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Combinations (Є) among controlled/living polymerizations and utilizations of efficient chemical reactions for the synthesis of novel polymeric materials

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Building on the 1st-generation method of living anionic polymerization in the 1950s, various 2nd-gen controlled/living polymerization (CLP) techniques were developed in the 1980s–1990s. The CLP techniques now include ionic, radical, ring-opening (metathesis), and condensation polymerizations, allowing us to precisely control molecular weight, polydispersity, and complex architectures. However, the polymerizable monomers restrict the use of single-initiation systems, thereby limiting the synthesis of innovative macromolecules. Polymer chemists are thus interested in investigating ways to design or overcome the obstacles presented by two-initiation or more methods. Our review mainly focuses on the investigations of such *combination* approaches, represented by the symbol "Є", in diverse and robust polymerizations. We also depict numerous combinations of revolutionary polymerizations and effective reactions to prepare novel polymeric materials and discuss their relevant, unique properties and applications. Notably, we further address the synthesis of novel macromolecules, including block copolymers (BCPs), bottlebrush polymers (BBPs), hyperbranched polymers (hbPs), and (miktoarm) star copolymers ((μ-)SCPs). This review aims to showcase the effectiveness of synthetic method combinations and highlight the diverse applications of these innovative materials.

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1. Introduction

Since the 1950s,[1] numerous controlled/living polymerization (CLPs) techniques have been developed, including the pioneering method of living anionic polymerization (LAP),[2,3] the fast method of living cationic polymerization (LCP),[4,5] preparations of bio-related materials of ring-opening polymerization (ROP), the significant contributions of ring-opening metathesis polymerization (ROMP), the great impact of controlled/living radical polymerization (CRP), and innovative designs of chain-growth condensation polymerization (CGCP) and catalyst transfer polymerization (CTP) as well as some other relevant techniques. CLPs practically enable the preparation of well-defined (co)polymers with predictable molecular weight (MW) and low polydispersity index (PDI). However, the early techniques, such as LAP and LCP of vinyl monomers, require strict conditions to conduct/control the polymerizations effectively. These requirements mainly involve avoiding moisture/water molecules during polymerizations and intolerance of vinyl monomers containing polar groups. The polar molecules can lead to uncontrolled/living trends in ionic polymerizations due to the influence of a combination between the active center and polar moiety. Despite several attempts to expand the variety of vinyl monomers, the inherent limitations of ionic polymerization still pose a challenge.

In the late 1980s to mid-1990s, several revolutionary CRPs were recognized.[6–9] Notably, robust CRPs were inspired by or extended from several efficient reactions. Among the most important examples, redox reactions of Kharash reaction[10–12] and similar atom transfer radical addition (ATRA)[13] typically proceed with a mono-addition reaction between an alkyl halide (RX) and a vinyl monomer (M) in the presence of a transition metal complex catalyst. A small molecule (RMX) is then acquired. Building upon these redox reactions, Matyjaszewski[14] and Sawamoto[7] independently reported the

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atom transfer radical polymerization (ATRP) methods that extend mono-addition toward multiple additions in large amounts of monomers, enabling the synthesis of well-defined macromolecules.[15,16] Furthermore, the development of "green" ATRPs has enhanced their robustness.[17–20] The core concept of the "green" ATRP is to decrease the amount of transition metal catalysts (down to a parts-per-million (ppm) level). Similar diminishing catalyst techniques, including activators regenerated by electron transfer (ARGET),[21,22] initiators for continuous activator regeneration (ICAR),[23] supplemental activator and reducing agent (SARA),[24,25] and organocatalyst-mediated (O-)[26–31] ATRPs, generally proceed with the aid of excess amounts of reducing agents (RAs) (*e.g.*, ascorbic acid,[32–36] zero-valent metals,[24,37] azo compounds[38–41] …*etc.*[42–47]). In addition, several other interesting and innovative ATRPs are conducted through external electrochemical (*i.e.*, *e*ATRP),[48–50] photochemical (*i.e.*, photoATRP),[51–53] mechanical (*i.e.*, mechano-ATRP),[54,55] or ultrasonic (*i.e.*, sono-ATRP) stimuli.[56,57]

Nowadays, ATRP is one of the most widely used methods in fundamental research,[58] application studies,[25,59] and industrial production.[60] Besides ATRP, two other CRPs, reversible addition–fragmentation chain transfer (RAFT) polymerization[9,61,62] and nitroxide-mediated radical polymerization (NMP),[8,63] are also extensively investigated. CRPs are one of the most potent platforms for obtaining specific macromolecules, including functional linear/branched polymers, periodic copolymers, block copolymers (BCPs), and conducting surface modifications. Different from ionic polymerizations of vinyl monomers, CRPs can not only afford well-defined (co)polymers with predictable MW and low PDI but also polymerize a wide range of vinyl monomers and obtain (co)polymers with various compositions/functionality as well as complex architectures. Through the combinations or transformation (symbolized as "Ŧ")[64] of different CLP techniques,[65–69] unique copolymers (*i.e.*, [amphiphilic/immiscible/various functional blocks] × [linear/non-linear copolymers]) can be synthesized effectively. Besides the robust tools mentioned above, several innovative synthetic methods are emerging in polymer science, such as (styrenics-assisted) atom transfer radical coupling ((SA) ATRC),[70–72] copper-catalyzed azide–alkyne cycloaddition (CuAAC),[73–75] multicomponent reaction (MCR),[76] complementary metallo-supramolecular coordination (CMSC),[77–79] and more. Toward the design of specific or complex macromolecules, several approaches or considerations could be examined:[64,80,81] (i) direct chain end transformation[82–84] or post-modification followed by initiation of another polymerization or followed by another effective reaction (such as click reaction, supramolecular reaction…*etc.*); (ii) utilization of a dual-functional initiator or inimer as a combination junction either *via* a multistep approach (generally two subsequent steps) or concurrent polymerizations *via* a one-step approach. These approaches should consider the influence of each initiating site or reactions toward the other polymerization technique or reactive end(s), especially in the one-step case; (iii) for non-linear copolymers (*e.g.*, bottlebrush polymers (BBPs) or star copolymers), "grafting-through", "grafting-to", "grafting-from", and recently developed "in–out" methods can be employed.

In this review, the diverse and robust combination (symbolized as "Є" herein) approaches among the abovementioned polymerizations and organic reaction methods in the synthesis of novel macromolecules, including BCPs, BBPs, hbPs (*i.e.*, hyperbranched polymers), and μ-SCPs (*i.e.*, miktoarm star copolymers), are mainly included. As shown in Scheme 1, we outline numerous combinations among various revolutionary polymerizations and effective reactions for the preparation of novel polymeric materials. Their relevant, unique properties and applications are also discussed. We thus attempt to present the effectiveness of the synthetic method combinations and demonstrate diverse applications to obtain innovative materials.

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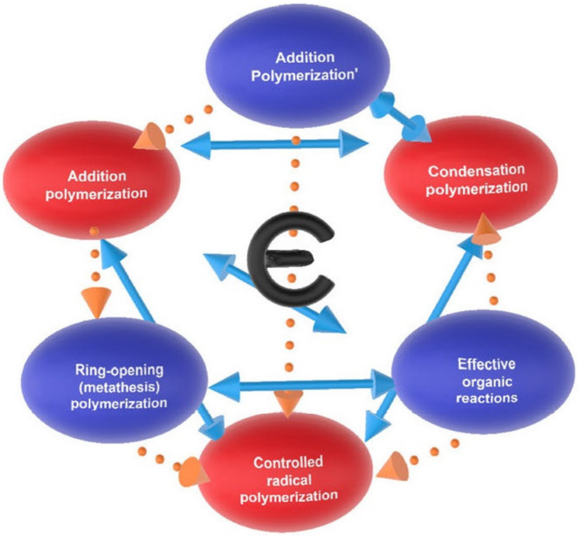

Scheme 1 Diverse combinations (Є) among controlled/living polymerizations (CLPs) and effective reactions.

2. (Addition polymerization)-Є-(addition polymerization′) and the relevant applications

We can efficiently synthesize a variety of block and star copolymers by using a single CLP technique through consecutive polymerizations. However, single-initiation systems are limited in their polymerizable monomers, restricting the synthesis of novel macromolecules. Thus, it is attractive and fascinating for polymer chemists to investigate how to design or overcome the interferences of two-initiation systems, especially in the challenging combinations of addition polymerization-Є-addition polymerization. This section addresses several representative varieties involving examples of (controlled/living) addition polymerizations, such as conventional free radical polymerization (FRP), ATRP, RAFT, NMP…*etc.* *via* several approaches (see Table 1).[81] ATRP is generally able to achieve good control over the polymerization of "more-activated" monomers (MAMs), including styrene (St), methyl acrylate (MA), *n*-butyl acrylate (nBA), *tert*-butyl acrylate (*t*BA), methyl methacrylate (MMA), hydroxyethyl methacrylate (HEMA), acrylonitrile (AN), and others. The limitations of ATRP are seen when polymerizing "less-activated" monomers (LAMs). The absence of resonance effects in LAM radicals, including vinyl acetate (VAc), *N*-vinylpyrrolidone (NVP), *N*-vinylcarbazole (NVK), and olefins, gives rise to their increased reactivity and instability. This inherent instability in the propagating radicals of these LAMs leads to rapid chain transfer or termination reactions, posing challenges in effectively controlling the ATRP of LAMs. Therefore, conventional FRP methods were often used to polymerize LAMs before the development of CRPs. However, it was later discovered that specific RAFT agents, such as thiocarbamates and xanthates, are suitable for achieving CRP fashions of LAMs. These agents, however, often exhibit poor or uncontrolled behaviors when used with MAMs. As a result, synthesizing poly(MAM)-*b*-poly(LAM) BCPs presents a challenge.

An approach for overcoming such limitations is to combine ATRP with other polymerization techniques. Using a bifunctional initiator, Destarac and co-workers first reported the combinations of ATRP and FRP (ATRP-Є-FRP) to prepare poly(MAM)-type diblock copolymers (diBCPs), comprising PnBA and PSt.[85] The first attempt to synthesize poly(MAM)-*b*-poly(LAM)-based diBCPs (wherein, LAM = VAc) was revealed by Matyjaszewski and coworkers.[86] They discussed and compared the two-way approaches involving mechanistic combinations between ATRP and FRP to obtain well-defined PVAc-based BCPs. The first polymerization sequence employed the mechanistic combination of FRP-to-ATRP in which an azo

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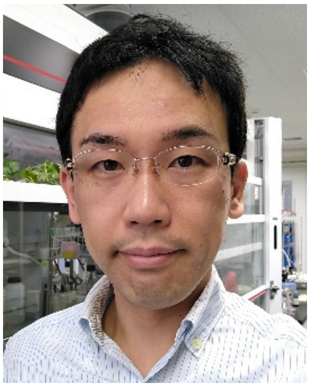

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compound containing an activated chlorine atom, 2,2′-azobis [2-methyl-*N*-(2-(4-chloromethyl benzoyloxy)ethyl) propionamide] (AMCBP), was used as a dual-functional initiator (see Scheme 2a). Whereas the second polymerization sequence employed an ATRP-to-FRP combination using 2,2′-azobis[2-methyl-*N*-(2-(2-bromoisobutyryloxy) ethyl) propionamide] (AMBEP) as a dual-functional initiator (see Scheme 2b). These dual-functional initiators can be facilely prepared by acylation of the hydroxyl-containing azo compounds with the acid halides. AMCBP was used to initiate the polymerization of VAc at 90 °C, resulting in PVAc terminated with an ATRP initiating site of benzylic chloride (M_n = 47 900, PDI (*i.e.*, M_w/M_n) = 2.21), which was then subsequently used as a macroinitiator for St to yield PVAc-*b*-PSt (M_n = 91 600, PDI = 1.80). In the other way, the dual-functional initiator (AMBEP) was first used to prepare nBA at 30 °C in the presence of CuBr/tris(2-(dimethylamino)-ethyl) amine (Me$_6$TREN) catalyst, resulting in PnBA (M_n = 7500, PDI = 1.15) with the preserved central azo unit which then helps to dissolve in VAc extending to PnBA-*b*-PVAc formation (M_n = 41 800, PDI = 3.56). One important point to note is that the second method allowed for preparation of a well-defined azo-macroinitiator without significantly losing the azo group. The acquisition of azo-macroinitiators can be attributed to the advantages of using CuBr/Me$_6$TREN as an effective catalyst to conduct ATRP of (meth)acrylates at a relatively low temperature (*e.g.*, <40 °C).

