Based on this mechanistic viewpoint, Barner-Kowollik *et al.* proposed a controlled polymerization mechanism termed enhanced spin capturing polymerization (ESCP),¹⁷⁸ which usually employed radical spin traps (*N-tert*-butyl- α -phenylnitron (PBN)) as controlling reagents to efficiently capture macroradicals by forming irreversibly terminating macro-nitroxides that not only enhanced but also controlled cross-termination reactions. This ESCP mechanism could be used to efficiently control the molecular weight and PDIs of polymers in radical polymerization of St, butyl acrylate (BA) and *N*-isopropylacrylamide (NIPAAm) monomers (Scheme 28). Similar to the NMRP mechanism, there was an alkoxyamine embedded into the polymers. However, there were still some differences of the nitrone mediated ESCP mechanism from the NMRP: the polymers made by the ESCP mechanism did not participate in any equilibrium reactions (*via* the capping and uncapping actions of nitroxide radicals with macroradicals) under the experimental conditions (at 60 °C or lower) because thermal cleavage of the C–O–N bond did not occur at such low temperatures. After ESCP polymerization, midchain functionalized polymers with an embedded alkoxyamine were achieved, which could be further used in the NMRP mechanism for ABA type triblock copolymers.¹⁷⁹

Alternatively, instead of using nitrones, monomers and propagating macroradicals in a one-pot style by the ESCP mechanism, a method using the reactions between nitrones and macroradicals generated directly from the preformed polymers was also presented by Barner-Kowollik *et al.* and termed nitrone-mediated

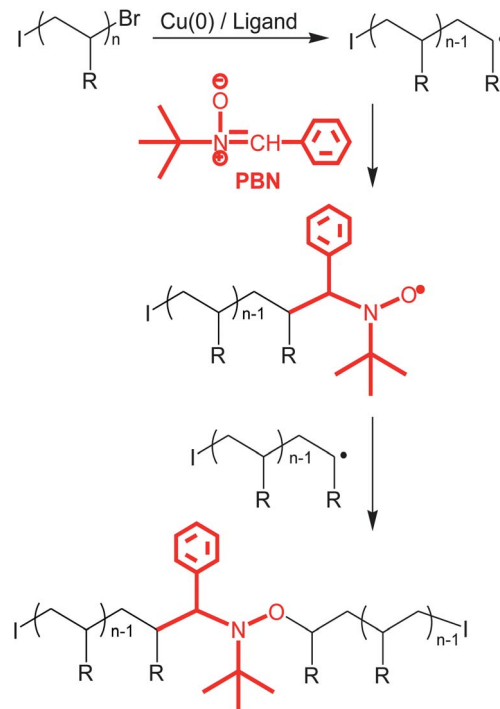


Scheme 28 The synthesis of PS, PNIPAAm and PBA via the ESCP mechanism.¹⁷⁸

radical coupling (NMRC) reaction (Scheme 29).⁹¹ Usually, the precursors were prepared by the ATRP mechanism and a halogen end group was retained to generate radicals using a copper catalytic system, and PBN was used as a radical spin trap. Because the precursors were obtained by the “living”/controlled ATRP mechanism, the well-defined architectures of coupled products could be inherited from the precursors with predicted molecular weight and low PDIs. Similar to the synthesis procedure for alkoxyamines, the formation of nitroxides upon reaction of a radical with nitron was utilized to enforce the combination with a second macroradical. Even in systems where radical disproportionation may be expected, only combination products would be found. Thus, the NMRC reaction was also an efficient and versatile radical–radical conjugation method for midchain functionalized polymers.

Besides the PBN agent, the applications of some other nitrones, such as *N*-methyl- α -phenylnitron (PMN), *N*-methyl- α -(4-bromophenyl)nitron (*p*BPMN) and so on, in the radical coupling reactions were also investigated (Scheme 30), and the results showed that steric effects of nitrones played an important role in the kinetics of the radical coupling reactions.¹⁸⁰ On the other hand, regardless of nitron assisted radical coupling reactions in ESCP mechanism and NMRC reaction procedure, the embedded midchain functionalities of alkoxyamines all originated from the nitron. Thus, when a functionalized nitron was employed, linkages such as alkynes, hydroxyl groups and so on could also be introduced into the polymers for subsequent polymer conjugation reactions.

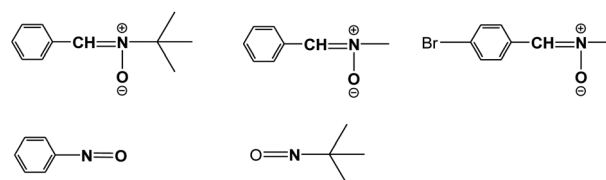
3.2.2 The synthesis of nonlinear polymers by nitron assisted radical coupling. Predicted by the above reports, when a nitron containing a functional group was designed and embedded into the polymers, some further modifications could



Scheme 29 The mechanism for NMRC reaction (I represents the polymer end group resulting from the initiator employed in the ATRP reaction).⁹¹

be performed to form polymers with complicated architectures after the nitron assisted radical coupling reactions (including the ESCP mechanism and NMRC reaction). For example, Barner-Kowollik *et al.* designed a novel nitron (α -4-(3-(trimethylsilyl)prop-2-ynoxy)-*N*-*tert*-butylnitron) with an alkyne group, and this compound was applied in the ESCP mechanism as well as the NMRC reaction.¹⁸¹ After the introduction of an alkoxyamine moiety and the following deprotection of the alkyne group by tetrabutylammonium fluoride trihydrate (TBAF), PS or poly(isobornyl acrylate) (PiBoA) featuring an alkoxyamine group and an alkyne group in the midchain position were obtained, and the alkyne group was selectively coupled to azide-terminated polymer for 3-arm star-shaped polymers by CuAAC chemistry (Scheme 31).

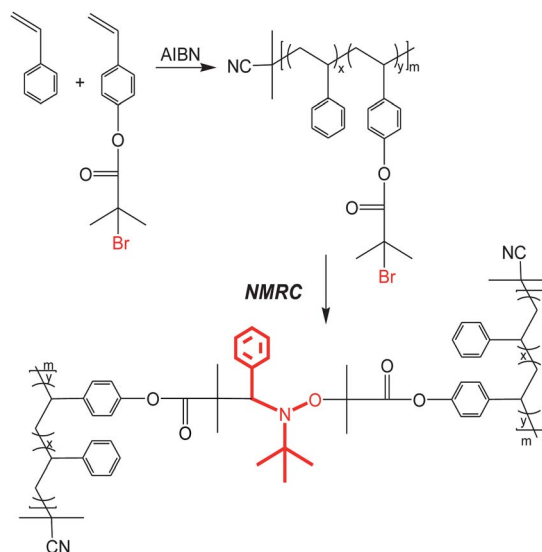
Similarly, by using the nitron related ESCP mechanism or NMRC reaction, reversible networks with controlled architecture and cleavable connections were also synthesized (Scheme 32).¹⁸² In the case of nitron assisted radical coupling reaction in an ESCP style, reversible polymeric networks were formed in the presence of PBN and divinylbenzene (DVB). However, the



Scheme 30 The structures of nitrones usually used in literatures.¹⁸⁰

cleaved fragments of polymer network by the ESCP method were composed from linear to branched or cross-linked fragments. In order to obtain linear polymer fragments after the cleavage, an alternative nitron assisted radical coupling reaction (in a NMRC reaction style) was adopted. After the conventional copolymerization of styrene and 4-vinylphenyl 2-bromo-2-methylpropanoate (VBMP), polymers with pendant bromide groups were obtained and the polymer network was formed in the presence of PBN and Cu(0)/PMDETA catalytic system. By optimizing the coupling conditions, some microspheres were obtained by conventional distillation precipitation polymerization in the presence of nitron. These microspheres featured alkoxyamine functionalities throughout their interior and on their surface, and the alkoxyamine functionalities on the surface were employed in subsequent NMRP of NIPAAm monomers to generate a stimuli-responsive layered PNIPAAm.

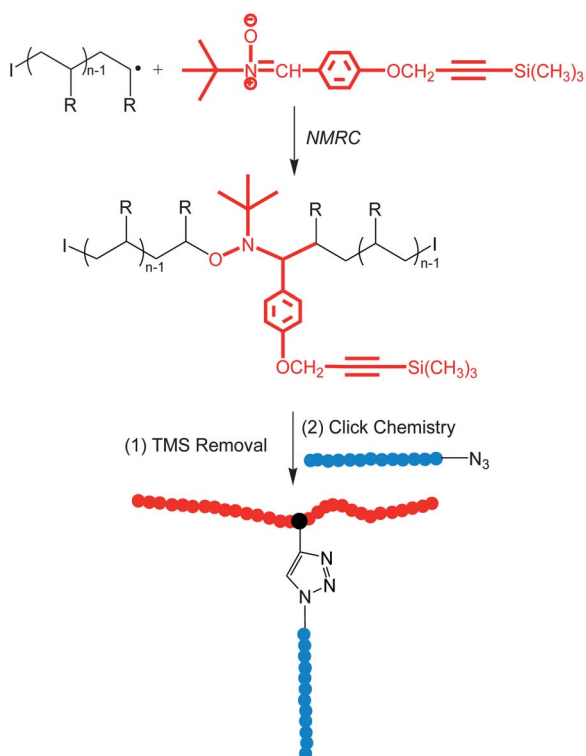
Also, by combination of nitron assisted radical coupling reaction (in a NMRC reaction style) and CuAAC chemistry, dendrimer polymers were realized by a divergent growth approach (Scheme 33).¹⁸³ In this approach, three compounds were the key points, including the design and synthesis of a core molecule containing three nitrones groups, an AB monomer bearing an azide functionality at one end and a 2-bromopropionate group at the other and a CD₂ monomer carrying one alkyne moiety and two nitron functions. In order to ensure there was enough flexibility while minimizing steric hindrance during the radical coupling reactions, both AB and CD₂ monomers were designed to have sufficiently long alkyl chain spacers between the functional groups. For the NMRC reaction



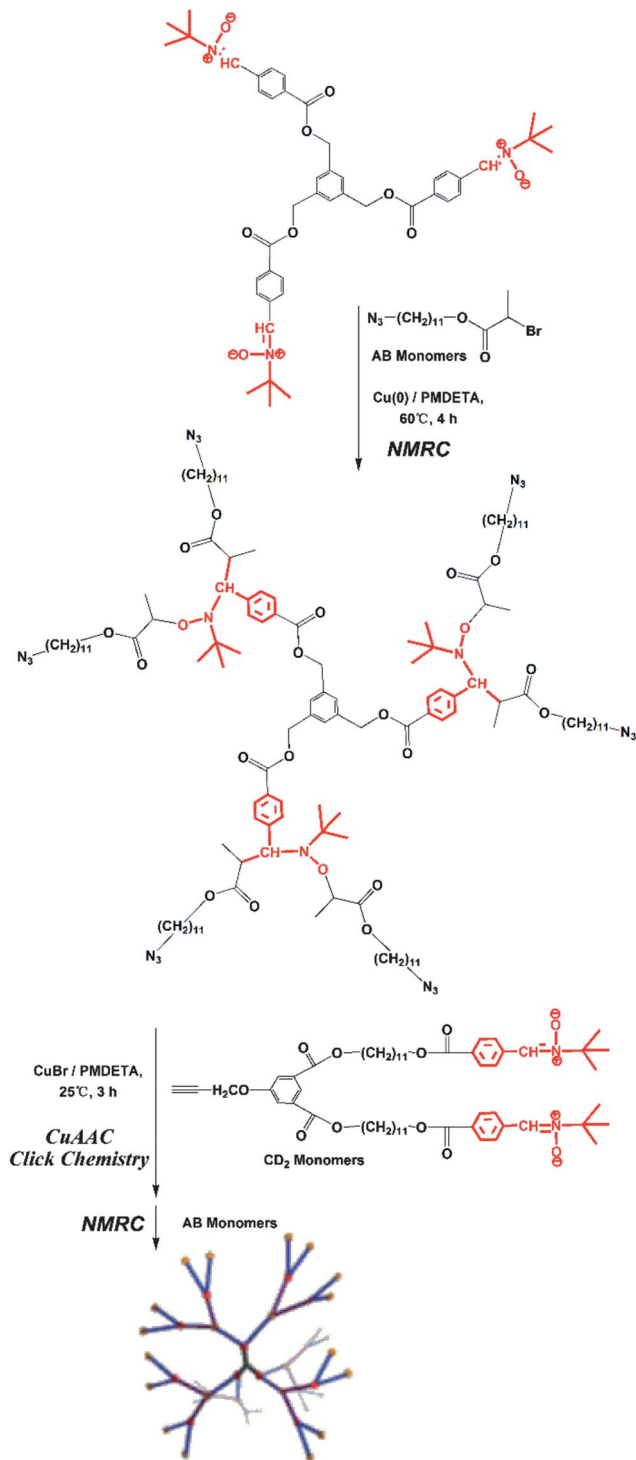
Scheme 32 The formation of reversible networks employing NMRC reaction.¹⁸²

between nitrones and AB monomers, Cu(0)/PMDETA was used as the catalytic system under 60 °C. Subsequently, CuAAC chemistry could proceed for the next generation of dendrimers by a simple purification procedure of removing the copper salts. Importantly, there were no conflicts between the four active groups of azide, alkyne, bromide and nitrones, and no protection/deprotection reaction procedure was needed in this strategy, which was a rather simple and efficient route to dendrimer polymers.

