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THE NOVEL METHODS OF POLYMERIZATION AT HAND

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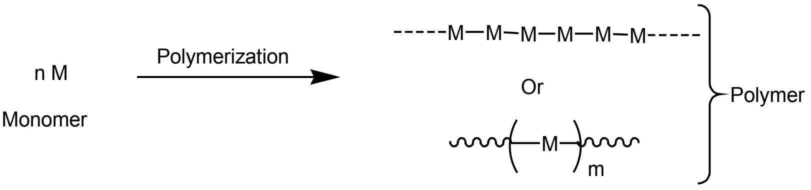
Abstract. In this account, the newly discovered methods of polymerization are briefly presented. Glances of their emergence, their characteristic features, their proposed mechanisms, and a few of their applications and uses are herein highlighted.

Keywords: catalyst, click, fragmentation, iodine, metathesis, polycondensation, polymerization, transfer

Introduction

Polymeric materials are nowadays integral parts of our modern life commodities. For their intrinsic characteristics, engineering polymers of high molecular weights, such as Kevlar and Nomex, equate metallic structures, and, in some instance, outdistance them. A polymer is a macromolecular build-up made of several covalently connected units called "monomers", realized via a chemical reaction called "polymerization" (Eq. 1). Commonly known are a homopolymer, made of one monomer unit, and a copolymer, made of two or more different monomer units. Polymerization of styrene (C_8H_8, M_{St} = 104 g/mol, liquid) provides a material called "polystyrene" (M_{PSt} = several thousand Daltons, solid), a ubiquitous plastic material (Eq. 2). Throughout the twentieth century, chemists have strived to develop and establish the requisite conditions for the monomer→polymer transformation, which are by now termed '*conventional* or *classical polymerizations*' (Moulay, 1999; Feldman, 2008). Every textbook in polymer science describes the two general and broad mechanisms of polymerization: (1) addition growth polymerization and, (2) step growth polymerization. The first one deals with free radical, anionic, cationic, and ring opening polymerizations of vinyl and cyclic monomers. The second one is mostly confined to condensation polymerization of monomers with functional groups other than vinyl.



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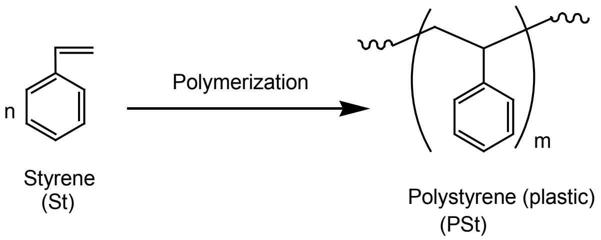

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Polymerization of some monomers such as the vinyl ones requires the use of a polymerization-inducing or -promoting species, generally called '*Initiator*' and '*Activator*', or '*Catalyst*' in some cases. Initiator/co-initiator (Kennedy & Marechal, 1981) and inifer/initiator system (Kennedy et al., 1981; Mah et al., 1987) were introduced as in Lewis acid-initiating cationic polymerization of some vinyl monomers; the term '*inifer*' refers to a species that acts both as initiator and transfer agent, such as cumyl chloride in cumyl chloride/BCl_3 initiating system in the cationic polymerization of isobutylene (IB), hence the *inifer polymerization*. Later, the term '*iniferter*' was invented to designate the following three actions of a compound, such as a dithiocarbamate, in radical polymerization (Otsu & Yoshida, 1982): initiator, transfer agent, and terminator; hence, the '*iniferter polymerization*'. A countless number of initiating systems have been invented and discovered within the 20th century, mostly for vinyl monomers. And, all of them exhibited either the conventional radical or ionic mechanism. Yet, the basic radical initiators have been diazo compounds such as 2,2'-azo*bis*isobutyronitrile (AIBN), 2,2'-azo*bis* (2,4-dimethyl)valeronitrile (AMVN), 4,4'-azo*bis*(4-cyanopentanoic acid) (ACP), and peroxides such as dibenzoyl peroxide (BPO) and dilauroyl peroxide (LPO); redox systems such as Fenton's reagent have been judiciously employed in aqueous radical polymerization. Alpha-olefins such as propylene and acetylenic or alkyne monomers undergo polymerization with special catalyst systems called Ziegler-Natta catalysts or with alike catalysts, affording polymers with high stereoregularity, and hence the term '*stereoregular or stereospecific polymerization*'.

Molecular weight distributions MWDs or polydispersity index PDIs ($\bar{M}_w/\bar{M}_n$) of the high polymers obtained by the above-mentioned methods are generally broad, particularly those achieved through polycondensation, usually greater than two. Highly polydisperse polymers are usually undesirable in that their intrinsic properties are ill-defined. Also, some polymerization methods lead to polymers with high molecular weights. Controlling the molecular weights of vinyl polymers is deliberately made with the use of chain transfer agents (CTA). However, living anionic polymerization (LAP) of vinyl monomers had been the method to resort to for making high polymers with narrow MWDs (Odian, 2004). Indeed, standard polystyrenes for the calibration of gel permeation chromatography (GPC) were accordingly made.

New ways of making polymers such as '*group-transfer polymerization* (GTP)' were described earlier (Ebdon, 1991). However, before the eclipse of the 20th century and at the dawn of the 21st century, novel methods of polymerization have startlingly emerged and widened further the polymer synthesis field. Each of these methods opened new insights with regards to the polymerization mechanism, the molecular weight controlling, the molecular weight distribution narrowing, the well-defined and tailored architecture, and other related features. Henceforth, in this paper, are tackled the following novel ways of polymerization in this order: *Atom transfer radical polymerization* (ATRP), *Reversible addition-fragmentation chain transfer* (RAFT), ***S**table free radical mediated polymerization* (SFRP), *Reverse iodine transfer polymerization* (RITP), *Click polymerization* (CP), *Acyclic diene metathesis polymerization* (ADMET), *Catalyst-transfer polycondensation* (CTP).