In other interesting works, Lee *et al.*[89] and Huang *et al.*[88] successfully synthesized PMMA-*b*-PNVP and PHEMA-*b*-PNVP diBCPs by combining ATRP with FRP with controlled molecular weight and moderate PDIs (see Scheme 2c). A well-defined azo-centred macroinitiator was prepared from AMBEP and the corresponding monomers using the ATRP technique in the synthesis procedures. This macroinitiator was then used to polymerize NVP *via* FRP. The authors further investigated the thermal properties and phase behavior differences between the synthesized diBCPs and their blends (including blends with other homopolymers). The homogeneity of the additional homopolymer in the PMMA-*b*-PNVP/PVPh [*i.e.*, poly (4-vinyl phenol)] blend system was identified. Interestingly, it was observed that PHEMA-*b*-PNVPs have higher glass transition temperatures (T_gs) than their corresponding PHEMA/PVP blends. This can be attributed to the stronger intermolecular hydrogen bonding interactions in the case of the diBCP.

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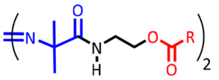
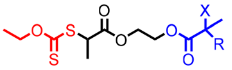
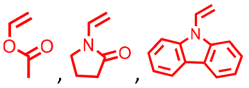
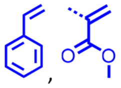
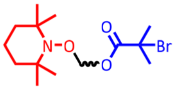
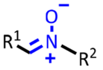
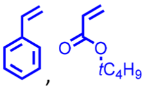
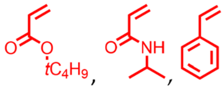
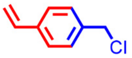
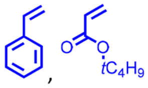
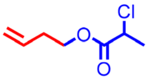
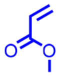
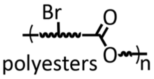
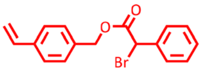
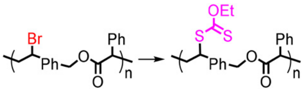
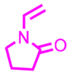
Compared with the mechanistic combinations of ATRP and other polymerization techniques, the use of RAFT in combination with other CRPs, such as RAFT-Є-ATRP,[90–92] RAFT-Є-NMP,[93–95] ATRP-Є-LCP,[96] and RAFT-Є-LAP/LCP,[97–102] to synthesize structurally well-defined BCPs is still relatively limited. In the case of RAFT-Є-ATRP combinations, BCPs comprising LAM and MAM can be synthesized.[64] As shown in Scheme 3, dual-functional initiators were synthesized, comprising an ATRP initiating site and an RAFT agent moiety. Such a combination can be applied interchangeably, one after the other. In most cases, "RAFT-first" was conducted to prepare LAM blocks. The resulting macroinitiators were then used to prepare the MAM blocks *via* ATRP (*i.e.*, step (i-to-ii) in Scheme 3). Matyjaszewski *et al.*[90,91,103] demonstrated that the synthesis of various diBCPs was described using "*iniferters*" of the halo-xanthates. These iniferters, first introduced by Otsu in 1982,[104] are named from the "*ini*tiator-trans*fer* agent-*ter*minator" concept and the synthesis of diBCPs can be accomplished using two interchangeable strategies. In the relevant reported studies, the RAFT polymerizations of LAMs (*i.e.*, VAc, NVP, and NVK) could be conducted before or after the ATRPs of MAM (*i.e.*, St, MMA, and MA). Their research results demonstrated that the predesigned sequential utilization of ATRP and RAFT combination polymerization techniques can affect the MW, PDI, and the degree of chain-end functionalization. When the "RAFT-first" approach was used in the diblock copolymerizations of PNVP with PMMA and PSt, the chloroxanthate iniferters displayed good controllability for RAFT polymerization of NVP, resulting in the synthesis of well-defined diBCPs of PNVP-*b*-PMMA. (M_n = 50 600, PDI = 1.3) and PNVP-*b*-PSt (M_n = 15 000, PDI = 1.4) through subsequent chain extension by ATRP. However, poor control was observed when the same sequence was attempted for PNVP-*b*-PMA synthesis due to a reshuffling reaction between the xanthate moiety of the PNVP chain end and the propagating acrylate radicals. This resulted in a loss of control over the MA chain extension process.[90] On the other hand, when "ATRP-first" was used (*i.e.*, step (iii-to-iv) in Scheme 3), a well-controlled ATRP was observed only for MMA monomer and resulted in poor control and a large PDI for the subsequent RAFT chain extension of NVP, similarly due to the occurrence of significant reshuffling

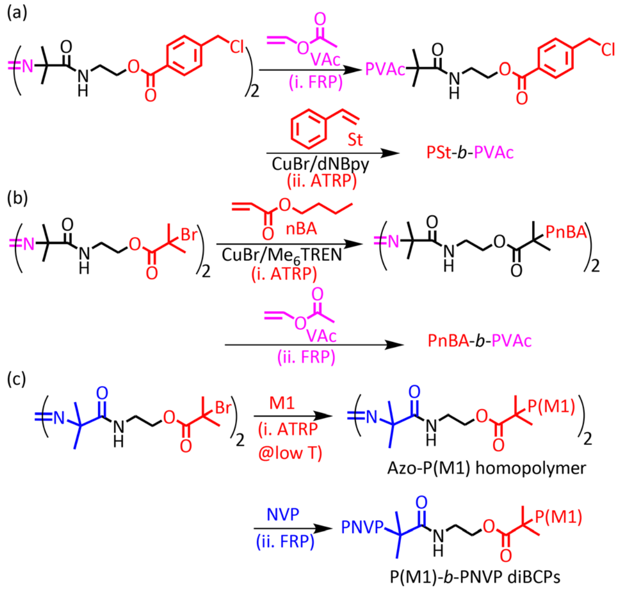
Table 1 Summary of combinations (Є), monomers, and products based on the addition polymerization-Є-addition polymerization' approaches

No.	Є case[a]	Є agent/notes	Monomer 1	Monomer 2	Products[b]
1	ATRP-Є-FRP	 R: 4-(chloromethyl)benzyl or 2-bromopropyl	nBA, HEMA, MMA	St, VAc, NVP	PnBA-*b*-PSt[85] PHEMA-*b*-PNVP[88] PMMA-*b*-PNVP[87]
2	RAFT-Є-ATRP	 (R= CH_3/H; X= Br/Cl)			PVAc-*b*-P(M)MA & PSt[103] PNVP-*b*-PMMA & PSt[90] PNVK-*b*-PMMA & PSt[91]
3	RAFT-SЄ-ATRP	(CDB & CuBr/TPMA)/simultaneous	MMA, St	BMA	HMW PMMA & PSt, HMW PMMA-*b*-PBMA[92]
4	NMP-Є-ATRP		St	MMA, *t*BA, AN	PSt-*b*-PMMA, PSt-*b*-PtBA, PSt-*b*-PAN[80]
5	ESCP-Є-NMP				PSt-*b*-PtBA-*b*-PSt[105] PSt-*b*-PNIPAM-*b*-PSt[106] $(PSt)_2$-μ-$(PtBA)_2$[107]
6	ATFRP-Є-ATRSCVP	Poor solvent for catalyst at the 1st & polar solvent at the 2nd/one-pot polymerization			(hb)PSt-*g*-PSt & PtBA[108]
7	ATRPA-SЄ-ATRP		Simultaneous ATRPA and ATRP		P(MA-*co*-ester)[109]
8	ATRPA-Є-ATRP	VBBiB; AA/BB type[c]		St; OEGMA	(polyester)-*g*-PSt;[110] (polyester)-*g*-P(OEGMA)[111]
9	ATRPA-Є-RAFT				PVBPA-*g*-PNVP[112]
10	CMRP-Є-TERP	Co(acac)$_2$ for VAc and (TeMe)$_2$ for the 2nd monomers	VAc	nBA, NIPAM, ADAME, IP, NVIm	PVAc-*b*-PnBA, PVAc-*b*-PNIPAM, PVAc-*b*-PDMEMA, PVAc-*b*-PIP, PVAc-*b*-PNVIm[113]

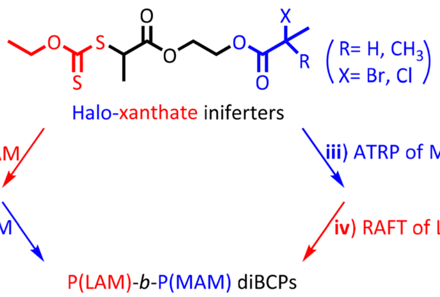
[a] SЄ: simultaneous polymerizations. ESCP: enhanced spin capturing polymerization. ATFRP: irreversible atom transfer-induced free radical polymerization. ATRSCVP: atom transfer radical self-condensing vinyl polymerization. CMRP: cobalt-mediated radical polymerization. TERP: organotellurium-mediated radical polymerization. ATRPA: atom transfer radical polyaddition. [b] nBA: *n*-butyl acrylate. HEMA: 2-hydroxyethyl methacrylate. MMA: methyl methacrylate. NVP: *N*-vinylpyrrolidone. VAc: vinyl acetate. NVK: *N*-vinylcarbazole. St: styrene. *t*BA: *tert*-butyl acrylate. NIPAM: *N*-isopropyl acrylamide. VBBiB: 4-vinylbenzyl 2-bromo-2-isobutyrate. VBPA: 4-vinylbenzyl phenylacetate. OEGMA: ethylene glycol methyl ether methacrylate. (TeMe)$_2$: dimethylditelluride. DMAEMA: 2-(dimethylamino)ethyl acrylate. NVIm: *N*-vinylimidazole. HMW: high molecular weight. hb: hyperbranched. *b*: for block copolymer. *μ*: for miktoarm star copolymer. *g*: for graft copolymer. [c] AA type: (4-vinylbenzyloxy)ethane. BB type: 1,2-bis(2-bromoisobutyryloxy)ethane and bis[2-(2-bromoisobutyryloxy)ethyl]disulfide.

reactions between the xanthate moiety and styryl/acrylate propagating radicals. The nature of the initiating sites and monomers used dramatically influences the polymerization effectiveness.[108] Despite the availability of various halo-xanthates, it is surprising that using bromo-xanthate iniferters prevented synthetic access to conduct RAFT polymerization of NVP or NVK. According to their research, bromo-xanthate iniferters were found to function as acid sources, resulting in protonation of the NVP and NVK monomers. A resulting byproduct of this reaction is the formation of an NVP or NVK dimer through an acid-catalyzed cationic mechanism.