Later, Barner-Kowollik *et al.* also synthesized some H-shaped polymers *via* the combination of nitron assisted radical coupling reaction (in a NMRC reaction style) and CuAAC chemistry.¹⁸⁴ Differently, the used precursors poly(vinyl acetate) (PVAc)-*b*-poly(acrylonitrile) (PAN)-Co(acac)₂ were not synthesized by the typical ATRP mechanism, but *via* cobalt-mediated radical polymerization (CMRP) mechanism, and nitron containing an alkyne functional group was used in the NMRC reaction. The obtained products of PVAc-*b*-PAN-*b*-PVAc triblock polymers bore an alkoxyamine functionality and an alkyne group in the midchain. Subsequently, CuAAC chemistry was carried out between PVAc-*b*-PAN-*b*-PVAc and bifunctional poly(ethylene glycol) (PEG) with two azide groups at each end to constitute a H-shaped structure (PVAc-*b*-PAN)₂-PEG-(PVAc-*b*-PAN)₂. The low PDI and double molecular weight of the target polymer compared to the precursors confirmed the successful synthesis of H-shaped polymers. Alternatively, using the nitron assisted radical coupling reaction (in a NMRC reaction style) mediated by 2-methyl-2-nitrosopropane (MNP), Huang *et al.* synthesized an amphiphilic H-shaped PEO₃-PS-PEO₃ polymer using PEO₃-(PS-Br) as precursor (Scheme 34).¹⁸⁵ The A₃B star-shaped precursor PEO₃-(PS-Br) was synthesized by the ATRP mechanism using three-arm star-shaped PEO₃-Br as macro-initiator. According to the NMRC procedure, the bromide group at the PS end was sequentially transformed into a carbon-centered radical and then a nitroxide radical by reacting with

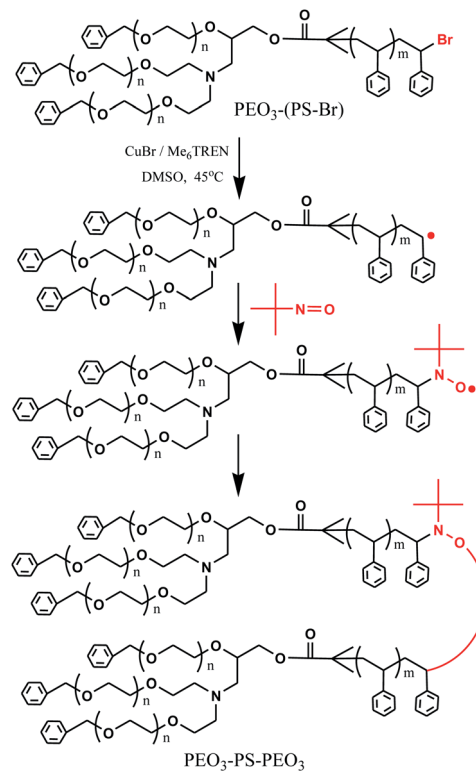


Scheme 31 The synthesis of 3-arm star-shaped polymers by NMRC reaction and subsequent CuAAC chemistry.¹⁸¹



Scheme 33 The strategy for the synthesis of third generation dendrimers via repetitive NMRC reaction and CuAAC chemistry.¹⁸³

MNP in dimethyl sulfoxide (DMSO)/THF mixed solvent in the presence of CuBr/Me₆TREN, and the *in situ* generated nitroxide radical could again capture another carbon-centered radical to form the target PEO₃-PS-PEO₃ polymer. The coupling reaction could reach a high efficiency of 90% within 60 min. However, after the product PEO₃-PS-PEO₃ was cleaved by ascorbic acid,

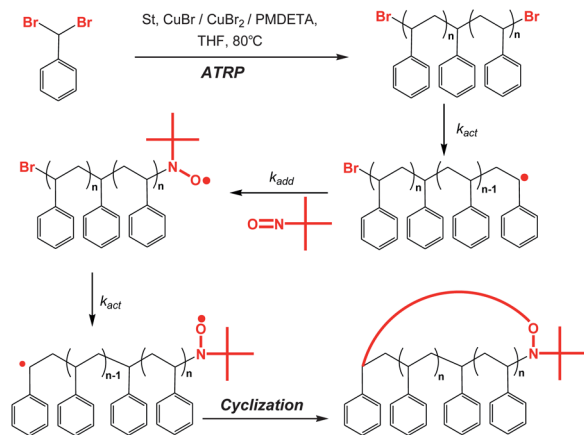


Scheme 34 The synthesis of H-shaped PEO₃-PS-PEO₃ by NMRC reaction.¹⁸⁵

the GPC results showed that there was about 30% fraction of product formed by direct radical coupling between carbon-centered radicals, which might result from the inappropriate ratio of MNP to precursors.

For macrocyclic polymers, the nitroxide assisted radical coupling reaction also showed its versatility in polymer science. In Section 2.2.3, one might notice that the intramolecular cyclization could be realized by ATRC reaction accompanied by some intermolecular coupling reaction.¹⁶² Using the nitroxide assisted radical coupling reaction (in a NMRC reaction style), the efficiency of cyclization could be greatly enhanced. For example, Tillman *et al.* synthesized macrocyclic PS with an alkoxyamine functionality by intramolecular NMRC reaction in the presence of a nitroso radical trap MNP (Scheme 35).¹⁸⁶ In their route, the linear α,ω -dibrominated Br-PS-Br produced by ATRP was subjected to the NMRC process under pseudodilute conditions. The yield of macrocyclic polymers was greater than 90%, with $\langle G \rangle$ values in the 0.8–0.9 range by GPC, which confirmed the success of the NMRC reaction in the synthesis of macrocyclic polymers.

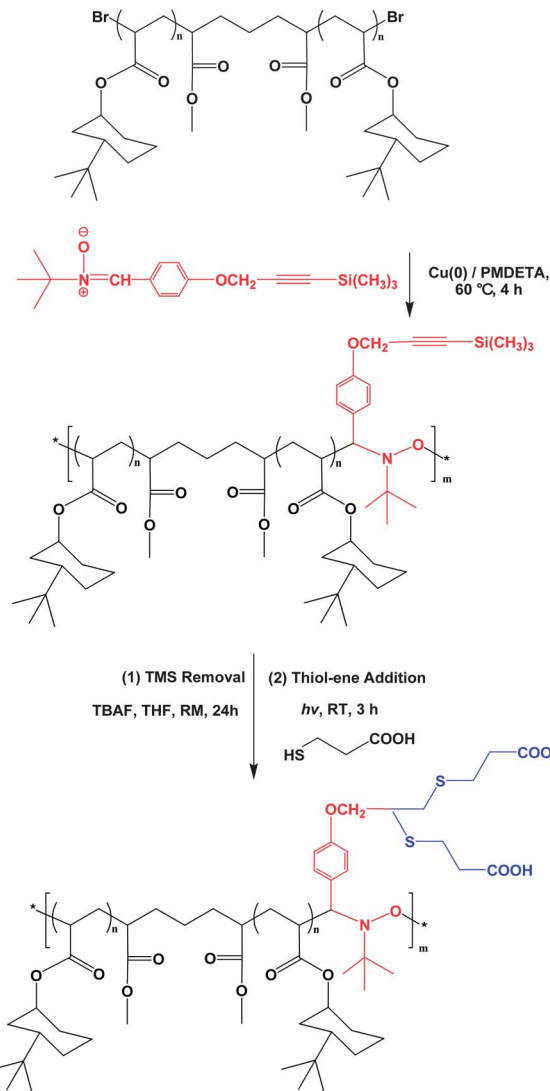
Thus, all the above works showed that the nitroxide assisted radical coupling reactions (including the ESCP mechanism and NMRC reaction) were efficient, simple and versatile methods for the synthesis of polymers with complicated structures. The key point was how to design and synthesize novel nitrones with additional functional groups, which must be tolerant to the conditions of NMRC reaction and ESCP mechanism, and how to apply this versatile method to construct various polymers.

Scheme 35 The synthesis of macrocyclic PS by NMRC reaction.¹⁸⁶

3.2.3 The application of nitroxide assisted radical coupling in step-growth polymerization.

Similar to the application of ATRC reaction in step-growth polymerization, the efficient nitroxide assisted radical coupling reaction could also be used in step-growth polymerization to obtain some novel polymers. Especially, the introduction of nitroxides could also enhance the polymerization rate and put the functional alkoxyamine into the polymer chain. For example, in the presence of α -4-(3-(trimethylsilyl)prop-2-ynyloxy)-*N*-*tert* butyl nitroxide, Barner-Kowollik *et al.* combined the nitroxide assisted radical coupling reaction (in a NMRC reaction style) with step-growth polymerization to generate higher molecular weight PiBoA (Scheme 36),¹⁸⁷ and the precursor, well-defined bifunctional Br-PiBoA-Br containing α,ω -dibromo end groups, was performed by ATRP mechanism. In the presence of Cu(0)/PMDETA, the generated macroradical could be efficiently captured by α -4-(3-(trimethylsilyl)prop-2-ynyloxy)-*N*-*tert*-butyl nitroxide, which resulted in a nitroxide radical. Then, the *in situ* formed nitroxide radical immediately underwent cross-coupling reaction with another macroradical, generating a block polymer bridged with alkoxyamine moieties. After the NMRC reaction, the embedded alkoxyamines with site specific functionalities were regularly separated along the polymer chain. Using the alkyne-functionalized nitroxide as a functional carrier, secondary functionalities could be easily incorporated into the polymer, for example, some 3-mercaptopropionic acid could be introduced *via* UV-induced thiol-yne reactions. Similarly, Wang *et al.* also prepared some degradable multisegmented polymers by combining the nitroxide assisted radical coupling reaction with step-growth polymerization.¹⁸⁸ In their work, α,ω -dibromo-PS, PtBA and PtBA-*b*-PS-*b*-PtBA polymers performed by ATRP mechanism were used as precursors, and MNP was used as radical spin trap. In the presence of Cu(0)/PMDETA, the nitroxide assisted radical coupling reaction (in a NMRC reaction style) proceeded in a step-growth manner. By varying the feed ratio of α,ω -dibromo precursor to MNP, the block number of multisegmented polymers could be tailored. Furthermore, the multisegmented polymer could be degraded in the presence of hydrogen atom donors or air.