Atom transfer radical polymerization (ATRP)

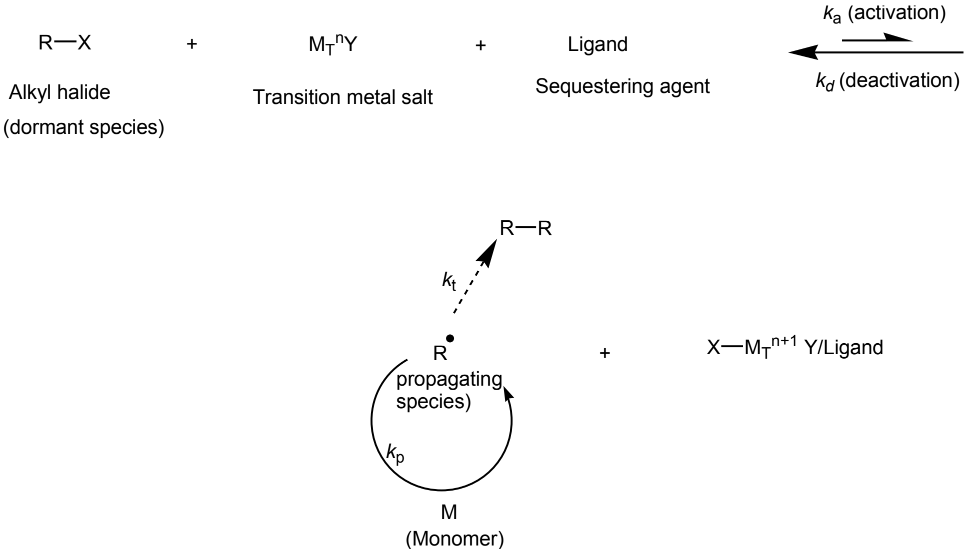
Atom transfer radical polymerization (ATRP) belongs to the class of living/controlled radical polymerizations (LCRP), also coined *reversible-deactivation radical polymerizations*. ATRP was brought forth in 1995, independently by Matyjaszewski in USA (Wang & Matyjaszewski, 1995a; 1995b) and Sawamoto in Japan (Kato et al., 1995). This nomenclature was adopted with analogy to atom transfer radical addition (ATRA) (Matyjaszewski, 2002). The novelty of this polymerization lies on the nature of initiating system which consists of an organohalide (R-X), a transition metal salt (M_T^nY), and a ligand; hence, ATRP is otherwise termed '*transition metal-mediated living radical polymerization'*. One can speak about copper-, cobalt-, nickel-, iron-, ruthenium-, rhenium-, rhodium-, molybdenium-, chromium-, palladium-, selenium-, telluride-, and stibine-mediated living radical polymerizations (Matyjaszewski & Xia, 2001; Yamago & Nakamura, 2013). Of these transition metal salts, cuprous chloride or bromide (Cu(I)X, X = Cl, Br) has been the most favored one. The commonly used ligands are polyamines such as 2,2'-bipyridine (Bipy) and *N*,*N*,*N'*,*N"*,*N"*-pentamethyldiethylenetriamine (PMDETA), polycarboxylic acids such as isophthalic acid (IPA), and amino polycarboxylic acid such as iminodiacetic acid (IDA), and phosphines such as triphenyl phosphine (PPh_3). ATRP has been mostly applied for styrenics and acrylic monomers, namely styrene and methyl methacrylate (Matyjaszewski & Xia, 2001). The generally accepted mechanism is depicted in Scheme 1 and involves: (a) the halogen atom transfer from the alkyl halide to the transition metal salt that is readily complexed by the ligand, leaving the alkyl as a free radical, (b) the latter radical then initiates and propagates the polymerization of vinyl monomer M; the concomitant oxidation of the transition metal occurred upon the halogen transfer. The built-up polymeric radical $P_m^{\bullet}$ (m = a degree of polymerization) from the propagating species $R^{\bullet}$ may reversibly be converted to P_m-X as a dormant species via a deactivation process. The polymerization experiment can be conducted in bulk, solution, suspension, and emulsion. A spectrum of solvents can be employed to carry out ATRP in solution, including polar ones such as DMF, DMSO, MeOH, NMP, MeCN, 1,4-dioxane, water, and less polar ones such as toluene and xylene, and green solvents such as ionic liquids and supercritical carbon dioxide. The reaction temperature generally fluctuated from ambient ones to 150 °C.

With ATRP method, the molecular weight can be established theoretically ($\bar{M}_{n,th}$) by rationalizing the monomer/initiator molar ratio (Eq. 3), and generally the theoretical molecular weights are closer to the measured ones. And, molecular weight distributions MWDs of lower than 1.5 can be achieved; to recall, MWDs higher than 1.5 are typical for conventional free radical polymerization.

$$\bar{M}_{n,th} = ([M]_0/[R\text{-}X]_0) \times M_{mon} \times \rho \tag{3}$$

where $[M]_0$, $[R\text{-}X]_0$, M_{mon}, ρ are the initial monomer concentration, the initial initiator (alkyl halide) concentration, the molecular weight of the monomer, and the conversion, respectively.

The living character of the ATRP method is demonstrated by the fact that molecular weight of the polymer increases linearly with monomer conversion, and by the plausible formation of a block polymer upon addition of a new monomer. For example, the first polystyrene made by ATRP method, using 1-phenylethyl chloride/CuCl/2,2'-bipyridine system and at 130 °C for 3 h, had a molecular weight of 3.8×10^3-1.05×10^5 g/mol with a MWD of 1.3-1.45 (Wang & Matyjaszewski, 1995a).

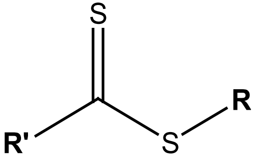


Scheme 1. General mechanism of ATRP method

Several variants of ARTP method based on activator regeneration process have been emerged in the last decade: Activators regenerated by electron transfer ATRP (ARGET ATRP), Initiators for continuous activator regeneration (ICAR ATRP), Supplemental activator and reducing agent ATRP (SARA ATRP), Electrochemical ATRP (eATRP), Photoinduced ATRP, Reverse ATRP, Simultaneous reverse and normal initiation (SR&NI ATRP), Activators generated by electron transfer ATRP (AGET ATRP), Metal-free ATRP, Surface-initiated ATRP (SI-ATRP). The latter variant is a valuable means for fashioning particle brush nanomaterials which find a wide application ranging from photonic inks and paints to advance nanocomposites with enhanced optical and mechanical properties (Hui et al., 2014).