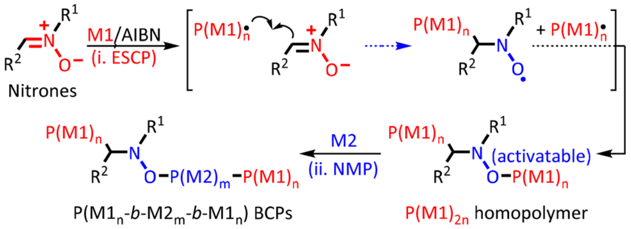
Rizzardo and co-workers first studied NMP in the mid-1980s. It allows us to synthesize a variety of polymers, including block, comb, star, and gradient copolymers with predictable MW and low PDIs.[81,114] NMP is recognized as one of the most commonly known reversible-deactivation radical polymerizations operating by the use of stable nitroxide radicals, such as 2,2,6,6-tetra methylpiperidine-1-oxyl (TEMPO). Several NMP-based combinations for the synthesis of functional and complex macromolecules have been reviewed.[64,80,81] Lately, an innovative and interesting method called enhanced spin capturing polymerization (ESCP) has been demonstrated. This method was extended from NMP and thoroughly investigated by the Jérôme, Junkers, and Barner-Kowollik groups.[106,115–117] As shown in Scheme 4, the ESCP method involves conducting the polymerization process under conventional FRP conditions by adding a nitrone compound. This allows secondary intermediates (*i.e.*, nitroxide radicals) to be efficiently formed through a cross-trapping reaction between propagating macroradicals and nitrones. These intermediates can then undergo cross-coupling with other propagating macroradicals, creating a new alkoxyamine moiety that can further conduct NMP from the middle of the polymer chains.[106,118] NMP and ESCP processes involve the formation of nitroxide radicals and incor-



Scheme 2 Synthesis of (a) PVAc-*b*-PSt, (b) PnBA-*b*-PVAc, and (c) PNVP-based diBCPs *via* ATRP-Є-FRP.[86–88]



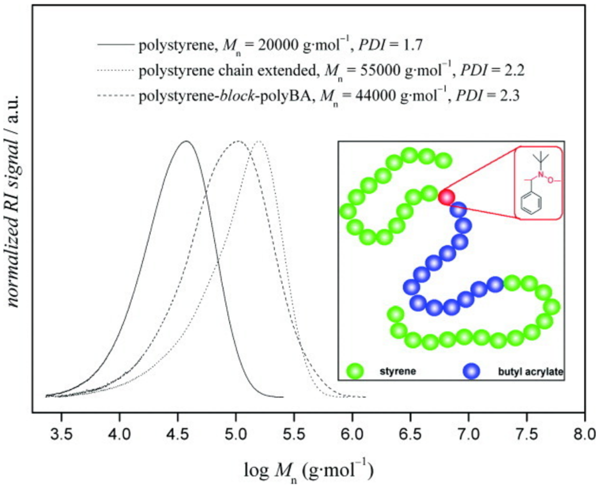
Scheme 3 RAFT-Є-ATRP for the synthesis of diBCPs of PVAc-*b*-P(M)MA & PSt,[103] PNVP-*b*-PSt & PMMA,[90] and PNVK-*b*-PSt & PMMA[91] [LAM: less-activated monomer (*e.g.*, VAc, NVP, and NVK); MAM: more-activated monomer (*e.g.*, St, MMA, and MA)].



Scheme 4 Consecutive mechanisms for (i) ESCP and (ii) NMP processes.[105–107]

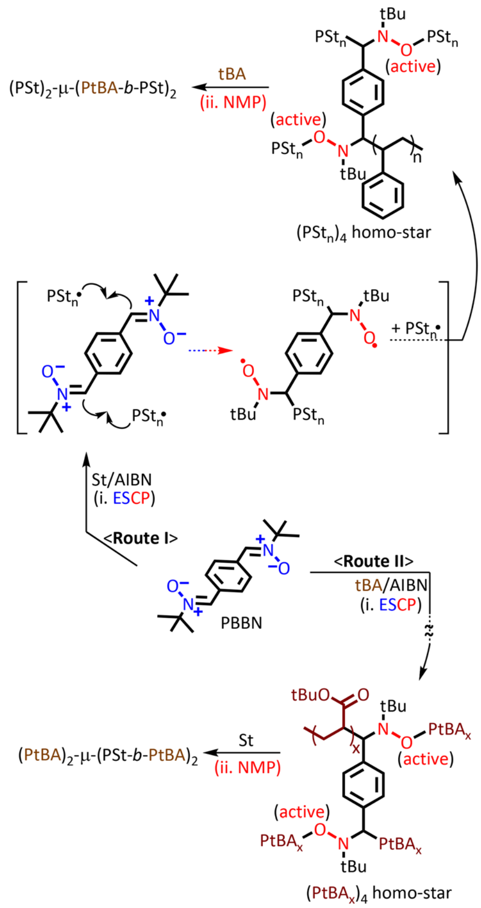
poration of the nitroxide moiety into the polymer chains, but their similarities are primarily due to this commonality. However, the two methods differ significantly in their reaction conditions and the systems used to establish equilibrium.[117] NMP operates at a high temperature (>100 °C) and participates in equilibrium reactions. In contrast, ESCP can be performed at a relatively low temperature (*i.e.*, 60–70 °C) without establishing any equilibrium reactions, relying only on the capping reactions between nitroxide radicals and macroradicals.[119]

Regarding the controllability and predictability of MWs and PDIs, ESCP is similar to the chain transfer polymerization or FRP method rather than CRPs. Thus, these two methods' overall kinetics and mechanisms are fundamentally different. As a matter of course, this tandem ESCP-to-NMP sequence (*i.e.*, ESCP-Є-NMP) would contribute to the synthesis of various BCPs. Junker *et al.*[120] explored the PDIs of ABA-type triblock copolymers (triBCPs) obtained by the chain extensions of ESCP-derived midchain alkoxyamine functional PSt using St and *t*BA as chain extenders *via* NMP. The efficiencies of NMP chain extensions with St and *t*BA were evidenced when the M_n of the midchain alkoxyamine functional PSt precursors were increased significantly. Similarly, Wong and co-workers studied the PDIs of PSt-*b*-PnBA BCPs using ESCP-Є-NMP with St and nBA, respectively.[117] Scheme 5 illustrates that successful chain shifts toward higher MW with moderate PDI values evince extensions of the ESCP-derived polymers. This verified its ability to act as a macro-nitroxide agent where a second monomer can be inserted in the ESCP-made polymer chain. ESCP allows manipulation of MWs for various monomers and provides an alternative approach for synthesizing multiblock polymers (multiBCPs) *via* subsequent NMP chain extensions. The same group demonstrated similar work by comparing experimental and simulation results. They found that if the radical initiator and nitrone are sensibly chosen in the ESCP-Є-NMP approach, a high degree of functionality (>90%) within the polymer chains can be achieved.[106] In addition, they conducted the first ESCP using *N*-*tert*-butyl-α-phenylnitrone, azobisisobutyronitrile (AIBN), and St monomer, resulting in the production of PSt precursors with different MWs. Subsequently, they conducted NMP chain extensions of the PSt macro-nitroxide agents using the hydrophilic monomer *N*-isopropyl acryl-



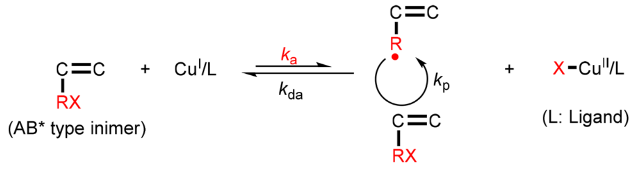
Scheme 5 MWs and PDIs after NMP midchain extensions from an ESCP-derived PSt with St and nBA.[117] Copyright 2023 John Wiley and Sons.

amide (NIPAM). As a result, the MW of the ESCP-prepared PSt precursor (M_n = 12 000) was substantially increased, resulting in the PSt-*b*-PNIPAM-*b*-PSt triBCP with an M_n of approximately 35 000. The triblock structure contains hydrophilic PNIPAM and hydrophobic PSt segments, allowing it to exhibit amphiphilic properties in aqueous solutions. Besides linear polymers, non-linear polymers such as dendrimers, (miktoarm) star polymers ((μ-)SCPs), hyperbranched polymers (hbPs), and bottlebrush polymers (BBPs) have demonstrated their various applications ascribing to their unique physical properties. Huang and co-workers[107] manifested a facile strategy for synthesizing μ-SCPs with adjustable/switchable interior and exterior polymer structures toward preparing various nanomaterials using ESCP-Є-NMP combination polymerization. As shown in Scheme 6, St and *t*BA were used either as first-step or second-step monomers in the sequential ESCP-Є-NMP combination (*i.e.*, route I or II) in the presence of the difunctional (1*Z*,1′*Z*)-1,1′-(1,4-phenylene)-bis(*N*-*tert*-butyl methanimine oxide) (PBBN) nitrone. This allowed the obtained four-armed star macroinitiators to be correspondingly switched into miktoarm star copolymers of $(\mathrm{PSt})_2$-μ-$(\mathrm{PtBA}$-*b*-$\mathrm{PSt})_2$ and $(\mathrm{PtBA})_2$-μ-$(\mathrm{PSt}$-*b*-$\mathrm{PtBA})_2$. The authors further conducted hydrolysis of the PtBA segments to poly(acrylic acid) (PAA), resulting in the formation of amphiphilic μ-SCPs of $(\mathrm{PSt})_2$-μ-$(\mathrm{PAA}$-*b*-$\mathrm{PSt})_2$ and $(\mathrm{PAA})_2$-μ-$(\mathrm{PSt}$-*b*-$\mathrm{PAA})_2$.