Alternatively, when the segments of the α,ω -dibromide functionalized precursor in step-growth polymerization by

Scheme 36 The NMRC reaction of α,ω -dibromide functionalized precursor and its post-modification with 3-mercaptopropionic acid *via* thiol-yne addition.¹⁸⁷

NMRC reaction were replaced by some small molecules, a real step-growth polymerization could be realized. The related work was pioneered by Wang *et al.* in recent years.¹⁸⁹ Initially, Wang *et al.* designed and synthesized a series of saturated and unsaturated α,ω -dibromo dibasic ester monomers. By using the nitroxide assisted radical coupling reaction based step-growth polymerization (also termed step-growth radical addition-coupling polymerization (RACP) by Wang *et al.*), the radicals generated from α,ω -dibromide monomers were used to attack the double bond of MNP compound followed by cross-coupling of the carbon-centered radical and the *in situ* formed nitroxide radical, which produces alternating copolymers with high molecular weight ($M_n = 44\,000\text{ g mol}^{-1}$) and low PDI (PDI = 1.98). Because there were plenty of separated ester and alkoxyamine groups along the main chain, the obtained polymer could be easily degraded. Thus, their work provided a novel strategy to produce new types of degradable polymer from

available monomers. Compared with the normal step-growth polymerization, especially with the above ATRC reaction based step-growth polymerization, the nitron assisted radical coupling reaction (in a RACP style) showed its advantage of achieving high polymerization degree under mild polymerization conditions. Interestingly, they also used this RACP mechanism to prepare some new types of periodic copolymers possessing ABAC, ABCD and ABCBCAD periodic structures from α,ω -dibromide compounds containing amide, ester, ether, and phenyl groups (Scheme 37).¹⁹⁰ The functional groups were periodically located in the main chain or side chain with tunable distances between the groups.

Enlightened by the application of nitron assisted radical coupling in step-growth polymerization, Wang *et al.* also introduced the dithioester group into radical coupling by substituting the above MNP nitron compound.¹⁹¹ In fact, other thiol-containing compounds have been used to produce multiblock polymers, such as cyclic trithiocarbonate 1,5-dihydrobenzo[e][1,3]dithiopyne-3-thione,¹⁹² cyclic trithiocarbonate (CTTC)¹⁹³ and 4,7-diphenyl[1,3]dithiopyne-2-thione,¹⁹⁴ which confirmed that the radicals in the ATRP and RAFT procedures resembled each other and could be integrated into one system. Similar to the MNP induced radical coupling reaction, using α,ω -dibromide functionalized polymer as precursor, a thermodegradable multisegmented polymer was synthesized in the presence of Cu(0)/ligand and ethyl dithiobenzoate (Scheme 38).¹⁹¹ Typically, the generated macroradical was added to ethyl dithiobenzoate, which results in an intermediate adduct radical, then, the *in situ* formed adduct radical immediately underwent cross-coupling reaction with macroradical, generating a segmented polymer bridged with C–S bonds. Because the

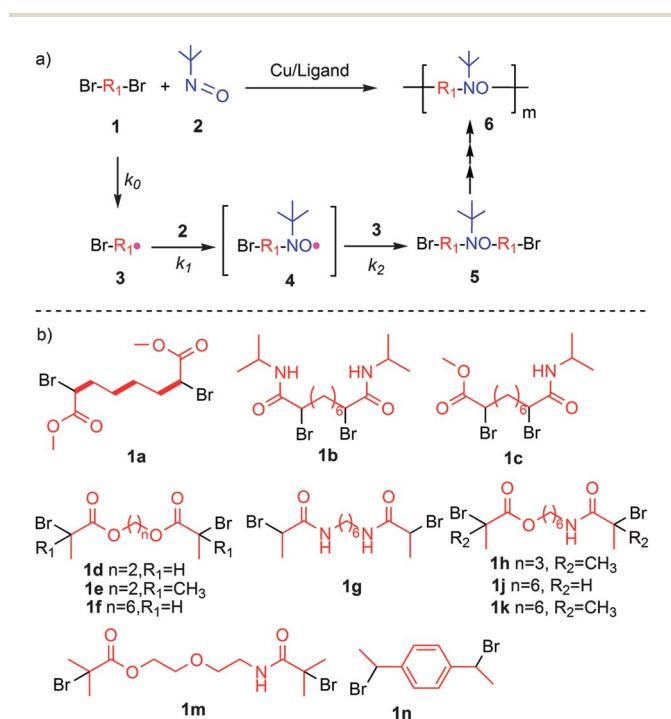
obtained polymer contained C–S bonds as repeat units, it could be thermodegraded or deprotected by using the *N*-bromosuccinimide (NBS)/DMSO system.

Compared to the previous ATRC reaction, nitron assisted radical coupling (including the ESCP mechanism and NMRC reaction) has an important improvement. The introduction of nitron compounds into the radical coupling reaction not only enhanced the efficiency of the radical coupling reaction, but also introduced some functional groups (such as alkoxyamine, alkyne, hydroxyl groups and so on) onto the polymers, which made it possible to prepare some functionalized polymers. All the above works showed that the nitron assisted radical coupling reaction might have some potential applications in polymer science from the simple midchain functionalized polymer to complicated polymers with various architectures, as well as the applications in step-growth polymerization.

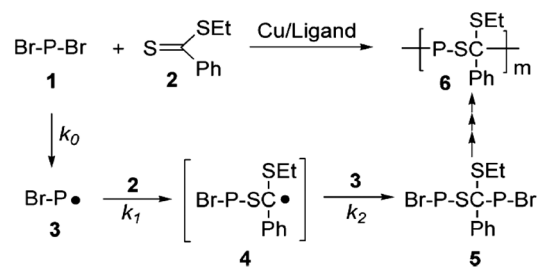
3.3 The diene assisted radical coupling reaction

As illustrated in the preceding sections, the block polymer PVAc-*b*-PAN-Co(acac)₂ polymers synthesized by the CMRP mechanism could undergo the nitron assisted radical coupling reaction (in a NMRC style), similar to the precursors from copper mediated ATRP or SETLRP mechanism, and the efficiency was rather high.¹⁸⁴ The CMRP mechanism could be used to prepare the polymers from vinyl acetate (VAc), acrylonitrile (AN), *N*-vinylpyrrolidone (NVP) or acrylic monomers, however, these monomers could not be successfully polymerized by the copper mediated ATRP or SETLRP mechanisms. Thus, one could suggest that some novel functionalized polymers might be obtained from the CMRP mechanism.^{195–206}

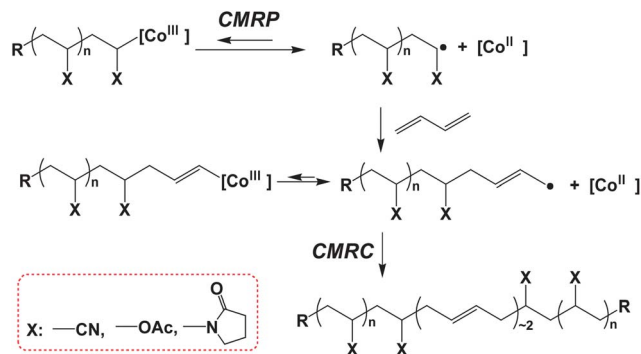
Recently, based on the CMRP mechanism, Detrembleur *et al.* developed a novel diene assisted radical coupling reaction termed isoprene-assisted radical coupling (IARC) or cobalt-mediated radical coupling (CMRC) (Scheme 39).^{92,93} Like the ATRC reaction or the above nitron assisted radical coupling reaction, the diene assisted radical coupling reaction was also a straightforward approach to the synthesis of symmetrical macromolecules that relied on the addition of 1,3-diene compounds onto polymer precursors performed by the CMRP mechanism. For example, the precursors were firstly performed by CMRP of VAc and AN monomers by temporary deactivation of the propagating radical with the bis(acetylacetonato)cobalt(II) complex [Co(acac)₂]. Subsequently, in the presence of diene



Scheme 37 The concept of RACP and the structures of various monomers.¹⁹⁰



Scheme 38 The synthesis of a multisegmented polymer by consecutive radical addition–coupling reaction of α,ω -macroiradicals and dithioester.¹⁹¹



Scheme 39 General scheme for CMRP mechanism and CMRC reaction.⁹²

monomers, the cobalt was released from the polymer chain and tiny amounts of isoprene were incorporated into the midchain of polymers. In contrast to the widely used ATRC techniques, diene assisted radical coupling reactions (in the IARC or CMRC style) were not restricted to short polymeric chains and homopolymers, and has been successfully applied to PAN-[Co] homopolymers with M_n of 25 000 g mol⁻¹ and to the coupling of PVAc-*b*-PAN-[Co] diblocks leading to PVAc-*b*-PAN-*b*-PVAc triblock polymers. Similarly, Detrembleur *et al.* also utilized this radical coupling reaction to PNVP precursors preformed by the CMRP mechanism,²⁰⁷ as well as to PVAc-*b*-PNVP-[Co] diblock polymers for the preparation of symmetrical PVAc-*b*-PNVP-*b*-PVAc triblock polymers. They found that the extents of coupling were different case to case, from high (>90%) for PAN to moderate (75–80%) for PVAc and PNVP precursors. As a rule, the shorter the precursor chain, the more efficient was the coupling reaction. Moreover, the efficiency of diene-assisted radical coupling varied in the order: PAN > PVAc > PNVP.

Later, Detrembleur *et al.* further investigated the mechanism of diene assisted radical coupling reaction on the basis of nuclear magnetic resonance (NMR) spectroscopy and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) analyses of the coupling product.⁹³ Their results showed that diene assisted radical coupling reaction proceeded *via* a radical mechanism. Using PAN as an example, the ease of cross-propagation from the cyanocarbyl to the allyl radical and the weak propensity of [Co(acac)₂] to deactivate the allyl radical terminated chains resulted in the release of a large amount of radical chains in the medium followed by a fast combination reaction instead of diene polymerization.

A key feature of diene assisted radical coupling was that the preferential insertion of two diene units in the midchain of the coupling product was mainly conducted according to a *trans*-1,4-addition pathway. Also, the tolerance of diene-assisted radical coupling towards the diene structure made it possible for midchain functionalization of polymers if the used diene compounds were deliberately designed (Scheme 40).⁹³ In addition to being a straightforward approach for the synthesis of symmetrical ABA copolymers, telechelic polymers by using α -functional precursors could also be realized by diene assisted radical coupling. Importantly, the diene assisted radical

coupling might go beyond the field of polymer chemistry, since it constitutes a novel carbon–carbon bond formation method that could be applied to small molecules.

To sum up, the agent (nitron or diene compound) assisted radical coupling reaction showed an important improvement to the ATRC reaction in the coupling efficiencies and the synthesis for topological polymers. However, the agent assisted radical coupling reactions still proceeded in a homocoupling style, and the nitron and diene agent should be cautiously designed for certain specific applications. In addition, the precursors for diene assisted radical coupling reaction were also limited to the CMRP mechanism. Thus, an enhanced version of the radical coupling reaction, NRC reaction, was presented and developed in polymer science, which was a rather efficient and versatile coupling reaction.