Reversible addition-fragmentation chain transfer polymerization (RAFT)

The second LCRP method is '*reversible addition-fragmentation chain transfer polymerization*', abbreviated as RAFT. It was discovered in 1998 by researchers of CSIRO (Commonwealth Scientific and Industrial Research Organization) at Australia (Le et al., 1998; Chiefari et al., 1998). The key feature of this method consists in the use of a thiocarbonylthio type (a dithioester) (1), a chain transfer agent (CTA) termed RAFT agent, along with a conventional radical initiator (peroxide or azo compound). The RAFT agent 1 is more effective if **R'** is aryl or alkyl group and **R** a good leaving group such as cumyl and cyanoisopropyl, and the ensued **R**• being able to reinitiate the radical polymerization. The polymerization experiment can be either carried out in bulk, solution, and aqueous dispersion, and under reaction conditions of classical free radical polymerization with the same precautions. The mechanism illustrated in Scheme 2 shows, besides the conventional steps of free radical polymerization (initiation, propagation, and termination), a step for the reversible addition/fragmentation chain transfer to provide the dormant/living species.



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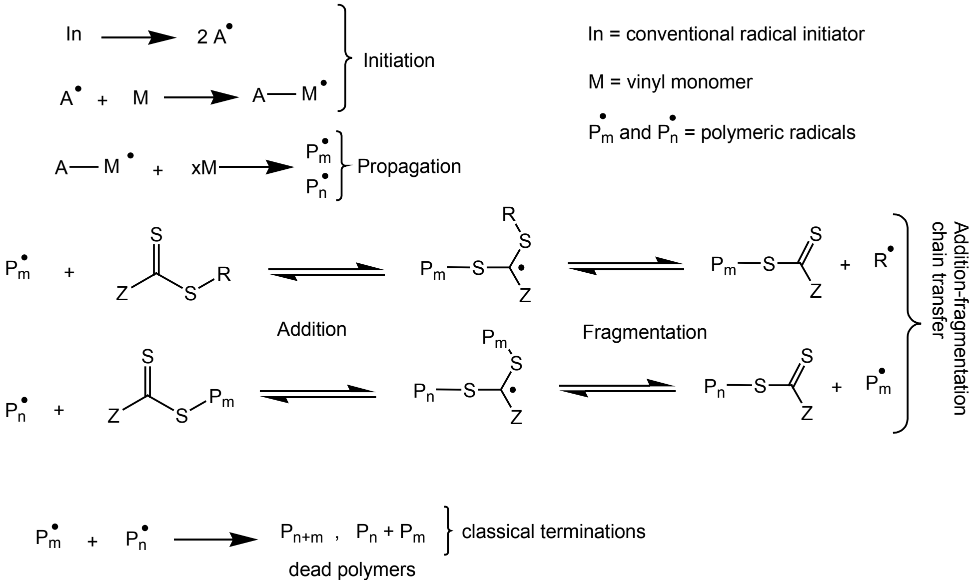
As with ATRP, a range of vinyl monomers can be polymerized via RAFT way, including styrenics, acrylics, and their corresponding functional ones. Also, the polymerization temperature varies from room temperature to 150 °C. The molecular weights of the thus-synthesized polymers ranged from low to high and the molecular weight distributions can be even smaller than 1.3. For example, the first poly(methyl methacrylate) (PMMA) made through RAFT polymerization was accomplished by polymerizing MMA in benzene using cumyldithiobenzoate, a RAFT agent 1 (**R'** = Ph, **R** = $C(CH_3)_2Ph$), and BPO as radical initiator at 60 °C for 18 h (Chiefari et al., 1998); its number-average molecular weight $\bar{M}_n$ and MWD were 47 kDa and 1.04, respectively. Very often, the CTA agents are prepared in laboratory, as they are not commercially available, and required intensive purification. Nearly, the same features as with ATRP, RAFT method proves the possibility of tailoring block copolymers and homopolymers with narrow molecular weight distributions, linear molecular weight-conversion relation, and the control of molecular weight ($\bar{M}_{n,th}$) by suitably setting monomer/RAFT agent molar ratio as given in Eq. 4. The measured molecular weights are usually not far from the predicted ones. A block copolymer, poly(MMA)-*b*-poly(NIPAAm) (MMA = methyl methacrylate; NIPAAm = *N-iso*propylacrylamide), with a molecular weight of 58 550 g/mol and of a MWD of 1.04 was successfully synthesized by RAFT method (Vega-Rios & Licea-Claveríe, 2011).



Scheme 2. General mechanism

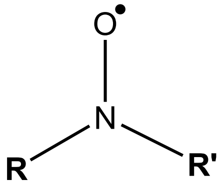
$$\bar{M}_{n,th} = ([M]_0/[CTA]_0) \times M_{mon} \times \rho \qquad (4)$$

where $[M]_0$, $[CTA]_0$, M_{mon}, and ρ are the initial monomer concentration, the initial chain transfer agent concentration, the molecular weight of the monomer, and the conversion, respectively.

One RAFT variant is the surface-initiated RAFT in which the RAFT agent, the thiocarbonylthio CTA, is covalently affixed to an organic (for example, Wang and Merrifield resins) or inorganic (for example, silica) material.

Stable free radical mediated polymerization (SFRP)

Another living/controlled radical polymerization that has gained a foothold in polymer science is '*stable free radical-mediated polymerization* (SFRP)'. This novel free radical polymerization was first advanced by Georges et al. (1993), proving that the use of a stable free radical (also termed persistent or long-lived radical), primarily nitroxide (2), along with a classical radical initiator (peroxides, azo compounds) would lead to polymer with a controlled molecular weight and a narrow MWD. Hence, the other adopted appellation of SFRP is ‘*nitroxide-mediated polymerization* (NMP)’. Of the several nitroxide radicals suggested for SFRP (Nicolas et al., 2013), the commercially available (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) ranks as the first choice. Monomer candidates for SFRP methods have been confined to styrenics, vinylpyridines, some acrylics, and some dienics (Nicolas et al., 2013). Reaction temperature higher than 80 °C and reaction time longer than 25 h are usually required to achieve high conversions. NMP polymerization can be carried out in bulk, solution (toluene, acetic acid, water, ionic liquids,…), and aqueous emulsion. The mechanism of the polymerization of vinyl monomers by SFRP method is depicted in Scheme 3.