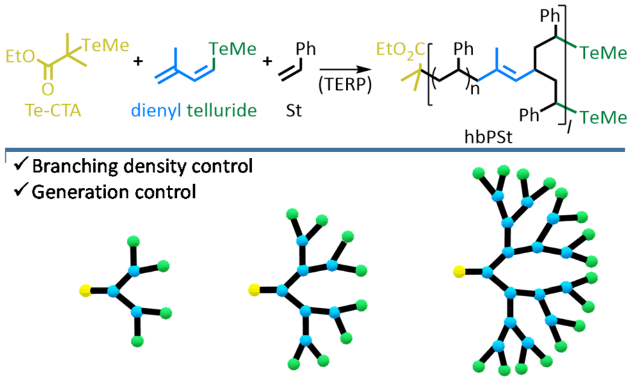


Scheme 6 ESCP-Є-NMP for the synthesis of various μ-SCPs.[107]

Besides SCPs, Fréchet and co-workers demonstrated an original idea and pioneering work on self-condensing vinyl polymerization (SCVP) through a cationic polymerization mechanism for synthesizing hbPs.[121] Matyjaszewski *et al.* proposed conducting SCVP through a radical polymerization mechanism. The designation of AB* is commonly used instead of AB_2 to allow a better understanding of the structure of monomers and macromolecules.[122–124] Accordingly, the A group is generally assigned to describe a double bond. It is separated from the B* group by a spacer (*e.g.*, alkyl, alkoxyl, *etc.*), while B* is assigned to represent a functional group that can generate an active center and initiate the polymerization of the double-bonds. The asterisks (*) indicate that a structural site/group can form either in an active center or dormant form.[123] The B* group can generate a radical, cationic, or anionic active center, and its activated form adds across the double bond A to form the dimer. Hawker *et al.*[125] and Matyjaszewski *et al.*[126] demonstrated SCVP through CRP mechanisms and synthesized hb(polystyrene) and hb(polyacrylates) from so-called "inimers", which are named from the combinations of *ini*tiator-monom*ers*. hbPs can be facilely synthesized from monomers that contain both a polymerizable unit and a functionality capable of initiating the polymerization of the former *via* atom transfer radical self-condensing vinyl polymerization (ATRSCVP) techniques. Scheme 7 depicts the general mechanism of ATRSCVP with an AB*-type inimer.[108] The AB*-type inimer can function as both initiating and propagating sites while having the external activator of $\mathrm{Cu^I/L}$ (L: ligand). As the initiation and the propagation sites have similar reactivity, chain propagation and re-initiation proceed simultaneously. Although SCVP encounters the significant disadvantages of large PDI values, several studies demonstrated their achievements in obtaining low PDI hbPs.[108,127] The SCVP approaches lead to hbPs with large PDI values. It is worth noting that several efforts have been designed using physical[128,129] or chemical[130–132] strategies to demonstrate the PDI controls for hbPs. In the first example of a radical mechanism, Yamago and coworkers[132,133] demonstrate the one-step copolymerization of dienyl telluride and St to produce highly branched hbPSts *via* organotellurium chain transfer polymerization (TERP), which can also conduct good control over LAMs. As shown in Scheme 8, this approach illustrates control over MW, branching density, and generation



Scheme 7 General mechanism of ATRSCVP with AB* type inimers.[108] This figure is reproduced from an open access MDPI journal (*Polymers*).

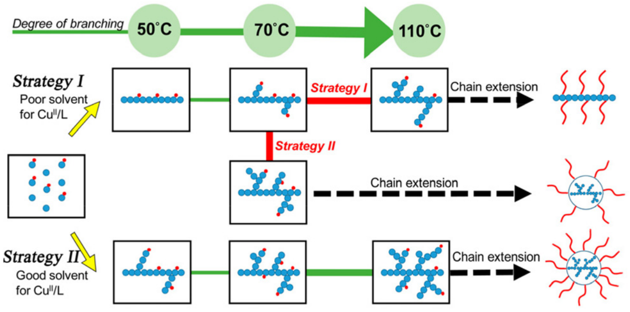


Scheme 8 Controllable synthesis of hbPSt by TERP.[132]

while reaching dendritic uniformity by manipulating the ratios of the highly efficient branching agent and dienyl telluride.

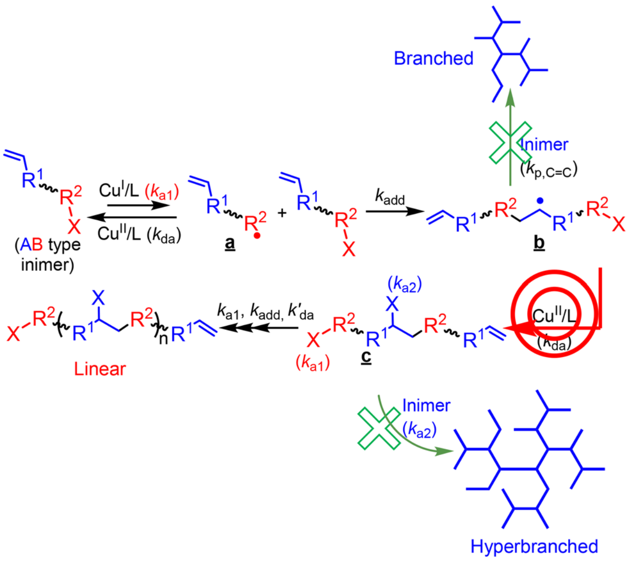
Regarding mechanistic combinations, Gong *et al.*[127] prepared an AB* monomer formed *in situ* by ATRA from commercially available 1-bromoethylbenzene (PEBr) and divinylbenzene (DVB). Simultaneously, ATRP of the *in situ*-formed AB* monomer occurred and afforded DVB-based hbPs with M_ns ranging between 27 380 and 109 600. Compared with the preparations of the preceding AB* monomers, the detail and polymerization mechanisms were intriguing. The study found that the DVB to 2,2′-bipyridine (Bpy) ratio and catalyst concentration significantly influenced the polymerization process. The pioneering works of Bannister *et al.*[134] and Wang *et al.*[135] demonstrated the preparation of hyperbranched polymers using the ATRSCVP-Є-ATRP strategy.

Recently, Huang *et al.*[108] reported the preparation of polymers with different topologies proceeding *via* ATFRP-Є-ATRP and ATRSCVP-Є-ATRP mechanistic combination by manipulating the phase homogeneity of CuBr$_2$/Bpy complex in a mixture of St, ethyl α-bromoisobutyrate (EBiB), and 4-vinyl benzyl chloride (VBC) monomers (Scheme 9). A monomer, an active initiator (*i.e.*, large activation rate constant (k_a)), a catalyst, and an inimer (*i.e.*, St, EBiB, Cu^{I}/L, and VBC) were mixed. In Strategy I, the heterogeneity and precipitation of the Cu^{II}/L complex resulted in irreversible atom transfer-induced free radical polymerization (ATFRP),[104] leading to linear or less-branched polymers (*i.e.*, $k_{\mathrm{a,VBC}} \ll k_{\mathrm{a,EBiB}}$). Subsequently, ATRP of the resulting P(St-*co*-VBC) macroinitiator (MI) with St could be conducted (*i.e.*, ATFRP-Є-ATRP). SCPs with a less-branched core were afforded. Increasing the copper complex's solubility can switch topology from linear to branched polymers (*i.e.*, Strategy II). The propagating chains and re-dissolved deactivators guided the recovery balance between activation and deactivation. Chain extensions were further performed on the resulting hyperbranched MIs. The chain extensions with either St or *t*BA were carried out. This one-pot process obtained hyperbranched core-star polymers of hbPSt-*g*-PSt and hbPSt-*g*-PtBA with M_ns ranging between 25 000 and 27 000 and PDI = *ca.* 1.8.



Scheme 9 Proposed strategies for controlling polymer topology *via* a one-pot procedure for the preparations of hyperbranched core-star polymers using ATFRP-Є-ATRP (*i.e.*, Strategy I) and ATRSCVP-Є-ATRP processes (*i.e.*, Strategy II).[108] This figure is from an open access MDPI journal (*Polymers*).

Another novel step-growth type polymerization technique based on radical chemistry, called atom transfer radical polyaddition (ATRPA),[136–138] is emerging. ATRPA is an innovative and conceptual combination of ATRP and polymer topology control.[139–141] ATRPA offers an intriguing approach for synthesizing functionalizable linear aliphatic polyesters. Scheme 10 illustrates the side reactions and general mechanism of Cu-catalyzed ATRPA for synthesizing aliphatic polyesters through the following steps: (i) activation (k_{a1}) of an ester-containing AB-type inimer with a Cu^{I}/L catalyst, resulting in the formation of a (macro)radical species **a** and a Cu^{II}/L deactivator; (ii) addition (k_{add}) of the produced radical to a vinyl bond, resulting in the formation of a monoadduct in radical form **b**; (iii) fast deactivation (k_{da}) of the monoadduct radical by the Cu^{II}/L deactivator (*i.e.*, the red route), resulting in the generation of an ester-containing halide species **c** and a Cu^{I}/L activator; and (iv) impeccably repeating the polyadduct steps of (i–iii), forming aliphatic polyesters. Compared with the above-men-

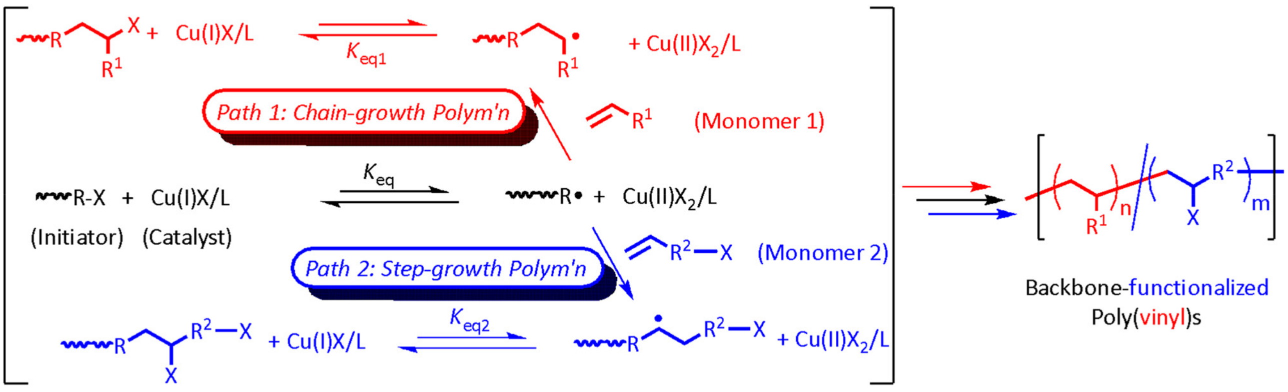


Scheme 10 Mechanism of suppression of ATRSCVP toward Cu-catalyzed ATRPA to synthesize aliphatic polyesters (*i.e.*, R^2 = ester group).

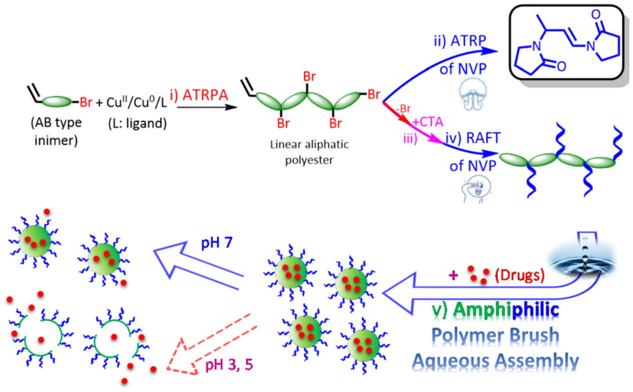
tioned, ATRPA and ATSCVP are two opposite cases of synthesizing linear and hyperbranched polymers based on fundamental ATRP mechanisms. Regarding linear topology control, one obstacle might be the propagation of the vinyl moiety of inimer from species **b** (*i.e.*, $k_{p,C=C}$ in the top green route), which results in the production of branched polymers. The other obstacle might be the re-activation of the backbone (*i.e.*, k_{a2} in the bottom green route), which can cause the generation of hyperbranched polymers. Thus, the intriguing design of the inimer structures with high ratios of k_{a1}/k_p and k_{a1}/k_{a2} can lead to a perfect ATRPA process.