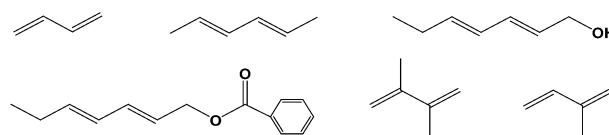
4 The nitroxide-radical coupling (NRC) reaction

4.1 The mechanism of NRC reaction

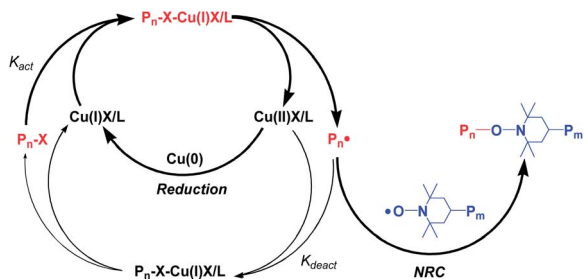
As described in Section 2.1, in the ATRP mechanism, when the quantity of deactivator was decreased or the activator was increased and the equilibrium was shifted, the concentration of the macroradicals would increase. Under certain conditions, in the absence of any monomers, if radical scavengers such as TEMPO or its derivatives were added, the generated macroradicals would be trapped by nitroxide radicals instantly. For example, using this reaction, Matyjaszewski *et al.*²⁰⁸ and Hawker *et al.*^{14,209} had synthesized various alkoxyamines derived from organic halides and TEMPO or its derivatives in one simple step with high yield. In 2008, Huang *et al.* applied this high efficiency reaction into polymer science and presented the Atom-Transfer Nitroxide-Radical Coupling (ATNRC) reaction (Scheme 41).^{94,95}

However, the macroradicals in ATNRC reaction were always generated at relatively high temperatures, which would lead to crosslinking, disproportionation termination, combination termination, chain transfer and other side reactions. Especially, for some active monomers, such as (methyl)acrylate, their corresponding polymers cannot be conducted smoothly in ATNRC reaction because of the significant β -hydrogen transfer from the macroradicals.^{210,211} Also, toxic toluene was used as the usual solvent in ATNRC reaction, while other polar solvents with low boiling point or less toxicity cannot be used. Thus, the search for milder conditions to carry out the ATNRC reaction was necessary.

Later, Percec *et al.*^{31–36} presented a SETLRP mechanism for the synthesis of ultrahigh molecular weight polymers from various functional monomers at ambient temperature, in which Cu(0) was used as catalyst. In a polar solvent, the *in situ*



Scheme 40 The structures of dienes used in the CMRC reaction.



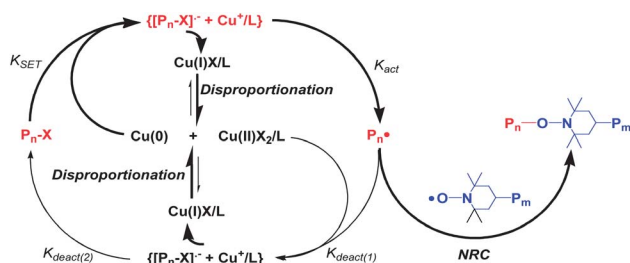
Scheme 41 The mechanism for ATNRC reaction.

disproportionation of CuBr into the highly active nascent Cu(0) species was the key step. Enlightened by their work, Huang *et al.* also presented Single-Electron-Transfer Nitroxide-Radical Coupling (SETNRC) (Scheme 42) based on the SETLRP mechanism.⁹⁶

Based on the mechanisms of ATRP and SETLRP, the generated radicals by atom transfer and single electron transfer (SET) procedures were all captured by TEMPO or its derivatives. Thus, ATNRC and SETRC were simplified as NRC reaction. Regardless of the argument about the activation mechanism of conventional atom transfer or single electron transfer, the possibility of bimolecular combination was extremely low and could be considered negligible in a NRC reaction.²¹² Importantly, as “click” reactions, the NRC reactions gave the products with near quantitative yields. Different from the above ATRC reaction and the agent assisted radical coupling reactions, the NRC reaction could proceed in a heterocoupling manner. There were also some published reviews on the development of the NRC reaction, which focused on the mechanisms²¹³ and their application in organic synthesis.^{13,214} In this review, we just showed the versatility of the NRC reaction for the construction of topological polymers, including the block,^{94,95,103} star-shaped, H-shaped, macrocyclic, graft polymers and so on, and finally, the application of the NRC reaction in dynamic covalent polymers was also mentioned.

4.2 The applications of NRC reaction in polymer science

4.2.1 The synthesis of functional polymers by NRC reaction. In 2009, Monteiro *et al.* reported that the NRC reaction could proceed in a rapid, selective, and reversible manner at ambient temperature (25 °C) in the presence of CuBr/Me₆TREN, and with toluene/DMSO (50% v/v) as solvent (Scheme 43).²¹⁵

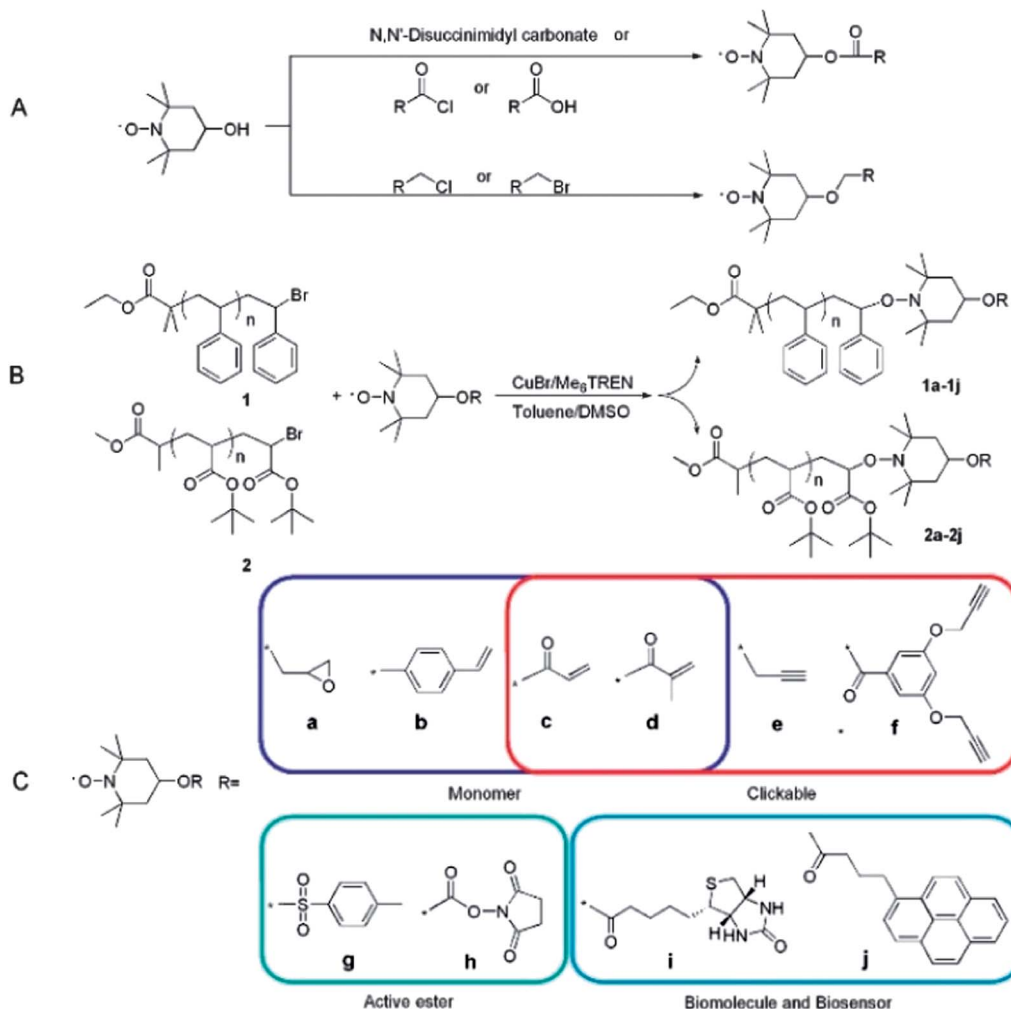
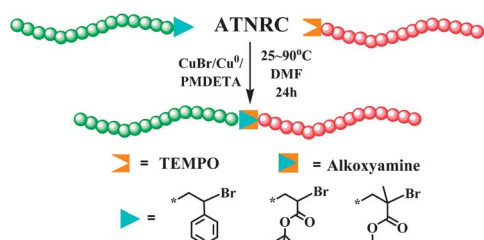


Scheme 42 The mechanism for SETNRC reaction.

When nitroxides containing functional groups were used, the NRC reaction between PS-Br and nitroxides would form functional polymers. Later, this NRC method was expanded to PtBA-Br and Br-PS-Br with a library of functional TEMPO-based compounds.^{216–218} Importantly, these NRC reactions were completed in less than 10 min, resulting in polymers with functionalities above 90% and near-quantitative coupling efficiencies of greater than 95%. Through the reversibility of this reaction, it showed the added advantage of permitting the exchange of chemical functionality on macromolecules. Utilization of this reversibility of the NRC reaction at elevated temperatures allowed the exchange of chain end groups with a variety of functional nitroxide derivatives. Also, by combination of thiol-ene coupling with NRC reaction, the successful post-modification of poly(oxanorbornene imide) (PONB) was realized by Tunca *et al.*²¹⁹

4.2.2 The synthesis of linear block copolymers by NRC reaction. As the initial and basic applications of NRC, not only in the synthesis of functional polymers, but also the synthesis of block polymers with different compositions, this reaction played a very important role. Using the NRC reaction, Huang *et al.* prepared several diblock copolymers under ambient temperature (25 °C) in the presence of the Cu(0)/PMDETA catalytic system.⁹⁶ The precursors PS-Br, PtBA-Br, PMA-Br, PMMA-Br with bromide end groups and PEO-TEMPO, PCL-TEMPO with TEMPO end groups were used as model polymers. The results confirmed that all the NRC reactions under ambient temperature showed high efficiency. Later, using the same precursors, Huang *et al.* further investigated the effects of temperature, catalytic system, and the structure of bromine connected groups on the NRC reaction in detail.²²⁰ The used catalytic systems were CuBr/PMDETA, Cu(0)/PMDETA and CuBr/Cu(0)/PMDETA, and the temperature was in the range from 90 to 25 °C, *N,N*-dimethylformamide (DMF) was used as solvent (Scheme 44). The result showed that the CuBr/Cu(0)/PMDETA catalytic system was the best one for all NRC reactions, and the NRC reactions could be conducted at high efficiency in a wide temperature range from room temperature to elevated temperature. The efficiency of NRC reaction between PtBA-Br and PCL-TEMPO was more than 85% in the temperature range from 25 to 75 °C, the efficiency between PS-Br and PCL-TEMPO was more than 90% from 25 to 90 °C, and the efficiency between PMMA-Br and PCL-TEMPO was more than 90% only at room temperature.