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Theoretical molecular weight can be calculated from Eq. 5. The livingness of SFRP is illustrated by the fact that the average molecular weight increases with conversion and by the possible formation of block copolymers. Well-defined copolymers for use in microelectronic or optoelectronic devices were made via NMP method (Nicolas et al., 2013). Beside linear block copolymers, macromolecules of complexed architectures such as comb polymers, star polymers, graft polymers, hyperbranched polymers, and dendrimers can be conceived through SFRP method.

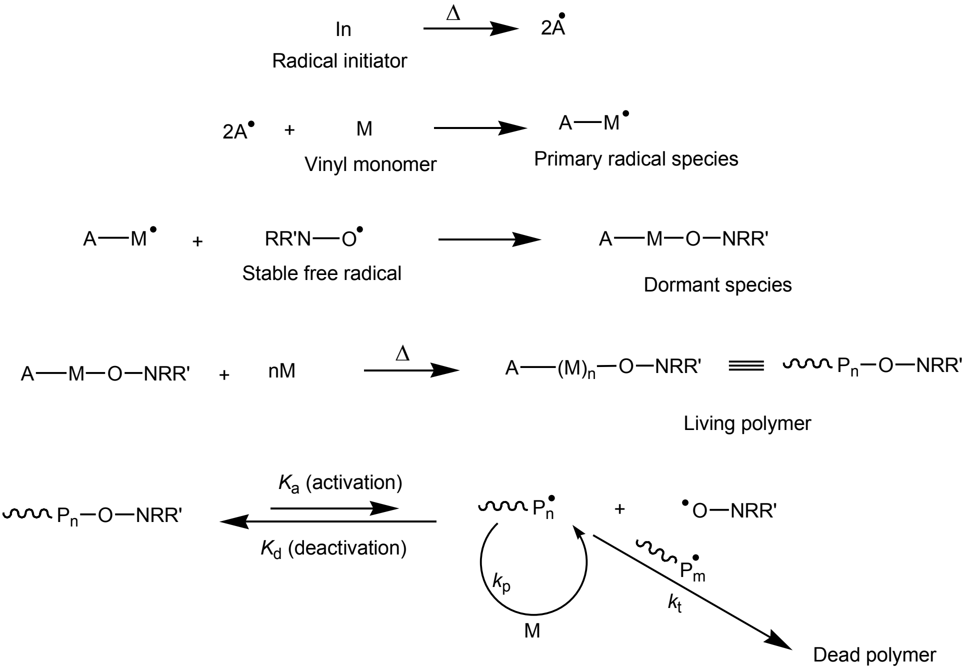
$$\bar{M}_{n,th} = ([M]_0/[\text{Nitroxide radical}]_0) \times M_{mon} \times \rho \qquad (5)$$

where $[M]_0$, $[\text{Nitroxide radical}]_0$, M_{mon}, and ρ are the initial monomer concentration, the initial nitroxide radical concentration, the molecular weight of the monomer, and the conversion, respectively.

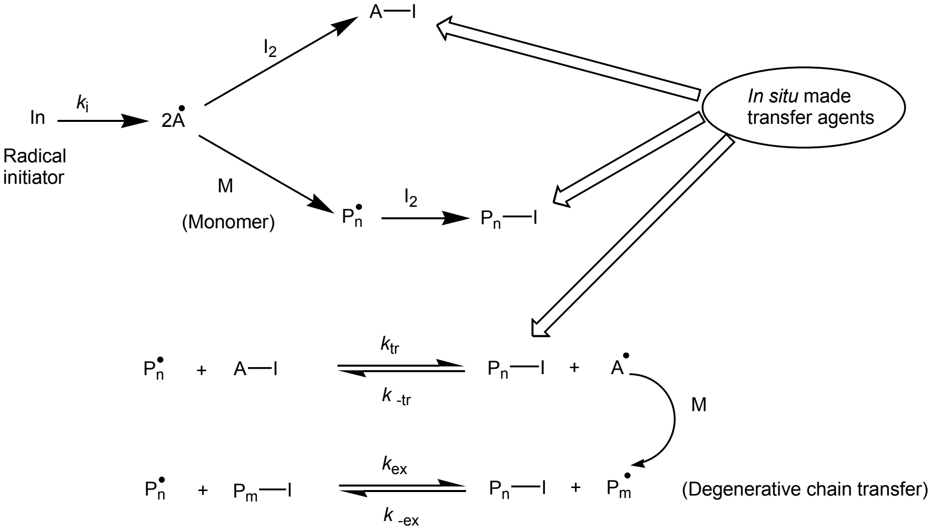
Polymerization of styrene employing TEMPO/BPO = 3 afforded polystyrene with polydispersity index of 1.19 ($\bar{M}_n$ = 18 200 g/mol; $\bar{M}_w$ = 21 700 g/mol) (Georges et al., 1993).

Reverse iodine-transfer polymerization (RITP)

Not only in organic synthesis does molecular iodine play a major role (Wang, 2004) but also in polymer synthesis (Moulay, 2014). A LCRP involv-



Scheme 3. General mechanism for SFRP method



Scheme 4. General mechanism for RITP method

ing the use of molecular iodine is known as '***r****everse iodine-transfer polymerization* (RITP)', a method developed by a French school (Lacroix-Desmazeset al., 2003).

The powerful radical-inhibiting property of molecular iodine manifested in the initiation step of the polymerization as depicted in Scheme 4. Indeed, the mechanism involves an induction period, where *in situ* formation of a chain transfer agent A-I and/or P_n-I and all formed radicals are deactivated by iodine and, consequently, monomer conversion is very low. This step is followed by a polymerization period controlled by a degenerative transfer process, where the polymerization takes place.