The first example of ATRPA was reported by Kamigaito and his co-workers, who successfully suppressed the formation of branched polymers. They utilized transition metals to catalyze radical polyaddition and produced linear polymers for several weeks.[136] This mainly uses AB- or AA/BB-type monomers to achieve precise control over polymer topology.[110,138] After that, Li *et al.*[110] designed a specific AB-type inimer, 4-vinylbenzyl 2-bromo-2-isobutyrate (VBBiB) inimer, that contains a styrenic group (A moiety) and a methacrylate-type ATRP initiating site (B moiety). By tuning the reaction factors accordingly, they synthesized a family of polymers with topologies ranging from linear to branched. The significance of the study is that it successfully produced the linear aliphatic polyesters and shortened the ATRPA process to less than a week. Huang and coworkers further studied the ATRPAs of VBBiB and designed another unsymmetrical AB-type inimer of 4-vinylbenzyl-2-bromo-2-phenylacetate (VBBPA). It was found that the linear polyester of PVBBiB was prone to undergoing ring-closure depolymerization. This was due to a group with strong leaving affinity from the side bromine atom, significantly contributing to self-degradation behavior. By changing the leaving group to chlorine and azido or using the VBBPA inimer with significant steric hindrance, several stable linear aliphatic polyesters could be obtained. In the study, Huang's group further studied the ATRPAs of VBBPA, comprising a styrenic group (A moiety) and a bromophenylacetate ATRP initiating site (B moiety). A high MW PVBBPA (M_w = *ca.* 2.6 × 10^4) could be obtained in just a few hours. Moreover, the MW can be further increased to approximately 4.0 × 10^4 when conducting Fe-catalyzed ATRPAs of VBBPA.[142–144] Developments of degradable or recyclable polymers have been an important issue for environmental concerns and the circular economy. Accordingly, Kamigaito and co-workers[109,136,137] perfectly demonstrated the metal-catalyzed simultaneous step-growth and chain-growth radical polymerization of vinyls and inimers. As shown in Scheme 11, we classify this technique as a simultaneous combination (herein symbolized as "SЄ") of ATRP and ATRPA (*i.e.*, ATRPA-SЄ-ATRP). Common vinyl monomer 1 and AB-type inimer 2 are utilized with an allyl group (A moiety) linked by an ester group to a reactive C–Cl bond (B moiety). They beautifully tagged the reaction as a "marriage of vinyl polymers and polyesters".[109] Linear random copolymers to multiblock copolymers, having different segment lengths of vinyl monomer units chopped by the polyester units, were obtained based on the transition metal complexes (catalysts), the feed ratio of monomers, and reaction conditions. For instance, ideal linear random copolymers containing both vinyl polymer and polyester units in a single polymer chain were formed when RuCpCl(PPh$_3$)$_2$- or CuCl/1,1,4,7,10,10-hexamethyltriethylenetetramine-catalyzed copolymerizations of MA for the ATRP and 3-butenyl 2-chloropropionate for the ATRPA was used. The copolymers can be easily degraded into lower MW vinyl polymers, oligomers, or polymers *via* methanolysis of the ester linkages in the main chain in the presence of sodium carbonate.

Moreover, it is easy to synthesize linear polyesters with brushes from AB-type monomers and perform post-reactions *via* the ATRPA-Є-CuAAC,[144] ATRPA-Є-ATRP,[111] or ATRPA-Є-RAFT[145] approaches. For instance, amphiphilic BBPs, consisting of a hydrophobic linear polyester grafted with hydrophilic PNVP chains, were investigated. As depicted in step i in Scheme 12, the resulting linear polyesters contain numerous bromides along the backbone. When ATRP chain extension with NVP was conducted (step ii in Scheme 12), near complete consumption of NVP was observed. Still, there were no significant changes in MW that might be ascribed to the bromides that served as acid sources that catalyze the dimerization of NVP.[90,91,112] An alternative approach was presented using ATRPA-Є-RAFT. As illustrated in steps iii and iv in Scheme 12, sequential post-reactions of substitutions and RAFT/MADIX



Scheme 11 Simultaneous chain-growth and step-growth polymerization (*i.e.*, ATRPA-SЄ-ATRP).[109,136–138]



Scheme 12 ATRPA-∈-RAFT for synthesizing amphiphilic polymer bottle brush for the applications of drug carriers in aqueous.[112,142–144]

(MADIX: macromolecular design *via* the interchange of xanthates) polymerization on the linear polyester can lead to the successful synthesis of (aliphatic polyester)-*g*-(PNVP). The BBPs exhibited critical micelle concentrations (CMC) below 0.5 mg mL^{-1}. The particle sizes range from 100 to 120 nm. The nanoparticles showed slow release and low efficiency of the Nile red drug model compound at pH 7. Fast release and high efficiency were observed at pH 5 and 3. In addition, low cytotoxicity and significant cell uptake were observed.

On the other hand, VAc is a vital monomer characterized by the fact that the PVAc can only be obtained by radical polymerization. Its polymerization is relatively difficult to control in most of the CRP methods. The methods to obtain PVAc with narrow molecular weight distribution and high molecular weight are limited to RAFT/xanthate or thiocarbamate, TERP,[146] and cobalt-mediated radical polymerization (CMRP)[147] methods.

Debuigne *et al.*[113] reported that a combination of CMRP to TERP (*i.e.*, CMRP-∈-TERP) was effectively utilized to synthesize BCPs comprising VAc and other typical vinyl monomers of MAM. BCPs with acrylates (*e.g.*, n-butyl acrylate (nBA)), acrylamides (*e.g.*, *N*-isopropyl acrylamide (NIPAM)), diene (*e.g.*, isoprene (IP)), and unconjugated monomer (*e.g.*, 1-vinylimidazole (Vim)) can be synthesized by adding dimethylditelluride to the PVAc macro-organo-cobalt complex in CMRP, followed by adding various monomers and radical sources. In this combination, the quantitative conversion of the Co(acac)$_2$ chain end group of CMRP (*i.e.*, PVAc-Co(acac)$_2$) to methyltelluride end group of TERP (*i.e.*, PVAc-TeMe) is based on the difference in thermal activation between these groups. Namely, the Co(acac)$_2$ end is reversibly activated at even mild temperatures (40 °C), whereas the temperature is insufficient to activate the telluride group.

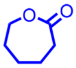
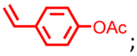
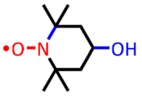
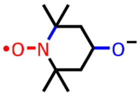
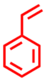
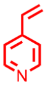
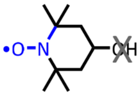
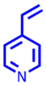
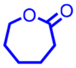
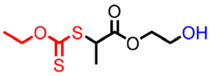
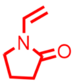
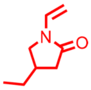
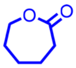
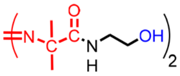
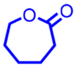
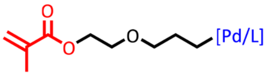
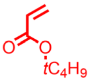
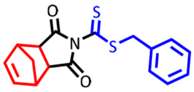
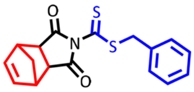
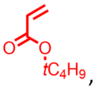
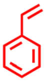
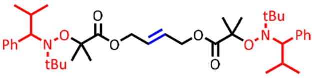
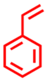
Another combination from CMRP to ATRP was reported by Peng *et al.*[148–150] They first conducted CMRP of VAc and subsequently added MMA and CuBr$_2$ to PVAc-Co(acac)$_2$ macrocomplex. When MMA is inserted into the end of PVAc, the equilibrium between corresponding dormant and chain-end radicals shifts to the latter. After that, this radical species is trapped by CuBr$_2$ and followed by ATRP to give the block copolymer. Although trapping of PVAc radicals by CuBr$_2$ is a competing reaction, the fast cross-growth reaction of PVAc macroradical to MMA monomer ($k = 3.37 \times 10^4$ M^{-1} s^{-1}) and suitable concentrations of CuBr$_2$ enable the chain extensions of PVAc with MMA. These authors intriguingly demonstrated a combination of CMRP-∈-ATRP and successfully afforded well-defined PVAc-*b*-PMMA BCPs.

3. (Addition polymerization)-∈-(ring-opening (metathesis) polymerization) and the relevant applications

Table 2 summarizes representative studies of such combinations. In this section, we focus on discussing representative copolymerizations between vinyl monomers and olefins, cyclic ethers, or lactones. Numerous studies have reported work based on the simple ROP-∈-ATRP approach.[151–158] For example, poly(vinyl phenol) (PVPh) can lead to enhanced miscible blends with several polymers through the formation of intermolecular hydrogen bond interactions between the pendent phenol and ester, hydroxy, pyridine, and ether groups. However, phenol derivatives can act as an effective radical scavenger, resulting in non-polymerization of vinyl phenol through free radical polymerization. In the case of no. 1 (Table 2), an acetoxystyrene (AS) precursor was utilized to overcome this issue. Kuo and co-workers[159] first conducted the ROP of ε-caprolactone (ε-CL) initiated by benzyl alcohol. It converted the hydroxyl chain end of PCL to an ATRP-initiating moiety of isobutyryl bromide. Subsequently, PCL-*b*-PAS can be attained through ATRP chain extension with AS. Importantly, selective hydrolysis of the acetyl protective group of the PAS segment can be achieved. The authors demonstrated a facile ROP-∈-ATRP approach for synthesizing PCL-*b*-PVPh BCP. Huang and co-workers[160] synthesized a novel PCL-*b*-PnBA-*b*-PMMA ABC-type BCP starting from the ROP of CL and then two ATRPs of nBA and MMA consecutively. The authors demonstrated that a facile ROP-∈-ATRP defined PCL-*b*-PnBA-*b*-PMMA BCP can be acquired. The novel triBCPs were used as an additive for epoxy resin for conducting a reaction-induced microphase separation (RIMPS) application. Interestingly, epoxy thermosets comprising diverse nanostructures, including sphere, lamellae, concentric circle lamellae, cylinder, and core/shell cylinder, were constructed with approximately 30–60 nm domain sizes.