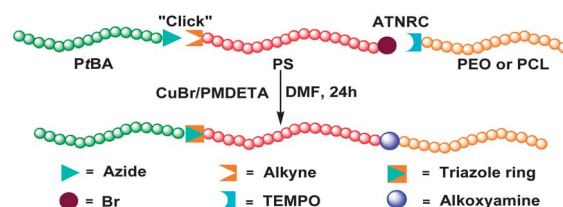
Besides the simple diblock polymers, some triblock polymers were also realized by combination of NRC reaction with other click chemistry in a simple way because of the tolerance of these coupling reactions. For example, Huang *et al.*⁹⁵ prepared ABC triblock copolymers *via* a one-pot method using the precursors heterofunctional alkyne-PS-Br, PEO-TEMPO or PCL-TEMPO, and PtBA-N₃. The final triblock copolymers, PtBA-*b*-PS-*b*-PEO and PtBA-*b*-PS-*b*-PCL, with controlled molecular weight and low PDIs were obtained with high efficiencies in CuBr/PMDETA at 90 °C (Scheme 45). Similarly, Huang *et al.* further synthesized ABC triblock copolymers by a one-pot strategy using α,ω -heterofunctionalized TEMPO-PEO-alkyne, PS-Br and PtBA-N₃ as precursors in Cu(0)/Me₆TREN at room temperature.²²¹

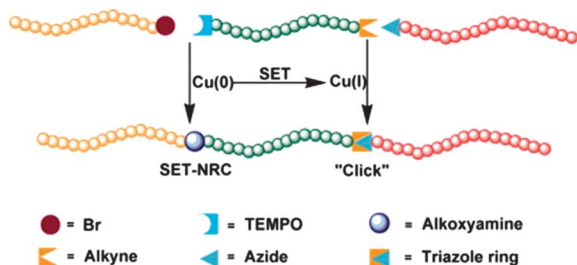
Scheme 43 End-group modification of PS-Br and PtBA-Br with nitroxide radical derivatives by NRC reaction.²¹⁵Scheme 44 The illustration of diblock polymers by NRC reaction.²²⁰

Specially, in this system, the author suggested that Cu(I) generated from Cu(0) by the SET mechanism was utilized to catalyze CuAAC chemistry, and no additional Cu(I) was needed (Scheme 46). Later, Tunca *et al.* combined CuAAC chemistry, Diels–Alder reaction and the NRC reaction in a one-pot fashion to generate tetrablock quaterpolymers PEG-*b*-PS-*b*-PtBA-*b*-PCL or PEG-*b*-PS-*b*-PnBA-*b*-PCL using Cu(0)/CuBr/PMDETA as the catalytic system, in DMF at 80 °C for 36 h (Scheme 47).²²² They also used sequential click reactions including thiol–ene addition, CuAAC chemistry, Diels–Alder reaction and NRC reactions

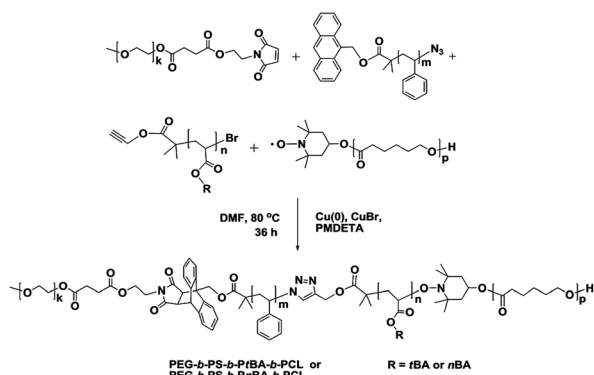
to synthesize cysteine-terminated linear PS-*b*-PCL-*b*-PMMA-*b*-PEG polymers (Scheme 48).²²³ Related research was also summarized in their reviews.^{100,101} These works confirmed that the NRC reaction showed similar characteristics, such as high efficiency and tolerance to the catalytic system, compared with the CuAAC chemistry or Diels–Alder reaction.

In the above works, DMF was used as the solvent due to its good solubility for nearly all polymer chains except polyisoprene (PI). However, Huang *et al.* found that THF could be used as the solvent in NRC reaction for copolymers containing PI segments, and a series of ABC triblock copolymers

Scheme 45 One-pot synthesis of ABC triblock copolymers PtBA-*b*-PS-*b*-PEO by combination of NRC reaction with CuAAC chemistry.⁹⁵



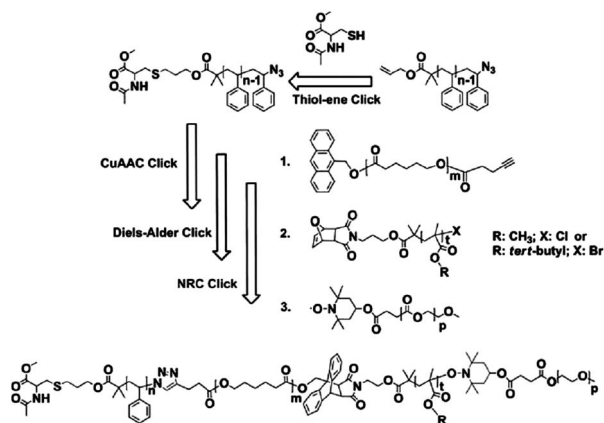
Scheme 46 One-pot synthesis of ABC triblock copolymer PS-*b*-PEO-*b*-PtBA by combination of NRC reaction with CuAAC chemistry.²²¹



Scheme 47 The synthetic pathway for the quaterpolymer via click reactions: CuAAC chemistry, Diels-Alder, and NRC reactions.²²²

PI-*b*-PS-*b*-PEO and PI-*b*-PtBA-*b*-PEO was prepared in THF using Cu(0)/Me₆TREN as the catalytic system at room temperature.²²⁴ The NRC reaction between PI-*b*-PS-Br and PEO-TEMPO was carried out with a coupling efficiency of up to 91.6% in only 2.0 h. In fact, this work further confirmed that other solvents (besides polar DMF) for ATRP or SETLRP mechanisms could all be used in NRC reactions.

Also, using the NRC reaction between Br-PS-Br and TEMPO dinitroxides, Matyjaszewski *et al.* prepared multisegmented degradable polymers with more than 10 cleavable units in the main chain using anisole as solvent and CuBr/PMDETA as



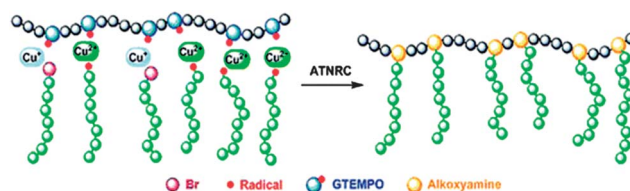
Scheme 48 The synthetic pathway for the cysteine-terminated multiblock polymers via click reactions: thiol-ene, CuAAC chemistry, Diels-Alder, and NRC reactions.²²³

catalytic system at 60 °C, and these multisegmented polymers could be chemically (*via* basic hydrolysis or disulfide reduction) and thermally (by heating in the presence of free nitroxides) degraded.²²⁵ Similarly, Monteiro *et al.* also used the NRC reaction to produce multiblock polymers with high molecular weights by coupling Br-PS-Br with a dinitroxide using DMSO as solvent and CuBr/Me₆TREN as catalytic system at 50 °C.²¹⁷

Thus, regardless of the linear diblock, triblock or multiblock polymers, the NRC reaction showed higher coupling efficiency than the previous ATRC reaction. Very importantly, the sequence of block polymers could be easily selected and modulated. The NRC reaction also showed its tolerance to efficient CuAAC chemistry, Diels-Alder and other click reactions, so it was possible to combine the NRC reaction with other coupling reactions in a simple and efficient one-pot style.

4.2.3 The synthesis of graft copolymers by NRC reaction.

Another application of NRC reaction was the synthesis of graft polymers, which actually could not be obtained by previous ATRC reaction. Initially, using the NRC reaction, Huang *et al.* prepared a series of graft copolymers poly(4-glycidyoxy-2,2,6,6-tetramethylpiperidin-1-oxyl-*co*-ethylene oxide) [poly(GTEMPO-*co*-EO)]-*g*-PS by using the linear precursor poly(GTEMPO-*co*-EO) with multi-pendant TEMPO groups and PS-Br with a bromide end group in CuBr/PMDETA system at 90 °C (Scheme 49).⁹⁴ The former was prepared first by ROP of 4-glycidyoxy-2,2,6,6-tetramethylpiperidin-1-oxyl (GTEMPO) and ethylene oxide (EO) monomers. Using a similar method, they also prepared the graft copolymer poly(GTEMPO-*co*-EO)-*g*-PtBA, and heterograft copolymer poly(GTEMPO-*co*-EO)-*g*-PS/PtBA.²²⁶ The results showed that the efficiency of NRC reaction for the graft copolymers was in the range of 90.2–95.9% for PS side chains and 82.3–88.4% for PtBA side chains when the number average molecular weight was in the range 1500–7800 g mol⁻¹ and the ratio of GTEMPO/EO in the copolymer was fixed. In the preparation of graft copolymers, the density of GTEMPOs on the precursor poly(GTEMPO-*co*-EO) and molecular weights of side chains PS-Br and PtBA-Br could exert a great effect on the coupling efficiency. The PS radicals were more reactive than that of PtBA in the coupling reaction, which was very consistent with the above work for ATRC reaction.^{90,141} Combining CuAAC chemistry with NRC reaction, Huang *et al.* also synthesized a special ABA type block-graft copolymer between a backbone with pendant TEMPO and azide groups and PtBA-Br, PS-alkyne precursors in a one-pot style (Scheme 50).²²⁷ Once more, the catalytic system CuBr/Cu(0)/PMDETA gave high efficiency. Later, using PEO with different densities of -C(CH₃)₂Br as main



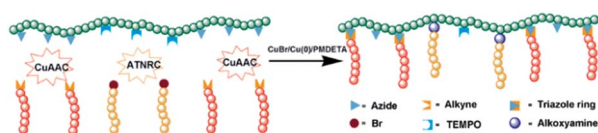
Scheme 49 The illustration of graft copolymers [Poly(GTEMPO-*co*-EO)-*g*-PS] and [Poly(GTEMPO-*co*-EO)-*g*-PtBA] by NRC reaction.⁹⁴

chain and TEMPO-PCL as precursors, the effects of bromide connected groups on NRC reaction were investigated by Huang *et al.*²²⁸ The results showed that the structure of bromide connected groups showed an important effect on NRC reaction, and the NRC reaction with high efficiency could be realized by transforming the more active bromide connected groups into less active ones by the addition of a small amount of St monomers, which was similar to the mechanism in styrene assisted ATRC reaction.

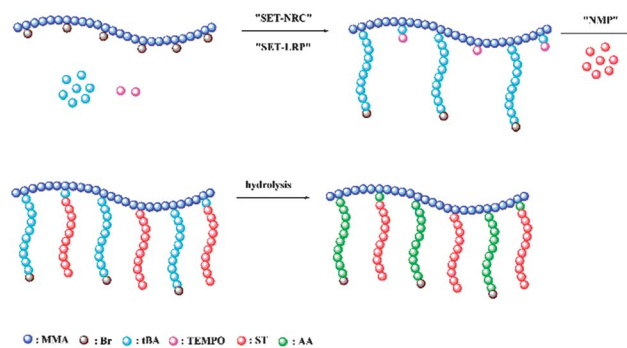
For the graft polymers with complicated side chains, the NRC reaction could also meet the requirement. For example, using the NRC reaction in the presence of CuBr/PMDETA, Huang *et al.* further prepared the graft copolymers methoxyl poly(ethylene oxide) (*m*PEO)-*b*-[poly(ethylene oxide-*co*-glycidyl) [poly(EO-*co*-Gly)]-*g*-(PS-*b*-PEO)] with amphiphilic PEO-*b*-PS as side chains.²¹⁴ By the combination of SETLRP, ATRP, NMRP mechanisms with NRC reaction, they also synthesized amphiphilic heterograft copolymers poly[methyl methacrylate-*co*-2-(2-bromoisobutyryloxy)ethyl methacrylate] [poly(MMA-*co*-BIEM)]-*g*-(PAA/PS), in which the SETNRC was used to partially functionalize the side bromide groups (Scheme 51).²²⁹ The macrocyclic molecular brushes *c*-PHEMA-*g*-(PS-*b*-PEO) consisting of macrocyclic poly(2-hydroxyethyl methacrylate) (*c*-PHEMA) as backbone and PS-*b*-PEO amphiphilic block copolymers as side chains were also obtained by the combination of ATRP mechanism with CuAAC chemistry and NRC reaction.²³⁰