RITP method has been applied to a wide range of monomers including the styrenics and the acrylics. The polymerization may be conducted in bulk, solution and dispersed aqueous media such as emulsion, miniemulsion, and suspension. The experiment is usually run in dark and under a slow stream of argon. Targeted molecular weight $\bar{M}_{n,th}$ can be computed from the following Eq. 6 or Eq. 7. The polydispersity index of RITP ranges from 1.20 to 2.00. The living character of the method is demonstrated by the ready formation of block copolymers. Besides, there are advantages of RITP technique over other LCRP methods: 1) it does not require the use of metals, 2) it yields uncolored polymers, and 3) it works at moderate temperatures (50-80 °C).

$$\bar{M}_{n,th} = (W_{mon})/(2n_{I2,\ initial}) + M_{A\text{-}I} \qquad (6)$$

where W_{mon}, $M_{A\text{-}I}$, and $n_{I2,\ initial}$ are weight of the monomer, the molecular weight of the chain ends, and the initial number of moles of iodine, respectively.

$$\bar{M}_{n,th} = (\rho[M]_0 M_{mon})/(2\ [I_2]_0 + M_{A\text{-}}) \qquad (7)$$

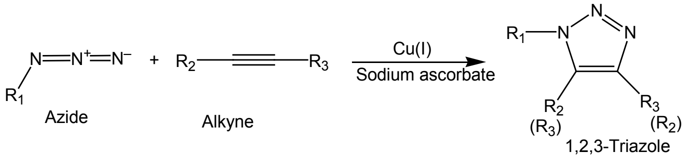
where $[M]_0$, $[I_2]_0$, M_{mon}, ρ, and $M_{A\text{-}I}$ are the initial monomer concentration, the initial iodine concentration, the molecular weight of the monomer, the conversion, and the molecular weight of the chain ends**,** respectively.

Application of RITP to the polymerization of MMA, using AIBN/I_2 system and at 70-80 °C, afforded PMMA with a controlled molecular weight and a polydispersity index of 1.5-1.6 (Boyer et al., 2006).

Click polymerization (CP)

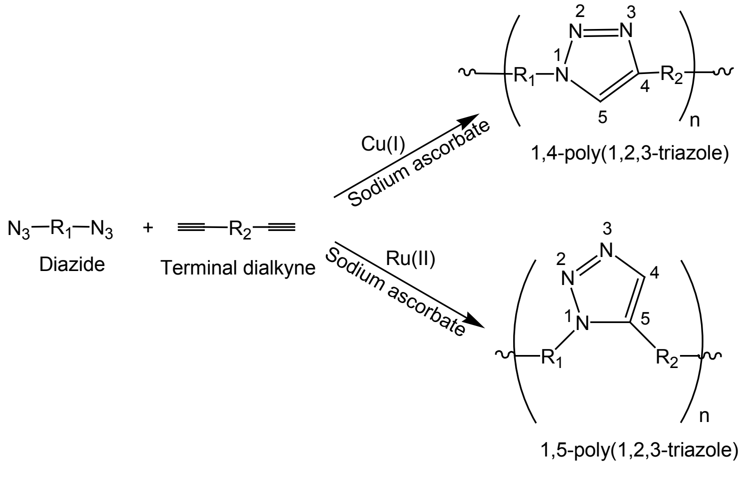
Since the birth of '***click chemistry***' in 2001 (Kolb et al., 2001), the research field of organic synthesis has become broader and more spellbound, particularly as far as designing therapeutic molecules is of great interest. The best known 'click reaction' is the one that involves an azide and an alkyne, commonly called '***azide-alkyne Huis-***

gen*_*cycloaddition', to afford a 1,2,3-triazole; the reaction usually requires a copper(I) catalyst in the presence of a reducing agent such as sodium ascorbate as shown in Eq. 8 (Rostovtsev et al., 2002), hence the appellation '*copper(I)-catalyzed azide-alkyne cycloaddition* (CuCAAC)'. The other variants of click chemistry involve thiol-yne and thiol-ene reactions. Polymer synthesis did take advantage of it to properly functionalize polymers (Moulay, 2015a; 2015b) or to make new ones (Qin et al., 2010a; 2010b). Coupling click chemistry with LCRP polymerization (ATRP, RAFT) created polymers with exotic architectures (Fournier et al., 2007; Golas & Matyjaszewski, 2010).



(8)

Also, one of the ***click polymerizations*** can be conceived by reaction of polyazides and polyalkynes under Huisgen conditions. Overall, the polymerization mechanism approaches that of the conventional polycondensation, offering the 1,2,3-triazole links. The overall polymerization can be exemplified by the reaction between a diazide and a terminal dialkyne, or a monomer having both azide and terminal alkyne groups, under Huisgen conditions (Eq. 9). The polymerization is usually run in media such as THF, DMF, acetonitrile, alcohols, and organic solvent/water system, at a temperature ranging from ambient one to 100 °C and for a time ranging from 1 to 250 h. Molecular weight of polymers are generally moderate, usually in the neighborhood of 10×10^3-50×10^3 g/mol, with a varying PDI (1.5-6.0). In some cases, the presence of a ligand such as triethylamine (TEA) is the key success of click polymerization.



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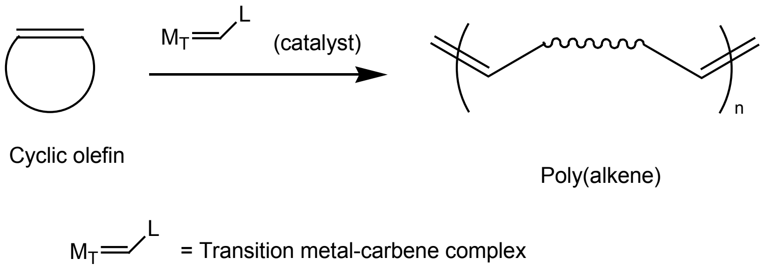
Polyazide and polyalkyne monomers with functionality higher than two would provide hyperbranched, star, graft, crosslinked, and brush polymers. Depending on its structure, the click polymer may be soluble, slightly soluble, or insoluble in common solvents. Worthy of note is the impact of the type of used catalyst on the stereoregioselectivity of the polymerization; that is, Cu(I) catalyst yields 1,4-poly(1,2,3-triazole), whereas Ru(II) gives 1,5-poly(1,2,3-triazole) (Eq. 9). Because of the onerous work-up for removal of the catalyst after the click reaction, a metal-free click polymerization was advanced for reactive alkyne monomers such as propiolates and aroylacetylenes (Qin et al., 2010b). In fact, click polymerizations of a series of bis(aroylacetylene)s and diazides in a DMF-toluene mixture and in the absence of a metallic catalyst, afforded linear poly(aroyltriazole)s with molecular weights $\bar{M}_w$ of 14×10^3-27×10^3 g/mol and PDIs of 2. Of interest is that click polymers containing 1,2,3-triazole moieties and well-chosen units (R_1 and R_2 of the two monomers in Eq. 9) exhibit some advanced functional properties such as nonlinear optical (NLO) activity, optoelectronic activity, and photovoltaic effect.