In the case of the ROP-∈-NMP approach, it also uses the strategy of combining dissimilar polymerizations *via* a dual-functional initiator.[172,173] As listed in no. 2 (Table 2), the literature has reported that 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-hydroxy-TEMPO) and its deprotonated compound can effectively be combined from anionic/cationic ROP to NMP, leading to afford PCL-*b*-PSt, PTHF-*b*-PSt, PEO-*b*-PSt, and PEO-*b*-P4VP BCPs. These studies mainly demonstrate a single-path synthetic route starting from ROP. An alternative approach of

Table 2 Summary of Є, monomers, and products based on the addition polymerization-Є-ring-opening (metathesis) polymerization approaches

No.	Є combo	Є agent or design	Monomer 1	Monomer 2(, 3)	Products[a]/notes
1	ROP-Є-ATRP	Acylation of PCL chain end		 ; nBA, MMA	PCL-*b*-PAS;[159] PCL-*b*-PnBA-*b*-PMMA[160]
2	ROP-Є-NMP	 ; 	ε-CL, THF, EO	 , 	PCL-*b*-PSt;[161] PTHF-*b*-PSt,[162] PEO-*b*-PSt;[163–165] PEO-*b*-P4VP[166]
3	NMP-Є-ROP				P4VP-*b*-PCL[167]
4	RAFT-Є-ROP		 , 		P(NVP-*co*-C_2NVP)-*b*-PCL[61]
5	FRP-SЄ-ROP, rATRP-SЄ-ROP[b]				PCL-*b*-PSt/one-step[168]
6	ROMP-Є-ATRP		Ethylene		PnBA-*g*-PE[169]
7	ROMP-Є-RAFT			 , 	PNB-*g*-PnBA, PNB-*g*-PSt[170]
8	ROMP-Є-NMP		Butadiene/isoprene		P(St-*b*-B-*b*-St), P(IP-*b*-B-*b*-IP), P(St-IP-*b*-B-*b*-IP-*b*-St)[171]

[a] L in no. 6: α-diimine-type ligand. AS: acetoxystyrene. 4VP: 4-vinylpyridine. NB: norbornene. C_2NVP: 3-ethyl-1-vinyl-2-pyrrolidone. B: butadiene. IP: isoprene. [b] SЄ: simultaneous polymerizations. rATRP: reverse ATRP. ROMP: ring-opening metathesis polymerization.

starting from NMP might have an intrinsic side reaction that could affect the following step of ROP. The study in no. 3 (Table 2) depicted an unexpected phenomenon observed during the mixing of benzoyl peroxide (BPO), 4-hydroxy-TEMPO, and styrene. Lu and Chang *et al.* found consumption of the 4-hydroxy-TEMPO within the mixture. They proposed a redox reaction mechanism at low temperatures between BPO and 4-hydroxy-TEMPO, which results in the formation of 2-phenyl-2-((2,2,6,6-tetramethyl-4-oxopiperidin-1-yl)oxy) ethyl benzoate (*i.e.*, a specific 4-oxo-*N*-alkoxyamine (OA) compound). During the NMP-first approach, the dual-functional initiator of 4-hydroxy-TEMPO loses its original integrity of the hydroxyl group for ROP. The authors converted OA to 1-(2-hydroxy-1-phenylethoxy)-2,2,6,6-tetramethylpiperidin-4-one (HOA) through hydrolysis. The HOA initiator can undergo consecutive ROP and NMP reactions to synthesize well-defined PCL-*b*-P4VP BCPs. The PCL-*b*-P4VP exhibits self-assembly behavior in a mixture of toluene and dichloromethane (90 : 10 (v/v)). The authors observed nanostructures in the form of spheres and rods with an approximate diameter of 50 nm. By utilizing P4VP segments as chelating ligands, furthermore, Au nanoparticles can be produced and stabilized inside the nanostructures with a diameter approximated 10 nm.

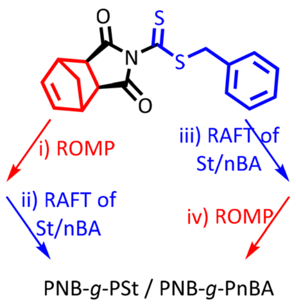
In addition to self-assembly behavior, the thermoresponsive properties in aqueous solution are also intriguing and captivating. Poly(*N*-isopropyl acrylamide) (PNIPAM) is one of the most popular and famous thermoresponsive polymers that have demonstrated their robustness in applications in bio-related fields. The reversible and significant aggregation at a particular temperature in an aqueous solution, referred to as the cloud point (CP), is attributed to the occurrence of the transition between intermolecular and intramolecular hydrogen bonding of amide groups and water molecules.[174] This specific temperature is the "lower critical solution temperature" (LCST). Based on amide group-induced CP, several examples of poly(vinyl)s comprising pendent lactam groups have demonstrated their tuneable thermoresponsive property, such as poly(*N*-vinylcaprolactam) (PNVCL) and poly(3-ethyl-*N*-vinyl-2-pyrrolidone) (PC_2NVP). As mentioned above, the *N*-vinyl lactam monomer belongs with analogs of LAMs, which can be mainly polymerized *via* xanthate or carbamate chain transfer agents (CTAs). In the case of the RAFT-Є-ROP approach, a dual-functional initiator was also utilized, consisting of a xanthate moiety and a hydroxyl group. As shown in no. 4 (Table 2), this approach was further applied for the RAFT copolymerizations of NVP and C_2NVP. These copolymers exhibited LCST characteristics. With various MWs and compositions, the CPs can be linearly tuned within a range of 29 and 51 °C. Subsequently, the ROP of P(NVP-*co*-C_2NVP)-OH macroCTA with ε-CL was conducted. The resulting P(NVP-*co*-C_2NVP)-*b*-PCL amphiphilic

BCP (M_n = 14 730, PDI = 1.59) possesses a CMC value of *ca.* 1.46×10^{-4} g L^{-1}. Among all the combinations, only a few studies demonstrated simultaneous combinations (*i.e.*, SЄ) that fulfill the orthogonality requirement between the polymerizations. One example is shown in no. 5 (Table 2), which studied the FRP-SЄ-ROP and rATRP-SЄ-ROP approaches.[168] One of the primary benefits of this methodology is its ability to conduct a straightforward and simultaneous polymerization process in bulk, and afforded PSt-*b*-PCL. This feature renders the process highly attractive to both industrial and academic settings. Several studies have demonstrated the combinations of ROMP-Є-ATRP/NMP/RAFT approaches.[169–171] In the case of ROMP-Є-NMP, Mahanthappa and co-workers[171] synthesized a difunctional acyclic alkoxyamine nitroxide agent containing a 2-butene olefin in the center. Using a specific approach of a chain transfer ring-opening metathesis polymerization (CT ROMP) of cyclododecatriene, followed by NMPs of St and isoprene (IP), the authors prepared a variety of perfectly regioregular poly(1,4-butadiene) (PB)-containing BCPs, including P(St-*b*-B-*b*-St), P(IP-*b*-B-*b*-IP), and P(St-IP-*b*-B-*b*-IP-*b*-St) BCPs. In the case of ROMP-Є-RAFT, Matson *et al.*[170] intriguingly designed a carbamate CTA containing a norbornene (NB) moiety (see Scheme 13). Due to the orthogonality and high selectivity among different polymerization reactions and vinyl monomers, targeted bottlebrush polymers (BBPs) can be synthesized using both the "skeleton-first" (ROMP-first) and "bristle-first" (RAFT-first) approaches. Eventually, the authors demonstrated an interesting study of the synthesis of PNB-*g*-PSt and PNB-*g*-PnBA BBPs.

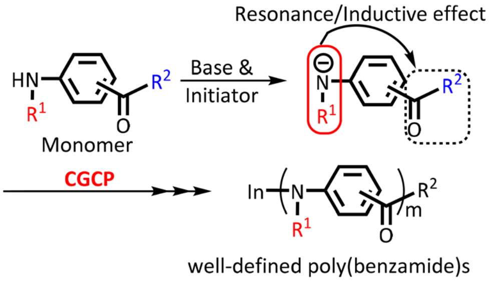
4. (Condensation polymerization)-Є-(addition polymerization) and the relevant applications

Various well-defined rod-like polymers have been synthesized by developing controlled/living condensation polymerizations. Two specific polymerizations will be discussed here: chain-growth condensation polymerization (CGCP) and catalyst transfer polymerization (CTP) techniques. Furthermore, many combinations used to synthesize particular rod-coil BCPs involve combining various dissimilar polymerization techniques, including (condensation polymerization)-Є-(addition polymerization), using dual-functional initiators and chain-end functionalized combinations.[175–178] For CGCP to be classified as one of the CLPs, it should exhibit living polymerization characteristics involving reactive monomers or species such as an ion or radical. Undeniably, the CGCP mechanism, inspired by natural biopolymers like DNA, polypeptides, and RNA, produces perfectly monodisperse condensation-type polymers.[179,180] As shown in Scheme 14, CGCP process can be achieved by manipulating the substituents to conduct inductive or resonance effects through aromatic rings to afford well-defined *meta*- and *para*-type poly(*N*-octyl benzamide)s (POBAs).[72,175,180,181] This approach can also be applied to the synthesis of well-defined aromatic-based polyesters,[182] polyethers,[183] and poly(ether sulfone)s.[184] CTP is also a living chain-growth polymerization for synthesizing conjugated polymers.[180] The benefits of using CTP as a conjugating method include low PDI and control over MW in the resulting polymers.[185] In 2004, the Yokozawa[186,187] and McCullough[188] groups independently demonstrated the living nature of CTP of 3-hexylthiophene (3HT). Many reports have shown that CTP can effectively polymerize a wide range of (hetero)aromatic monomers, resulting in conjugated polymers with excellent physical properties for various applications.[189–200] In this section, we will discuss the combinations as mentioned earlier (*e.g.*, LAP-Є-CGCP, ATRP-Є-CGCP, and RAFT-Є-CGCP), as well as the catalyst transfer-induced living polycondensation (*e.g.*, CTP-Є-ATRP), among others.

Kim *et al.*[178] synthesized well-defined *para*-benzamide-based rod-coil BCPs by combining living anionic polymerization and CGCP (*i.e.*, LAP-Є-CGCP). This approach involved first preparing COOH-terminated PSt *via* LAP with *sec*-butyllithium, ended by quenching with dry ice. The PSt-COOH was then converted to PSt-COOPh as macroinitiators (MIs) (M_n = *ca.* 2300–9200, PDI = 1.02–1.06) with phenol, 4-(dimethyl amino) pyridine, *N*,*N*′-dicyclohexylcarbodiimide, and *p*-toluenesulfonic acid monohydrate. CGCP chain extensions were conducted using phenyl 4-(octylamino)benzoate, initiating from the terminal phenylbenzoate moiety of the PSt MIs. The diBCPs synthesized in this manner have both PSt coil and *para*-POBA rod segments with controlled MW and low PDI.