Similarly, by combination of RAFT mechanism with NRC reaction, Huang *et al.* prepared a series of well-defined amphiphilic graft copolymers consisting of hydrophilic poly(acrylic acid) backbone and hydrophobic poly(propylene oxide) (PPO) side chains (Scheme 52).²³¹ The NRC reaction between the Br containing P*t*BA-based backbone and PPO-TEMPO was conducted by using CuBr/PMDETA or Cu(0)/PMDETA as the catalytic system. Later, they expanded this method to amphiphilic star graft copolymers by a similar method using CuBr/PMDETA or Cu(0)/PMDETA as the catalytic system.²³² Additionally, amphiphilic graft copolymers bearing hydrophobic P*t*BA backbone and hydrophilic PEO side chains were also prepared by the reaction of Br-containing P*t*BA-based backbone and PEO-TEMPO side chain using Cu(0)/PMDETA as the catalytic system at ambient temperature, and the coupling efficiency of the NRC reaction was as high as 90%.^{233,234}

In another group, the NRC reaction was also used to design and synthesize various graft polymers by Tunca *et al.* Using the NRC reaction catalyzed by the CuBr/Cu(0)/PMDETA catalytic system in DMF solvent at room temperature, they synthesized graft polymers PONB₂₀-*g*-PEG₁₁ or PONB₂₀-*g*-PCL₂₃ with PEG₁₁-TEMPO or PCL₂₃-TEMPO as side chains and ROMP-generated

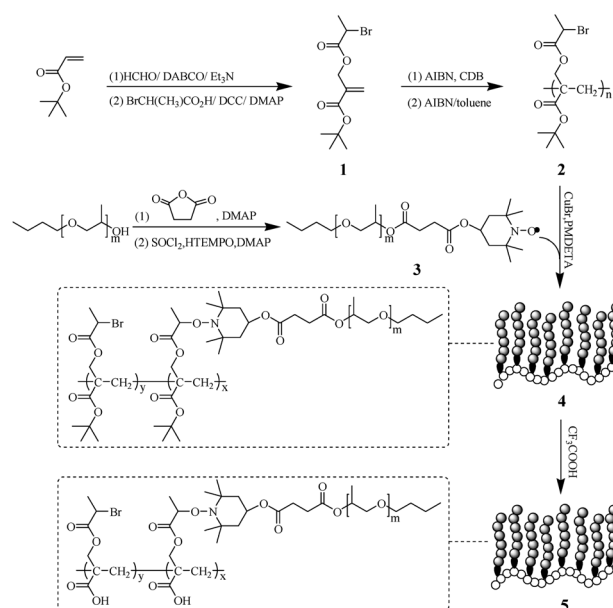


Scheme 50 The illustration of ABA type block-graft copolymers by NRC reaction.²²⁷

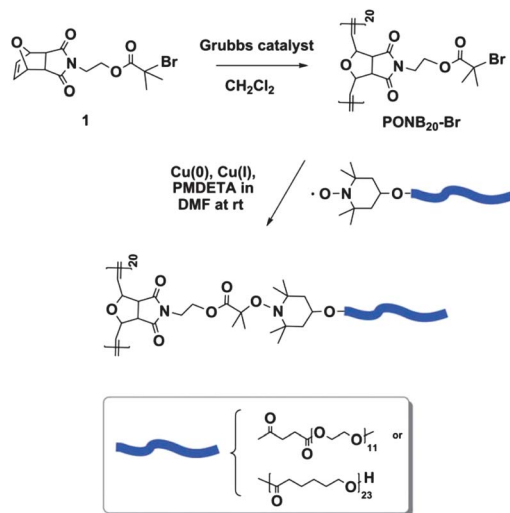


Scheme 51 The synthesis of the amphiphilic heterograft copolymers poly(MMA-*co*-BIEM)-*g*-(PAA/PS).²²⁹

polyoxanorbornene with bromide pendant groups (PONB₂₀-Br) as backbone (Scheme 53).²³⁵ Using a similar method, the ROMP-generated graft copolymer PONB₉-*g*-[(PMMA)₂₄-Cl] was reacted with PEG₁₁-TEMPO or PCL₂₃-TEMPO precursor *via* the NRC reaction, and corresponding brush terpolymers PONB₉-*g*-(PMMA₂₄-*b*-PEG₁₁) or PONB₉-*g*-(PMMA₂₄-*b*-PCL₂₃) were formed. For the former, the efficiency of the NRC reaction was as high as 97%, however, the efficiency of the NRC reaction for the latter was calculated to be 56%. This lower efficiency might be attributed mainly to the hydrogen abstraction *via* TEMPO and the steric hindrance caused by the highly dense structure of the starting brush copolymer. Later, by sequential Diels-Alder reaction, NRC reaction and CuAAC chemistry, a heterograft polymer was also obtained by reaction between furan protected maleimide-terminated PMMA, TEMPO-terminated PEG, alkyne-terminated PCL-alkyne and main chain poly(ONB-anthracene-*co*-ONB-Br-*co*-ONB-OTs)₁₀, the latter was synthesized by ROMP using an equimolar mixture of oxanorbornenylanthracene (ONB-anthracene), oxanorbornenyl-bromide (ONB-Br), and



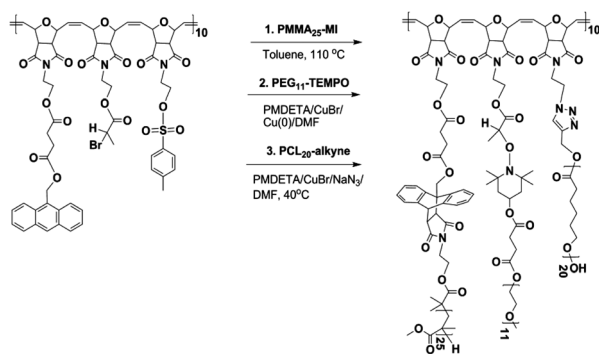
Scheme 52 The synthesis of well-defined amphiphilic graft copolymer PAA-*g*-PPO.²³¹



Scheme 53 The synthesis of graft copolymers, PONB₂₀-g-PEG₁₁ or PONB₂₀-g-PCL₂₃, via NRC reaction of PONB₂₀-Br with PEG₁₁-TEMPO or with PCL₂₃-TEMPO, respectively.²³⁵

-tosylate (ONB-OTs) monomers in CH₂Cl₂ at room temperature (Scheme 54).²³⁶

The NRC reaction was very versatile and it could also be used for organic/inorganic composites. For example, after modification of TEMPO groups onto nanotubes (MWNTs) by esterification of HO-TEMPO and carboxylic acid groups on the surface of MWNTs, MWNTs-g-PS was obtained by coupling PS-Br onto MWNTs through NRC reaction using CuBr/PMDETA as the catalytic system by Sui *et al.* (Scheme 55).²³⁷ The final content of grafted polymers was 46.7% by TGA measurements. Also, Huang *et al.*²³⁸ anchored a radical scavenger species, TEMPO, onto graphene oxide (GO) to afford TEMPO-functionalized graphene sheets (GS-TEMPO). Then the GS-TEMPO was reacted with bromide functionalized PNIPAM homopolymer by NRC reaction in the presence of CuBr/PMDETA to form PNIPAM grafted graphene sheets (GS-PNIPAM) nanocomposite (Scheme 56). Their results also showed that the PNIPAM-modified graphene sheets were easily dispersible in organic solvents and water, and a temperature-induced phase transition was found in the water suspension of GS-PNIPAM. Very recently,



Scheme 54 The synthesis of poly(ONB-g-PMMA-co-ONB-g-PEG-co-ONB-g-PCL)₁₀ heterograft graft copolymer.²³⁶

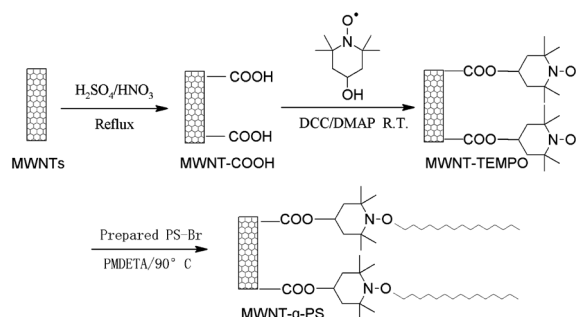
based on the NRC reaction, Yagci *et al.* prepared some polymer/clay nanocomposites by using the NRC reaction (Scheme 57).²³⁹

Thus, one could notice that the NRC reaction could find many applications in the synthesis of graft polymers, which could not be realized by the previous ATRC reaction. Importantly, the NRC reaction could be adopted not only in the construction of topological polymers, but also in organic/inorganic composites, and the main chain and side chains in NRC reaction could be elaborately selected and designed.

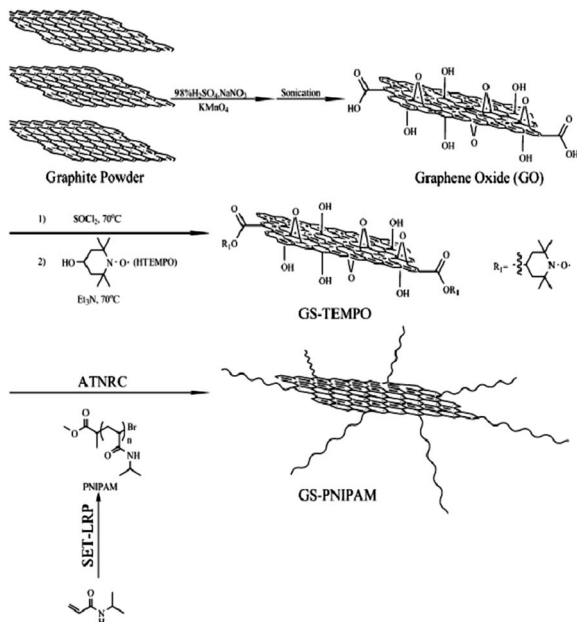
4.2.4 The synthesis of star-shaped copolymers by NRC reaction. Among the polymers with defined structure, the synthesis of star-shaped polymers was always a challenge work. By combination of CuAAC chemistry with NRC reaction, Huang *et al.* prepared a 3-miktoarm star-shaped terpolymer star (PtBA-PS-PEO) using a one-pot strategy.²⁴⁰ The CuAAC chemistry and NRC reaction between precursors PtBA-N₃, TEMPO-PEO or TEMPO-PCL and PS-alkyne/Br proceeded using the CuBr/Cu(0)/PMDETA catalytic system at 90 °C for 24 h (Scheme 58). The coupling efficiency of NRC was as high as that for CuAAC chemistry. Also, amphiphilic 3-miktoarm A₂B star-shaped copolymers PS-*b*-PEO₂ were synthesized via the combination of NRC reaction with ROP and ATRP mechanisms (Scheme 59).²⁴¹ The precursor V-shaped TEMPO-PEO₂ with a TEMPO group at the middle chain was obtained by ROP of EO monomers using 4-(2,3-dihydroxypropoxy)TEMPO and diphenylmethyl potassium (DPMK) as coinitiator. Through the sequential Diels-Alder reaction, CuAAC chemistry and NRC reactions in a two-step reaction mode, Tunca *et al.* synthesized some well-defined 3-miktoarm star-shaped terpolymers star(PEG-PCL-PS) and star(PEG-PCL-PONB) with narrow PDIs, and linear furan-protected maleimide-terminated PEG-MI, PCL-TEMPO, and PS-N₃ or PONB-N₃ were used as precursors (Scheme 60).²⁴²

Similarly, using the NRC reaction, Monteiro *et al.* prepared 3-arm PS stars.²¹² Also, by combination of NRC reaction with CuAAC chemistry, they synthesized 3-miktoarm AB₂ star-shaped polymers in a one-pot strategy (Scheme 61).^{243,244} Especially, cyclic building blocks could be introduced into the AB₂ stars. The conditions for NRC reaction were optimized by using PMDETA and Me₆TREN as ligands and varying the ratio of solvent of DMSO to toluene over a wide temperature range.