Several sulfur-bearing polymers have been also prepared through the thiol-yne click polymerization that can be either, thermo-, photo-, amine- or transition metal-mediated (Yao et al., 2013). Functional poly(vinylene sulfide)s were successfully synthesized via a catalyst-free thiol-yne click polymerization (Yao et al., 2014).

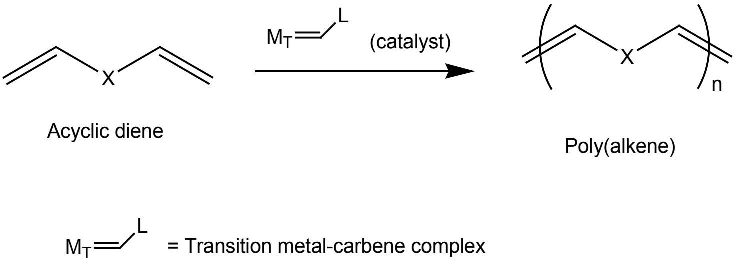
Acyclic diene metathesis polymerization (ADMET)

Strained cyclic olefins (cyclobutene, cyclopentene, *cis*-cyclooctene and norbornene) are prone to the polymerization by a ring opening metathesis mechanism, ending up with linear unsaturated polymers as illustrated in Eq. 10, a polymerization commonly known as '*ring-opening metathesis polymerization* (ROMP)' (Sutthasupa et al., 2010). The most favorable metathesis catalysts are metal-carbene complexes of transition metals Mo, W, Ru, Ta, and Ti (Buchmeiser, 2009); of these catalysts, the Grubbs' catalysts (for example, benzylidene-*bis*(tricyclohexylphosphine)dichlororuthenium) are the most prominent, yielding stereoregular and monodisperse polymers. The living character of ROMP was demonstrated for some monomer/catalyst systems, enabling to design copolymers (Schrock, 1990; Bielawski & Grubbs, 2007). Besides, surface-initiated ring-opening metathesis polymerization (SI-ROMP) has opened up new avenues of research (Kim et al., 2000). Very recently, a metal-free ROMP of cyclic olefins was claimed to be feasible (Ogawa et al., 2015).



(10)

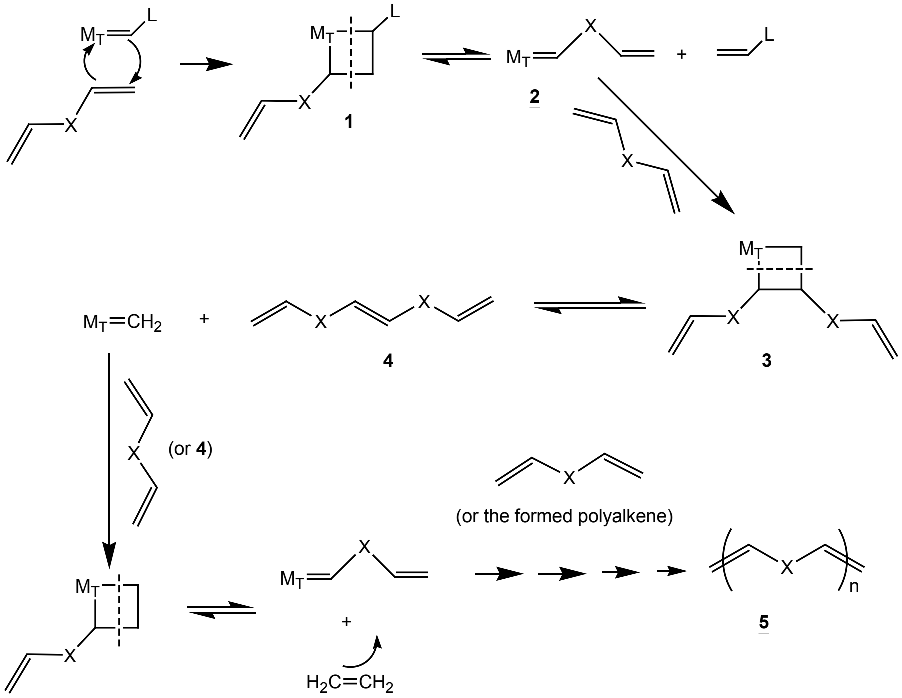
While ROMP has been known since the 1960s (Ivin, 2000), the metathesis polymerization has been successfully applied to acyclic dienes only in 1991 by Wagener's group, a polymerization coined ADMET (Eq. 11) (Wagener et al., 1991). The most efficient ADMET catalysts, as far as high molecular weights are desired, are those of Schrock's and Grubbs' (Mutlu et al., 2011). Poly(octenylene) and polybutadiene with molecular weights of 108 and 28 kDa, respectively, were made by polymerizing 1,9-decadiene and 1,5-hexadiene, respectively, by ADMET technique using Grubbs' first generation catalysts (Brzezinska et al., 1996). Although ADMET polymerization can be conducted in solvents such as toluene and xylene to achieve high conversions, its run in bulk may prevent the formation of cyclic compounds. Polymerization temperature ranges from 40 to 90 °C.



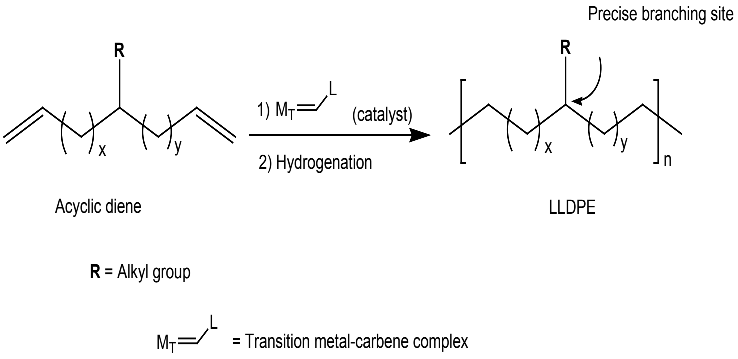
(11)

The mechanism of ADMET polymerization is depicted in Scheme 5 where a reversible [2+2] cycloaddition of metal carbene complex with one carbon carbon double bond of the diene monomer took place. The formed metallocycle **1** will then brake up to afford metal-monomer adduct **2**, which reacts with a second monomer molecule to lead to another metallocycle **3**; the break-up of latter one **3** yields triene **4**. This cycle is repeated until all diene molecules are consumed to produce a high molecular weight polyalkene **5**. The formation of ethylene is an unshakable evidence of the proposed mechanism, which suggests a step-growth nature of ADMET polymerization (Rogers & Timothy, 2003).