Scheme 13 ROMP-Є-RAFT for the synthesis of PNB-*g*-PSt/PNB-*g*-PnBA bottlebrush polymers.[170]

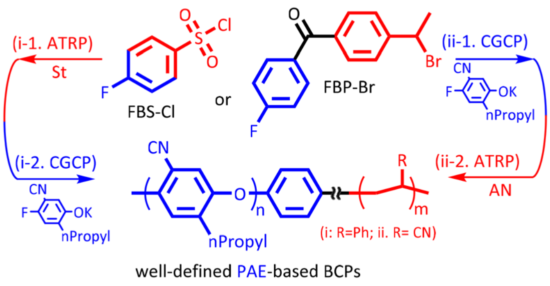


Scheme 14 An example of CGCP mechanism for the synthesis of well-defined poly(benzamide)s.[179]

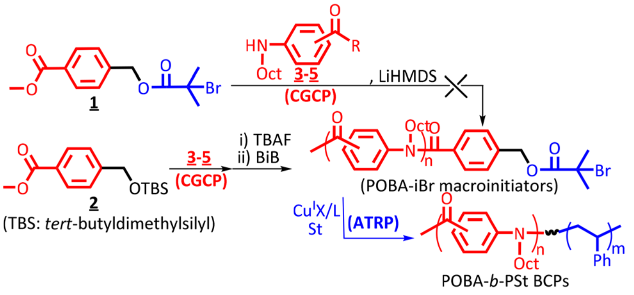
Other kinds of rod-coil BCPs (*e.g.*, PSt-*b*-poly(aromatic ether) (PAE)[176]) have been synthesized *via* the ATRP-Є-CGCP approach using orthogonal initiators. With an orthogonal initiator, one initiating site is activated for one type of CLP while remaining inert concerning the other polymerization, and *vice versa*. Using an orthogonal initiator is more convenient than preparing MIs by converting the polymer end group through several steps.[80] Two sequential strategies can be applied in this combination system: "ATRP-to-CGCP" or *vice versa*. For example, Ajioka *et al.*[176] synthesized well-defined diBCPs of PSt and PAE *via* the "ATRP first" approach using 4-fluorobenzenesulfonyl chloride (FBS-Cl) or 4-(1-bromoethyl)-4′-fluorobenzophenone (FBP-Br) as an orthogonal initiator (see Scheme 15). The PSt precursors were first synthesized *via* ATRP of St using FBS-Cl/FBP-Br, initiated from the 1-bromoethylbenzene or benzenesulfonyl chloride moiety. The terminal halogen of the precursors was then dehalogenated to obtain FBS-PSt-H and FBP-PSt-H MIs. CGCP chain extensions of the PSt MIs with potassium 5-cyano-4-fluoro-2-propylphenolate (PCFPP) were carried out in sulfolane at 150 °C. The fluorobenzene moiety, which exerts a strong electron-withdrawing effect at the *para* position, initiates the CGCP chain extensions with PCFPP monomer and affords a PAE segment. As a result, well-defined PSt-*b*-PAE rod-coil BCPs were acquired with low PDI particularly. Notably, macrocyclic PCFPP oligomers can be obtained using the FBS-PSt-H MI, probably due to transetherification occurring between the *p*-sulfonyl phenyl ether linkage of the FBS-PSt-H MI and the PCFPP unit. The authors also observed that the obtained BCPs exhibited self-assembly in THF and proposed an intriguing micelle structure with onion-like interiors. The particle sizes can vary widely (300 nm–1 μm). Using the same orthogonal initiator,[201] syntheses of different rod-coil diBCPs of PAE and PAN (polyacrylonitrile) were investigated by sequential strategies. When PAN MI was first synthesized *via* ATRP of acrylonitrile (AN), the following CGCP process decomposed the PAN backbone. While the aromatic polyether was first synthesized by CGCP and followed by an ATRP initiator unit, well-defined diBCP of polyether-*b*-PAN was obtained with low PDI. It was also revealed that the self-assembly of the obtained diBCP in *N*,*N*-dimethylformamide (DMF) formed spherical or bundle-like aggregates, depending on the length of the PAN chains.

Afterward, Huang *et al.*[175] synthesized well-defined POBA-*b*-PSt BCPs with controlled MW and small PDI (*i.e.*, M_n = 37 200, PDI = 1.25) by conducting the CGCP technique first, followed by ATRP. As shown in Scheme 16, *para*- and *meta*-substituted monomers and two dual-functional initiators were investigated for the CGCP procedure. An appropriate dual-functional initiator with a *tert*-butyldimethylsilyl (TBS)-protecting group was selected to avoid the problem associated with quenching between the aminyl anion of monomer and the halogen atom of the ATRP initiating site during CGCP. The results indicated that employing the "CGCP-to-ATRP" is the primary synthetic strategy to avoid interference between the halogen atoms and the lithium base to deprotonate OBA monomers during the CGCP step.

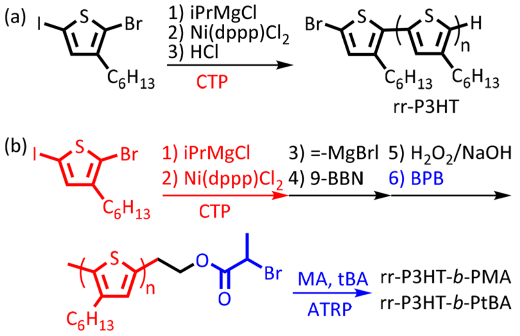
To date, most chain-growth polycondensations, including CTP, rely on electron-rich monomers like thiophene derivatives and thiophene analog monomers (*e.g.*, pyrrole and selenophene).[185,202,203] Few studies have reported the synthesis of polymers from electron-deficient monomers, such as pyridine derivatives and naphthalene derivatives.[191,204] The CTP technique has been extensively utilized in Suzuki–Miyaura, Kumada,[186–188,198,205] Buchwald–Hartwig,[206] Stille,[207] Sonogashira, and Negishi[208] cross-coupling reactions. These allow us to obtain various alkyl or ester-functionalized polythiophenes, polyfurans, polyfluorenes, poly(phenylene)s, poly(phenylene ethynylene)s, poly(benzo[1,2,3]triazole)s, poly(phenylene vinylene)s, poly(aryleneamine)s, poly(3,6-phenanthrene)s, and so on. Among them, regioregular polythiophenes, particularly poly(3-alkylthiophenes) (rr-P3AT), embody a class of polymers with good solubility, electrical conductivity, and environmental stability.[200] However, their practical utility often faces challenges due to low processability, poor film forming, and brittle mechanical properties.[189] These properties can be enhanced by integrating rr-P3AT into copolymer structures with various blocks that display better-desired properties *via* a combination of CTP with other CLP techniques such as LAP, RAFT, NMP, and ATRP. In 2005, the McCullough groups innovatively presented their works on synthesizing rr-PATs through CTPs.[199,200,205] A typical synthetic method of rr-P3ATs *via* CTP is presented in Scheme 17a. Subsequently, several reports[195,216–218] synthesized various rr-P3HT-based diBCPs containing PSt (*via* CTP-Є-RAFT or CTP-Є-LAP) and PIP



Scheme 15 ATRP-Є-CGCP for the synthesis of well-defined (i) PSt-*b*-PAE and (ii) PAE-*b*-PAN.[176,201]



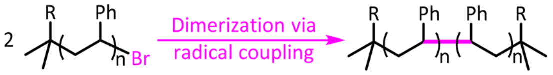
Scheme 16 CGCP-Є-ATRP for the synthesis of POBA-*b*-PSt BCPs.[175] Copyright 2023 John Wiley and Sons.



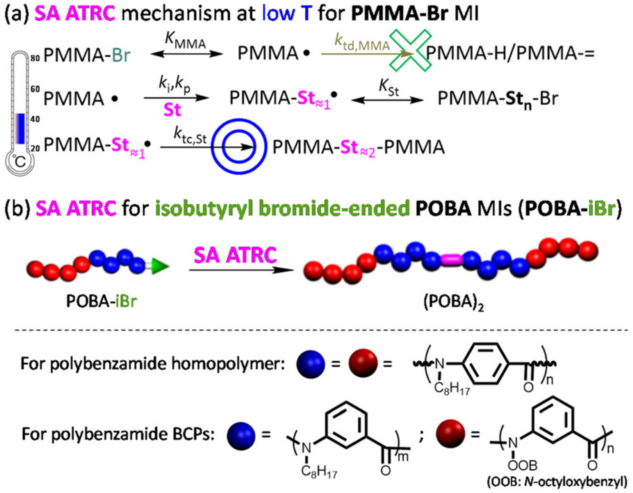
Scheme 17 (a) Typical CTP steps for the synthesis of rr-P3HT. (b) CTP-Є-ATRP for the synthesis of rr-P3HT-*b*-PMA and PtBA.

(*via* CTP-Є-NMP). Generally, the rr-P3HTs prepared by CTP were used as MIs, followed by the addition of St or IP monomer *via* ATRP, LAP, RAFT, or NMP. Syntheses of other rr-P3AT-containing BCPs, such as poly(3-(2-ethylhexyl) thiophene)-*b*-poly(methyl (meth) acrylate)s (P3EHT-*b*-PM(M)A) poly (3-(2-ethylhexyl) thiophene)-*b*-polylactide (P3EHT-*b*-PLA), rr-P3HT-*b*-PtBA, and P3HT-*b*-PM(M)A were demonstrated by using CTP-Є-ATRP.[200,219] For example, Iovu *et al.*[200] demonstrated the synthesis of rr-P3HT precursor prepared from 3-hexylthiophene monomer *via* the CTP mechanism. Because of a single reactive chain end, sequential modifications were conducted on the vinyl-terminated P3HT precursor, which included hydroboration/oxidation in 9-borabicyclo[3.3.1] nonane (9-BBN) and NaOH/H_2O_2, and acylation using 2-bromopropionyl bromide (BPB) and the terminal hydroxyl group, to ultimately obtain the P3HT MI (see Scheme 17b). The P3HT MI was easily used for ATRP chain extensions. The ATRP process was performed by adding acrylate monomers (*i.e.*, MA and *t*BA) in a toluene solution using CuBr/PMDETA at 80 °C. The resulting rr-P3HT-*b*-PMA and rr-P3HT-*b*-PtBA rod-coil diBCPs demonstrated good solubility in organic solvents and excellent processing and electrical properties.

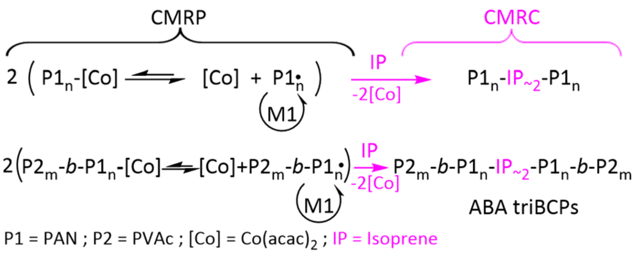
The reversible reaction between the dormant species and the propagating chain end radicals is controlled by the CRP's balance of deactivation and activation reactions. On the other hand, exceeding activation of the dormant species changes the reaction mode from propagation to selective termination. As shown in Scheme 18, several studies found the utility of the termination of propagating chain end radicals *via* selective radical coupling reactions.[210,215,220] Sarbu and Matyjaszewski reported the dimerization of poly(methyl acrylate)-Br in the presence of styrene and excess reductive Cu(0) reagents at ambient temperature through simultaneous insertion of styrene to the propagating chain end radical followed by



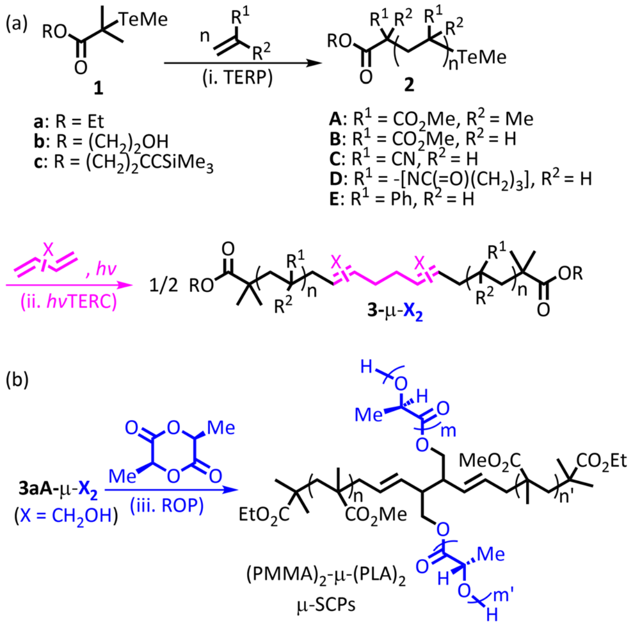
Scheme 18 A dimerization approach for atom transfer radical coupling reaction (ATRC) of PSt-Br.[215]