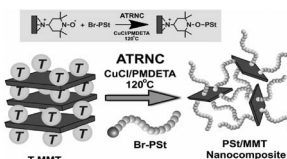
Alternatively, star-shaped copolymers with PS-*b*-PEO as arm chains and hyperbranched polyglycerol (HPG) as core were



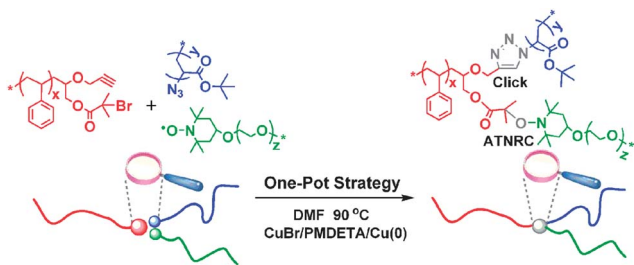
Scheme 55 Preparation of PS-grafted MWNTs.²³⁷



Scheme 56 Preparation of PNIPAM-functionalized graphene sheets by NRC reaction.²³⁸



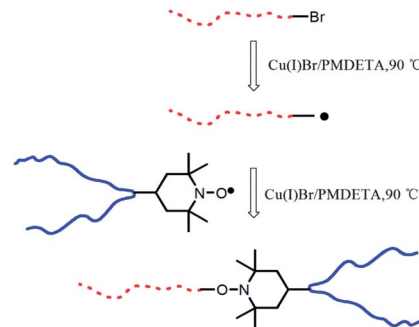
Scheme 57 Preparation of PS/MMT nanocomposites by NRC reaction.²³⁹



Scheme 58 The synthetic illustration of star(PtBA-PS-PEO) by CuAAC chemistry and NRC reaction.²⁴⁰

synthesized by combination of ATRP mechanism with NRC reaction in the presence of the CuBr/PMDETA catalytic system (Scheme 62).²⁴⁵ The multiarm PS with bromide end groups on HPG-*g*-(PS-Br)_{*n*} graft polymer originated from the HPG core by ATRP mechanism, and the heterofunctional TEMPO-PEO was then coupled by NRC reaction. The results showed that the coupling efficiency of the NRC reaction in the preparation of star-shaped polymers was satisfactory (90%) even if the density of coupling sites on HPG was rather high.

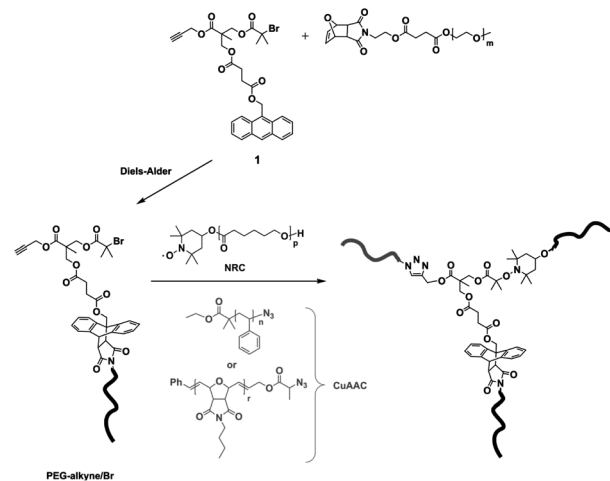
4.2.5 The synthesis of macrocyclic polymers by NRC reaction. Besides the above ATRC reaction and nitron assisted radical coupling reaction, the NRC reaction could also be



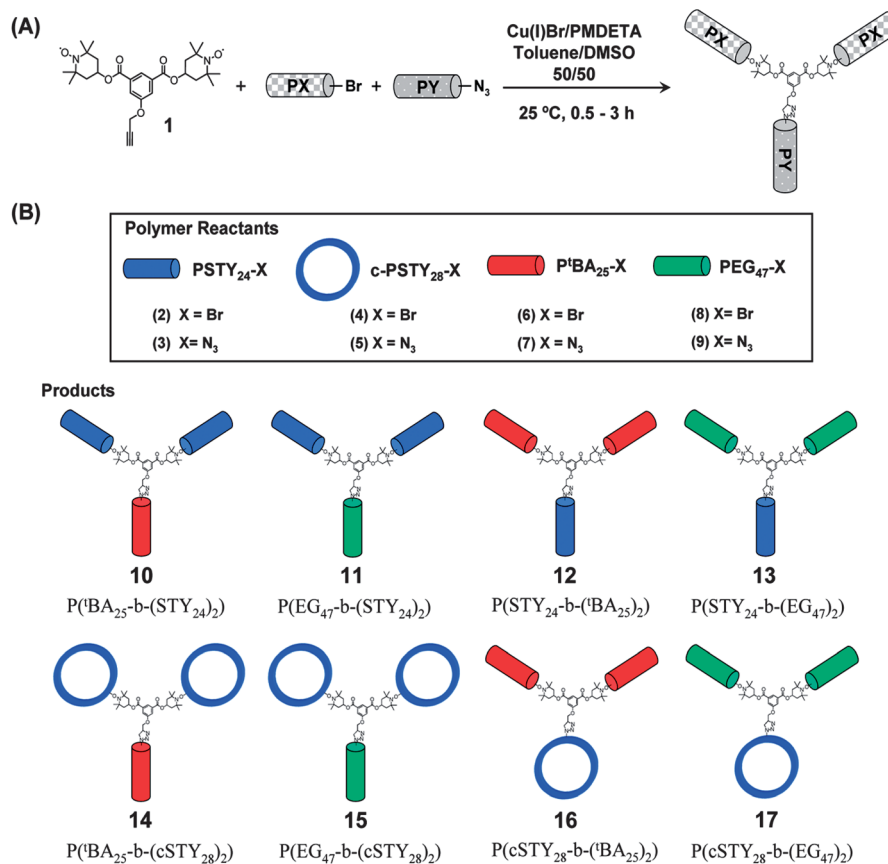
Scheme 59 The synthetic illustration of A₂B star-shaped copolymers of PS-*b*-PEO₂.²⁴¹

adopted to produce macrocyclic polymers. Initially, Monteiro *et al.*²¹⁷ aimed to produce multiblock polymers with high molecular weights by coupling a difunctional telechelic Br-PS-Br with a dinitroxide using the NRC reaction. However, in their experiment, some macrocyclic polymers were observed. Also, this work pointed out that the NRC reaction might be used as a cyclization method.

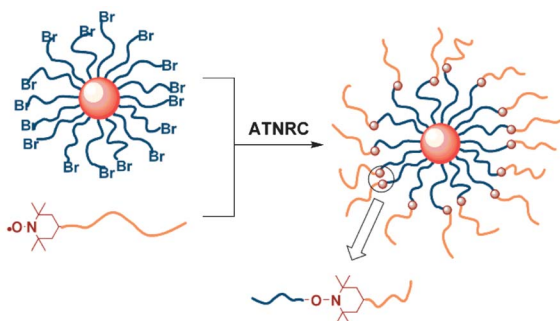
Later, using the NRC reaction, Matyjaszewski *et al.* presented a novel approach to prepare macrocyclic polymers (Scheme 63).²⁴⁶ A functional ATRP initiator possessing an alkoxyamine group was synthesized and used to prepare well-defined linear telechelic α -nitroso, ω -bromide polymers *via* ATRP mechanism and subsequent thermal deprotection of the α -terminal nitroxide function. Cyclization reactions were then achieved by intramolecular NRC reaction under high dilution, and well-defined cyclic PMA, PS and cyclic PMA-*b*-PS block copolymers with low molecular weights were obtained. In another group, Tunca *et al.*²⁴⁷ designed a trifunctional initiator containing anthracene, bromide and hydroxyl group functionalities and subsequently used it as an initiator of ATRP for St monomers to yield linear PS with α -anthracene/hydroxyl groups, ω -bromide terminal groups. By combination of the CuAAC chemistry with the Diels-Alder



Scheme 60 The synthetic pathway for star(PEG-PCL-PS) and star(PEG-PCL-PONB) using Diels-Alder, CuAAC chemistry and NRC reactions.²⁴²



Scheme 61 The synthetic strategy for the star-shaped polymers by NRC reaction and CuAAC chemistry.²⁴³

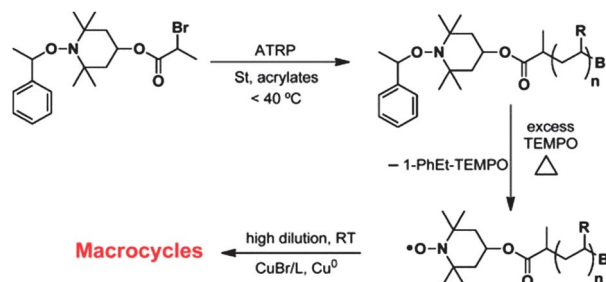


Scheme 62 The synthetic illustration of HPG-*g*-(PS-*b*-PEO)_{*n*} by ATRP mechanism and NRC reaction.²⁴⁵

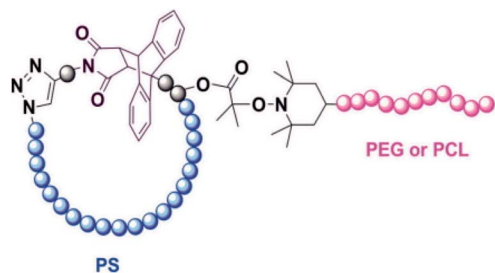
reaction, cyclic PS with one hydroxyl group on the ring, (c-PS)-OH, was formed. The c-PS-OH was further reacted with 2-bromoisobutyl bromide to yield the cyclic PS with one bromide functionality, (c-PS)-Br, and subsequent NRC reaction with TEMPO-PEG or TEMPO-PCL afforded the target tadpole polymer, (c-PS)-*b*-PEG or (c-PS)-*b*-PCL (Scheme 64).

4.2.6 The synthesis of dendrimer-like polymers by NRC reaction. Using the CuAAC chemistry and NRC reaction, Monteiro *et al.* synthesized a second-generation dendrimer by either a convergent, divergent or simultaneous pathway with very high yields and purities by tuning the type of solvent and ligand

employed (Scheme 65).²⁴⁸ Their results showed that, by modulating the ratio of co-solvents and the structure of employed ligand, the routes to dendrimers might be changed. For example, the combination of Me₆TREN ligand with 30% DMSO and 70% toluene resulted in a divergent pathway, in which the formation of the second generation dendrimer by NRC reaction was completed in less than 2 min, followed by the coupling of the third generation layer in 30 min. Changing ligand, using PMDETA to replace Me₆TREN, and 50% DMSO and 50% toluene gave similar rates of CuAAC chemistry and NRC reaction, resulting in the third generation of dendrimer through a parallel process. Using PMDETA and 100% toluene gave much faster CuAAC chemistry than NRC reaction. The dendron was



Scheme 63 The synthesis of macrocyclic polymers via a combination of ATRP mechanism and ATRC reaction.²⁴⁶



Scheme 64 The synthesis of tadpole polymers (c-PS)-b-PEG and (c-PS)-b-PCL using the triple click reaction strategy.²⁴⁷

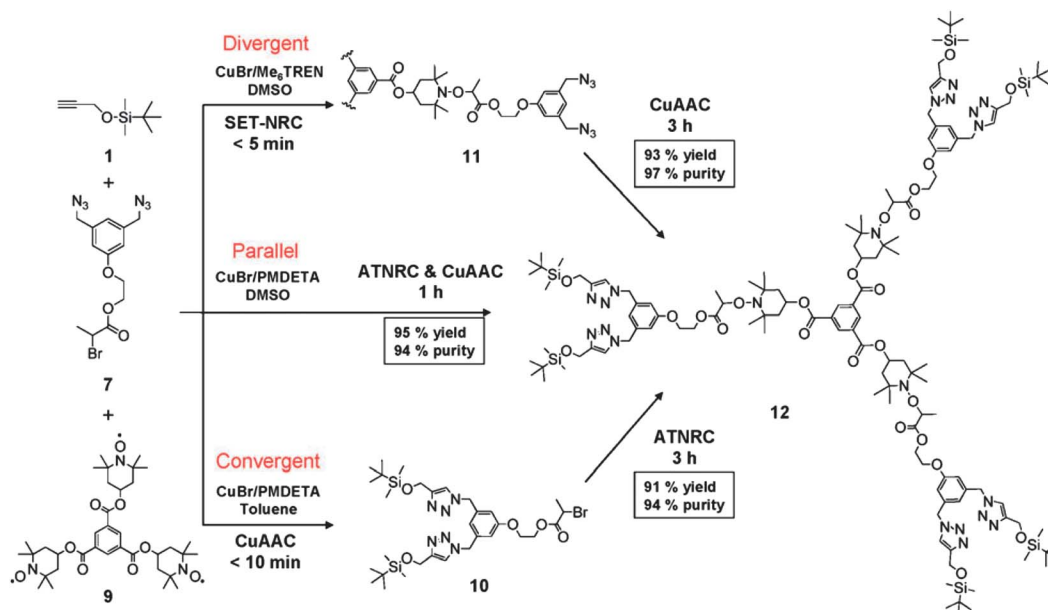
formed first after a few minutes, but the coupling of the dendrons to the core was slow, taking up to 24 h. To increase the speed of the convergent pathway, 15% DMSO was added as a co-solvent, and the reaction was completed in 2 h. Similarly, the synthetic utility of this method was further extended to coupling linear telechelic polymer building blocks, consisting of PS, PtBA, PEG, and PNIPAM, to form a range of dendrimer-like polymers in high yields.²⁴⁹ This approach reduced the steps of purification and chemical protection. By selecting the experimental conditions, the structures of polymers and the routes could all be controlled.