Wagener and his group conceived a linear low density polyethylene (LLDPE) with precise branching sites by polymerizing the proper acyclic dienes with ADMET approach (Wagener et al., 1997; Smith et al., 2000; Baughman et al., 2006) (Eq. 12). The branching **R** in Eq. 12 is not restricted to alkyl groups but is extended to other functional ones such as hydroxyl, alcohol, ester, ether, phenyl and halogen, giving rise to the so-called "precision polymers" (Sauty et al., 2014). ADMET technique has been a versatile tool for making defect-free precision polymers as electronic components, such as poly(arylenevinylene)s (Haque& Nomura, 2015).



Scheme 5. General mechanism for ADMET polymerization



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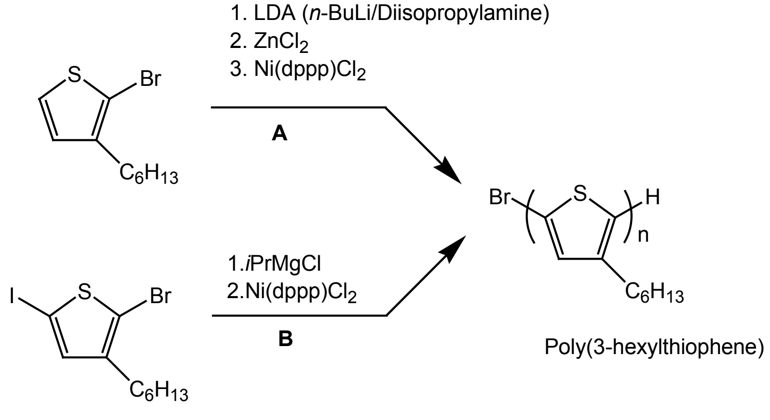
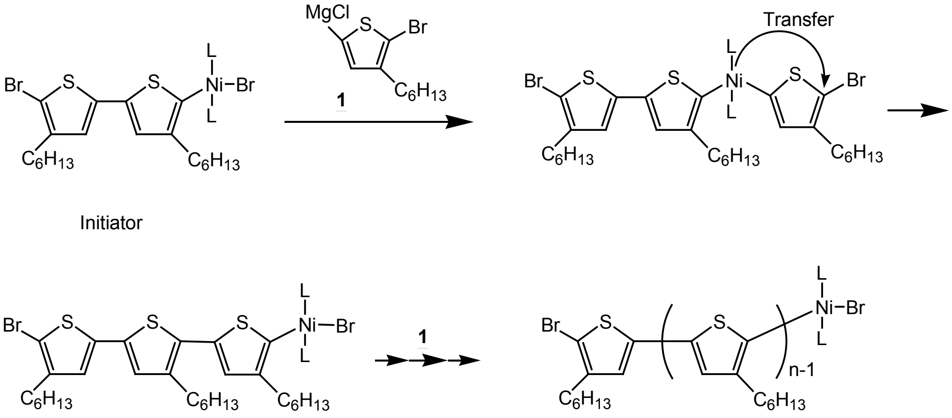
Catalyst-transfer polycondensation (CTP)

'*Metal-catalyzed polycondensation*' with a chain growth mechanism, yielding polymers with controlled and well-defined molecular weights and low polydispersity indexes, was reported in 2004 by two independent research groups, McCullough's (Sheina et al., 2004) and Yokozawa's (Yokoyama et al., 2004; Miyakoshi et al., 2004). Both research teams demonstrated such a polycondensation with chain growth mechanism on the polymerization of 2-bromo-3-hexylthiophene in the presence of [1,3-bis(diphenylphosphino)-propane]dichloronickel(II), Ni(dppp)Cl_2, as a catalyst (Eq. 13: **A**, McCullough pathway; **B**, Yokozawa pathway). Its chain-growth character was supported by: (1) The instantaneous formation of high molecular weight of poly(3-hexylthiophene), (2) The linear increase of molecular weight with conversion, and (3) The polymerization rate increase with increasing Ni(dppp)Cl_2 concentration. At a conversion of 81% and for [2-bromo-3-hexylthiophene]/[Ni(dppp)Cl_2] molar ratio of 57, a molecular weight $\overline{M}_n$ of 9 400 g/mol and a polydispersity index of 1.29 were measured (Sheina et al., 2004). Moreover, the polymerization can be advantageously conducted at room temperature.



(13)

The polymer chains, prepared by this method, are usually terminated with covalently attached catalyst. The monomer will couple with this polymer chain via the catalyst site which is transferred intramolecularly to the newly attached monomer as illustrated in Scheme 5, hence the name "*Catalyst-transfer polycondensation*" (CTP). This polymerization is also referred to as "*Kumada catalyst-transfer polycondensation* (KCTP) or *Kumada chain-growth polycondensation* (KCGP)" because the mechanism involves the Kumada cross-coupling, and as in "*Grignard metathesis polymerization*". Several conductive polymers such as polythiophenes, polypyrroles, poly(phenylene)s, polycarbazoles, and polyfluorenes were made via CTP approach (Bryan et al., 2013). Indeed, KCTP was successfully applied for the synthesis of polyfluorenes with $\bar{M}_n$ ranging from 30 to 90 kDa and polydispesity index from 1.4 to 1.9 (Sui et al., 2015). As can be remarked on Scheme 6, the KCTP is featured by a living character as long as the catalyst remained bonded at the polymer end. This living facet would allow to control the molecular weight of a polymer and to set well-defined diblock copolymers. Surface-initiated polymerization has been conceived for CTP, in which the initiator is covalently attached to inorganic (silica) or organic (polystyrene resin) substrate (Bryan & McNeil., 2013).



Scheme 6. Proposed mechanism for CTP (Miyakoshi et al., 2005)

REFERENCES

Baughman, T.W., Sworen, J.C. & Wagener, K.B. (2006). Sequenced ethylene-propylene copolymers: effects of short ethylene run lengths. *Macromolecules*, *39*, 5028 – 5036.