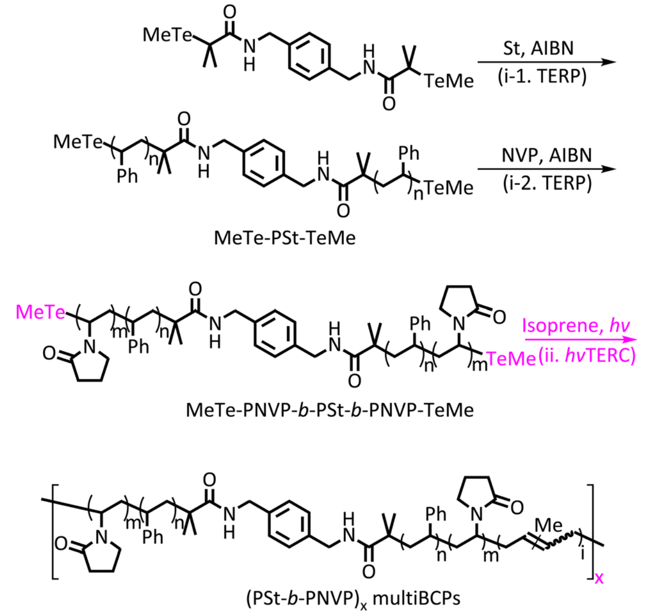
Scheme 19 (a) SA ATRC mechanism at low temperature (≤50 °C) for PMMA-Br. (b) CGCP-Є-SA ATRC for the dimerizations of POBA MIs.[212]



Scheme 20 Distinct mechanisms of CMRP and IP-assisted CMRC.[222–224]



Scheme 21 (a) TERP-Є-*hv*TERC. (b) TERP-Є-*hv*TERC-Є-ROP further for the synthesis of (PMMA)$_2$-μ-(PLA)$_2$ μ-SCPs.[213]

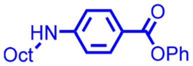
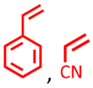
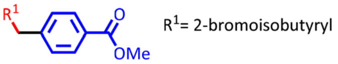
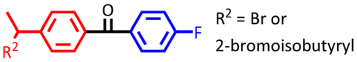
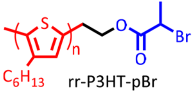
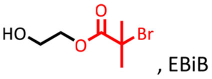
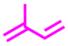
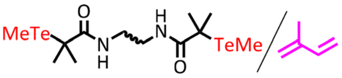


Scheme 22 TERP-Є-*hv*TERC for the synthesis of (PSt-*b*-PNVP)$_x$ multiBCPs.[214]

radical coupling dimerization in >90% yield.[211] This method opened up the synthetic usability of radical coupling of polymer-end radicals (*i.e.*, ATRP-Є-ATRC). As reported by Huang and Yokozawa *et al.* (Scheme 19), products of PMMA-Br and isobutyryl bromide-terminated POBA were effectively coupled using cupric reagents through styrenics-assisted ATRC (*i.e.*, ATRP-Є-SA ATRC and CGCP-Є-SA ATRC)[212] and others.[221]

In the case of the cobalt-mediated system, Debuigne and Detrembleur *et al.* reported a dienes-assisted dimerization approach that reached a high conversion stage of CMRP (*i.e.*, CMRP-Є-CMRC).[222–224] As shown in Scheme 20, it works well for the precursors of PAN-[Co] homopolymers (M_n = 25 000 g mol^{-1}) and PVAc-*b*-PAN-[Co] diBCPs, forming (PAN$_n$)$_2$ and PVAc-*b*-PAN-*b*-PVAc triBCPs, respectively. [Co]-containing PAN, PVAc, or PNVP precursors can perform cobalt release from chains and minor diene integration. CMRC is versatile for longer chains and diverse polymers. From the mechanism viewpoint, CMRC involves facile cross-propagation from cyano-carbyl to allyl radicals. Meanwhile, Co(acac)$_2$ exhibits limited deactivation capacity toward the allyl-terminated radicals. Consequently, this leads to a significant release of radical chains within the medium, promptly followed by rapid chain combination reactions, deviating from the conventional diene polymerization pathway. Notably, the distinct inclination of the CMRC is to favor the selective incorporation of two diene

Table 3 Summary of Є, monomers, and products based on the condensation polymerization-Є-addition polymerization approaches

No.	Є case[a]	Monomer 1	Є agents/design	Monomer 2/additive	Products/notes[b]
1	LAP-Є-CGCP		modifying chain end of PSt-COOH to PSt-COOPh		PSt-*b*-P4OBA[209]
2	ATRP-Є-CGCP		 	3OOBBA/4OBA; PCFPrPh; PCFPrPh	PSt-*b*-P3OOBBA & P4OBA;[175] PSt-*b*-PPrNPO;[176] PAN-*b*-PPrNPO[201]
3	CGCP-Є-RAFT	4OBA	modifying iodo-terminated P(4OBA) to P(4OBA)-benzyl dithiocarbonyl	St	PSt-*b*-P4OBA[177]
4	CTP-Є-ATRP	3-(2-ethylhexyl) thiophene (3HT)		MA or *t*BA	rr-P3HT-*b*-PMA and PtBA[200]
5	ATRP-Є-(SA) ATRC	St, MA; MMA		—, St; St	(PSt-OH)$_2$, (PMA-OH)$_2$;[210,211] (PMMA)$_2$[212]
6	CGCP-Є-SA ATRC	3OBA, 3OOBBA	POBA-iBr, POBA-*b*-POOBBA-iBr	St	(POBA)$_2$, (POBA-*b*-POOBBA)$_2$ triBCP[212]
7	CMRP-Є-CMRC	Vac		NVP	(PVAc-*b*-PNVP)$_2$ triBCP
8	TERP-Є-*hv*TERC-Є-ROP	Vac		LA	(PMMA)$_2$-μ-(PLA)$_2$[213]
9	TERP-Є-*hv*TERC	St		NVP	(PSt-*b*-PNVP)$_x$ multiblocks[214]

[a] LAP: living anionic polymerization. CGCP: chain-growth condensation polymerization. CTP: catalyst transfer polymerization. CMRC: cobalt-mediated radical coupling. *hv*TERC: photoirradiation organotellurium-mediated radical coupling. (SA) ATRC: (styrenics-assisted) atom transfer radical coupling. [b] OBA: *N*-octyl benzamide. OOBBA: *N*-(octyloxy)benzyl benzamide. PCFPrPh: potassium 5-cyano-4-fluoro-2-propylphenolate. PrNPO: propyl nitrile phenyl oxide. MA: methyl acrylate. EBiB: ethyl α-bromoisobutyrate. iBr: isobutyryl bromide.

units within the dimerized polymers, setting it apart as a promising method for precise functionalization along the mid-chain region. This reaction can not only make symmetrical ABA copolymers but also enable telechelic polymers through α-functional precursors.

The St or IP-inserting radical coupling dimerization was further investigated by Nakamura and Yamago *et al.* in TERP under photoirradiation (*i.e.*, TERP-Є-*hν*TERC).[213] As shown in Scheme 21a, they found the high selectivity of two-molecule insertion of isoprene (IP) into the resulting polymer (97%) for PMMA dimerization along with the high yield of dimerization (>90%). The reaction with IP showed a superior yield of dimerization and two-molecule insertion selectivity. These are accounted for by the higher radical coupling termination selectivity of allyl radical (from IP, *ca.* 100% selectivity) than styryl radical (from St, *ca.* 90% selectivity) and the lower propagating rate of IP ($k_{\mathrm{p,IP}}$ = 125 $\mathrm{M^{-1}\ s^{-1}}$) than St ($k_{\mathrm{p,St}}$ = 340 $\mathrm{M^{-1}\ s^{-1}}$), respectively. As shown in Scheme 21b, they further synthesized μ-SCP by sequential radical coupling dimerization with 1-hydroxy-2,4-butadiene and ring-opening polymerization of lactide (*i.e.*, TERP-Є-*hν*TERC-Є-ROP). Because of the insertion of two dienes in the radical coupling, the reaction selectively gives a $\mathrm{(PMMA)_2}$-μ-$\mathrm{(PLA)_2}$ μ-SCP. Due to the simplicity of this radical coupling dimerization method, high yield and high selectivity of the reaction, it can synthesize polymers with various functionalities and topologies, including telechelic, block, star, and cyclic.

In addition to the versatility for various polymers, the combination of TERP to radical coupling dimerization was further utilized in synthesizing amphiphilic multiblock copolymer. The radical coupling polymerization (oligomerization) of α,ω-methyltellanyl PNVP-*b*-PSt-*b*-PNVP triBCPs prepared by TERP was allowed to undergo radical coupling reaction in the presence of isoprene to give $\mathrm{(PSt\text{-}\mathit{b}\text{-}PNVP)_{\mathit{x}}}$ multiBCP with M_{n} = 51 000, PDI = 1.52, and averaged total segment number (x) of 7 (see Scheme 22).[214] Our described and other examples[225,226] of (condensation polymerization)-Є-(addition polymerization) approach are included in Table 3.

Scheme 23 Robustness and diversity of combination among CLPs and organic reactions for the designs of novel macromolecules.

5. Conclusions and outlook

In summary, various techniques have been developed to manipulate macromolecules' structural diversity and topology through polymerization mechanisms involving two or more types of monomers. This review highlights recent advancements in combining multiple polymerization methods to synthesize desired polymers with increased complexity. The progress in mechanistic reactions includes addition polymerizations, condensation polymerizations, and RO(M)Ps approaches, which enable the synthesis of novel macromolecules using existing and newly synthesized monomers.

The combinations can be achieved sequentially or simultaneously, allowing for integration of different monomer types using post-modification techniques or dual-functional initiators. The former approach, known for its ease of implementation and versatility across other polymerization methods, has gained widespread application. While including post-modification, it is necessary for a reactive functional group to be introduced during the initiation or the termination steps of the polymerization of the first monomer. This requirement leads to the need for further combination steps and intermediate protection. Alternatively, dual-functional initiators provide another route to designing, synthesizing, and applying functional copolymers compared with the post-modification technique. When combining mechanistically incompatible monomers, dual-functional initiators offer numerous advantages over the post-modification process. They allow for the design of well-defined macromolecules with desired properties, making them highly innovative. This approach has become a significant research direction in polymer chemistry.

For the future challenge, the key to further combinatory polymerization mechanisms, such as in three-method approaches, lies in multistep synthesis. Therefore, other efforts should be focused on developing more complex and efficient combination (organic) reactions or screening multi-functional initiators (*e.g.*, trifunctional initiators). Recent developments incorporating multifunctional reactions and polymerizations are emerging as critical trends, although much work remains. With the progress of polymer chemistry, moreover, a few recent reports have revealed the possibility of using polymerization newly extended from efficient organic reactions (such as from multicomponent reactions (MCRs) to multicomponent polymerizations (MCPs)) to prepare macromolecules novel in topology, compositions, and functionality. Accordingly, the developed methodology will continuously enrich the combinations with robustness and diversity (as outlined in Scheme 23).

Conflicts of interest

There are no conflicts to declare.

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