Again, the NRC reaction showed its versatility in the synthesis of star-shaped, macrocyclic and dendrimer polymers. However, because of the difficulties in the synthesis procedure, the examples for these polymers were rarely realized and reported. Thus, for the applications of NRC reaction in synthesis of polymers with complicated structures, challenges and opportunities might coexist.

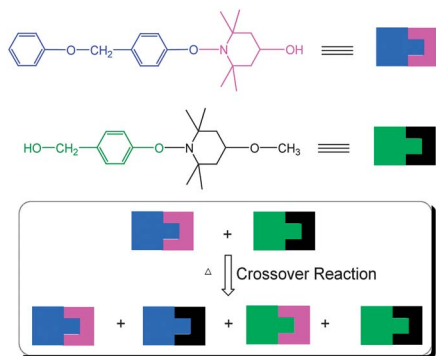
4.2.7 The applications of NRC reaction in radial crossover reaction. As concluded in literature, alkoxyamine groups

could be recombined under certain conditions because the alkoxyamine was formed by thermally reversible covalent bonds.¹⁴ Under normal conditions (below 60 °C), the alkoxyamine was rather stable, even at high concentration. However, once they were exposed to external stimuli such as heating, they could be reorganized. Because of these reasons, TEMPO containing alkoxyamine derivatives were frequently used as unimolecular initiators for NMRP mechanism in polymer synthesis,^{14,250,251} in which the key step was the reversible capping of the polymer chain by the nitroxide radical.²⁵² In fact, even though there was no monomer in the system, the alkoxyamine unimolecular initiators could also be expected to dissociate and associate reversibly by means of heating and exchange through a radical crossover reaction, which actually proceeded according to the NRC reaction mechanism (Scheme 66).²⁵³

Based on the radical crossover reaction, Takahara *et al.* developed some “dynamic covalent polymers”, whose structures and properties were changeable and tunable after polymerization.^{254,255} The radical crossover reaction between alkoxyamines on “dynamic covalent polymers” occurs in a radical process that was tolerant to many functional groups.^{256,257} Also, the radical crossover reaction rate strongly depended on the time, concentration and reaction temperature. Usually, the higher the reaction temperature, the faster the molar ratio reached equilibrium. Importantly, the radical crossover reaction might be used as a novel synthetic method to new polymers. By selectively incorporating alkoxyamine units into the main chains or side chains of polymers, various topological polymers had been realized, such as graft,^{258–260} star-shaped,^{261–266} crosslinked,^{267–270} macrocyclic²⁷¹ and block polymers.^{254,272,273} Related work was reviewed by Takahara *et al.*,¹⁰² and the detailed progress is not described here any further.



Scheme 65 The synthetic pathways for divergent, parallel and convergent formation of a highly branched dendrimer-like architecture in a one-pot strategy.²⁴⁸



Scheme 66 The radical crossover behaviour of TEMPO-based alkoxyamine derivatives.²⁵³

5 Conclusions and outlook

Based on the radical coupling reaction, the homocoupling of ATRC reaction and the agent (including styrene, nitrene and diene) assisted radical coupling reactions has been developed; the heterocoupling of NRC reaction between nitroxide radicals and carbon-centered radicals was also studied in detail. These methods facilitated the design and synthesis of polymers with various complicated topological architectures, such as telechelic, H-shaped, star-shaped, grafted, crosslinked, dendritic, macrocyclic polymers and so on. Comparing with the ATRC reaction and the agent assisted radical coupling reactions, the NRC reaction showed many advantages in polymer science because the precursors used for NRC reaction could be pre-designed and prepared with different structures and compositions.

However, there were still some challenges for these radical based coupling reactions. In the ATRC reaction, because of the side reaction attributed to the carbon-centered radicals, this reaction was mainly limited to PS-based precursors and low molecular weights ($M_n < 5000 \text{ g mol}^{-1}$), and poly(methyl)acrylate precursors always displayed low coupling efficiencies because of the tendency to disproportionation termination of the radicals. For the nitrene assisted radical coupling reaction, the feed ratio of nitrenes to the functional precursors was the key point, the selection of efficient nitrenes (especially those containing a functional group) for the coupling reaction was also a complicated task. In the diene assisted coupling reaction, the kind of precursor was limited because the monomers adapted to the CMRP mechanisms were rare. For the NRC reaction, to a great extent, it was limited by the available TEMPO containing precursors and the kind of nitroxide radicals. Usually, halogen containing precursors for ATRC or NRC reactions could be obtained by direct ATRP or SETLRP mechanisms. However, TEMPO containing precursors were majorly obtained by modification of certain polymers with small molecule TEMPO, and only limited precursors could be obtained by direct polymerization using TEMPO or its derivatives as initiators.

Thus, the extension of the above ATRC and NRC reactions in polymer science was still challenge work, including the optimization of coupling conditions, enriching the kinds of polymers adapted to the coupling reactions, as well as

expanding the application of these reactions for more complex polymers and so on. From the mechanistic viewpoint, if possible, we could also envision that the radicals generated in RAFT mechanism (not only in ATRP or SETLRP mechanisms) could also be used in radical coupling, for either ATRC or NRC reactions. Instead of bromide terminated precursors, iodine terminated precursors could be widely used because of the weaker connection of iodine with the carbon atom, and the Co-mediated “living” controlled polymerization should also be hugely developed and used in radical coupling reactions. Also, the application of radical based coupling reactions in step-growth polymerization may be another orientation in polymer science, because this mechanism could be used to generate various functional polymers.

Abbreviations

AGET	Activators generated by electron transfer,
AN	Acrylonitrile,
ATRA	Atom transfer radical addition,
ATRC	Atom transfer radical coupling,
ATRP	Atom-transfer radical polymerization,
ATNRC	Atom transfer nitroxide radical coupling,
BA	Butyl acrylate,
BBr_3	Boron tribromide,
CMRC	Cobalt-mediated radical coupling,
CMRP	Cobalt-mediated radical polymerization,
CTTC	Cyclic trithiocarbonate,
CuAAC	Copper-catalyzed azide/alkyne click chemistry,
DA	Diels–Alder reaction,
DBCP	1,3-Diyl-bis(2-chloro-2-phenylacetate),
dHBipy	4,4'-Di-(<i>n</i> -heptyl)-2,2'-bipyridine,
DMF	<i>N,N</i> -Dimethylformamide,
DMSO	Dimethyl sulfoxide,
DPMK	Diphenylmethyl potassium,
DVB	Divinylbenzene,
EO	Ethylene oxide,
ESCP	Enhanced spin capturing polymerization,
GO	Graphene oxide,
GPC	Gel permeation chromatography,
GPEC	Gradient polymer elution chromatography,
GTEMPO	4-Glycidyoxy-2,2,6,6-tetramethylpiperidin-1-oxyl,
HMTETA	1,1',4,7,10,10'-Hexamethyltriethylenetetramine,
HPG	Hyperbranched polyglycerol,
IARC	Isoprene-assisted radical coupling,
MALDI-MS	Matrix-assisted laser desorption ionization mass spectrometry,
Me_6TREN	Tris[2-(dimethylamino)ethyl]amine,
NBS	<i>N</i> -Bromosuccinimide,
NIPAAm	<i>N</i> -Isopropylacrylamide,
NMR	Nuclear magnetic resonance,
NMRC	Nitrene-mediated radical coupling,
NMRP	Nitroxide mediated radical polymerization,
NVP	<i>N</i> -Vinylpyrrolidone,
PAN	Poly(acrylonitrile),

PBN	<i>N</i> -tert-Butyl- α -phenylnitron, <i>N</i> -Methyl- α -(4-bromophenyl)nitron,
pBPMN	
PC	Poly(bisphenol A carbonate),
PCL	Poly(γ -caprolactone),
PDI	Polydispersity index,
PEG	Poly(ethylene glycol),
PEO	Poly(ethylene oxide),
PHEMA	Poly(2-hydroxyethyl methacrylate),
PI	Polyisoprene,
PiBoA	Poly(isobornyl acrylate),
PMA	Poly(methyl acrylate),
PMDETA	1,1,4,7,7-Pentamethyldiethylenetriamine,
PMMA	Poly(methyl methacrylate),
PMN	<i>N</i> -Methyl- α -phenylnitron,
PNVP	Poly(<i>N</i> -vinylpyrrolidone),
Poly(EO-co-Gly)	Poly(ethylene oxide-co-glycidyl),
Poly(FABu)	Poly(butyl- α -fluoroacrylate),
Poly(GTEMPO-co-EO)	Poly(4-glycidyoxy-2,2,6,6-tetramethylpiperidin-1-oxyl-co-ethylene oxide),
Poly(MMA-co-BIEM)	Poly[methyl methacrylate-co-2-(2-bromoisobutyryloxy)ethyl methacrylate],
PONB	Poly(oxanorbornene imide),
PP	Polypropylene,
PPO	Poly(phenylene oxide),
PS	Polystyrene,
PtBA	Poly(<i>tert</i> -butyl acrylate),
PVAc	Poly(vinyl acetate),
RACP	Step-growth radical addition-coupling polymerization,
RAFT	Reversible addition fragmentation transfer polymerization,
RATRP	Reverse atom transfer radical polymerization,
RITP	Reverse iodine transfer polymerization,
ROMP	Ring-opening metathesis polymerization,
ROP	Ring-opening polymerization,
SET	Single electron transfer,
SETLRP	Single electron transfer living radical polymerization,
SETNRC	Single electron transfer nitroxide radical coupling,
SETRC	Single electron transfer radical coupling,
Sn(EH) ₂	Tin ethyl hexanoate,
SnOct ₂	Stannous octanoate,
SRAA	Silane radical atom abstraction,
St	Styrene,
TBAF	Tetrabutylammonium fluoride trihydrate,
tBB	<i>tert</i> -Butylbenzene,
TEMPO	2,2,6,6-Tetramethylpiperidin-1-oxyl,
THF	Tetrahydrofuran,
VAc	Vinyl acetate.
VBMP	4-Vinylphenyl 2-bromo-2-methylpropanoate,

Acknowledgements

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