Bielawski, C.W. & Grubbs, R.H. (2007). Living ring-opening metathesis polymerization. *Progr. Polym. Sci.*, *32*, 1 – 29.

Boyer, C., Lacroix-Desmazes, P., Robin, J.-J. & Boutevin, B. (2006). Reverse iodine transfer polymerization (RITP) of methyl methacrylate. *Macromolecules*, *39*, 4044 – 4053.

Bryan, Z.J. & McNeil, A.J. (2013). Conjugated polymer synthesis via catalyst-transfer polycondensation (CTP): Mechanism, scope, and applications. *Macromolecules*, *46*, 8395 − 8405.

Brzezinska, K., Wolfe, P.S., Watson M.D. & Wagener, K.B. (1996). Acyclic diene metathesis (ADMET) polymerization using a well-defined ruthenium based metathesis catalyst. *Macromol. Chem. Phys.*, *197*, 2065 – 2074.

Buchmeiser, M.R. (2009). Polymer-supported well-defined metathesis catalysts. *Chem. Rev.*, *109*, 303 – 321.

Chiefari, J., Chong, Y.K., Ercole, F., Krstina, J., Jeffery, J., Le, T.P.T., Mayadunne, R.T.A., Meijs, G.F., Moad, C.L., Moad, G., Rizzardo, E. & Thang, S.H. (1998). Living free-radical polymerization by reversible addition-fragmentation chain transfer: the RAFT process. *Macromolecules*, *31,* 5559 – 5562.

Ebdon, J.R. (1991). *New methods of polymer synthesis*. New York: Chapman & Hall.

Feldman, D. (2008). Polymer history. *Des. Monom. Polym.*, *11*, 1 – 15.

Fournier, D., Hoogenboom R. & Schubert, U.S. (2007). Clicking polymers: a straight forward approach to novel macromolecular architectures. *Chem. Soc. Rev.*, *36*, 1369 – 1380.

Georges, M.K., Veregin, R.P.N., Kazmaier, P.M. & Hamer, G.K. (1993). Narrow molecular weight resins by a free-radical polymerization process. *Macromolecules*, *26*, 2987 – 2988.

Golas, P.L. & Matyjaszewski, K. (2010). Marrying click chemistry with polymerization: expanding the scope of polymeric materials. *Chem. Soc. Rev., 39*, 1338 – 1354.

Haque, T. & Nomura, K. (2015). Acyclic diene metathesis (ADMET) polymerization for precise synthesis of defect- free conjugated polymers with well-defined chain ends. *Catalysts*, *5*, 500 – 517.

Hui, C.M., Pietrasik, J., Schmitt, M., Mahoney, C., Choi, J., Bockstaller, M.R. & Matyjaszewski, K. (2014). Surface-initiated polymerization as an enabling tool for multifunctional (nano-)engineered hybrid materials. *Chem. Mater.*, *26*, 745 – 762.

Ivin, K.J. (2000). ROMP and related chemistry: past, present, and future. (pp. 1-16). In: Khosravi, E. & Szymanska-Buzar, T. (Eds.). *Ring-opening metathesis polymerization and related chemistry: state of the art and visions for the new century*. Dordrecht: Kluwer.

Kato, M., Kamigaito, M., Sawamoto, M. & Higashimura, T. (1995). Polymerization of methylmethacrylate with the carbon tetrachloride/dichlorotris-(triphenylphosphine)ruthenium(II)/methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system: possibility of living radical polymerization. *Macromolecules*, *28*, 1721 – 1723.

Kennedy, J.P. & Marechal, E. (1981). Chemistry of initiation in carbocationic polymerization. J. Polym. Sci. Macromol. Rev., 16,123 – 198.

Kennedy, J.P., Ross, L.R., Lackey, J.E. & Nuyken, O. (1981). New telechelic polymers and sequential copolymers by polyfunctional initiator-transfer agents (inifers). *Polym. Bull.*, *4*, 67 – 74.

Khosravi, E. & Szymanska-Buzar, T. (2000), *Proceedings of the NATO Advanced Study Institute*, Polaica-Zdroy (Poland), September 3 – 15.

Kim, N.Y., Jeon, N.L., Choi, I.S., Takami, S., Harada, Y., Finnie, K.R., Girolami, G.S., Nuzzo, R.G., Whitesides, G.M. & Laibinis, P.E. (2000). Surface-initiated ring-opening metathesis polymerization on Si/SiO$_2$. *Macromolecules*, *33,* 2793 – 2795.

Kolb, H.C., Finn, M.G. & Sharpless, K.B. (2001). Click chemistry: diverse chemical function from a few good reactions. *Angew. Chem. Int. Ed.*, *40*, 2004 – 2021.

Lacroix-Desmazes, P., Severac, R., Otazaghine, B. & Boutevin, B. (2003). Reverse iodine transfer polymerization (RITP): use of elemental iodine as a versatile control agent in living radical polymerization. *Polym. Prepr., 44*, 683 – 684.

Le, T.P., Moad, G., Rizzardo, E. & Thang, S.H. (1998). PCT Int. Appl. WO 9801478 A1 980115. *Chem. Abstr. 128*, 115390.

Mah, S., Faust, R., Zsuga M. & Kennedy, J. P. (1987). New telechelic polymers and sequential copolymers by polyfunctional initiator-transfer agents (inifers). *Polym. Bull.*, *18*, 433 – 440.

Matyjaszewski, K. (2002). From atom transfer radical addition to atom transfer radical polymerization. *Curr. Org. Chem.***,** *6***,** 67 – 82.

Matyjaszewski, K. & Xia, J. (2001). Atom transfer radical polymerization. *Chem. Rev.*, *101*, 2921 – 2990.

Miyakoshi, R.,Yokoyama, A. & Yokozawa, T. (2004). Synthesis of poly(3-hexylthiophene) with a narrower polydispersity. *Macromol. Rapid Commun.*, *25*, 1663 – 1666.

Miyakoshi, R.,Yokoyama, A. & Yokozawa, T. (2005). Catalyst-transfer polycondensation: mechanism of Ni-catalyzed chain-growth polymerization leading to well-defined poly(3-hexylthiophene). *J. Amer. Chem. Soc.*, *127*, 17542 – 17547.

Moulay, S. (1999). Bref historique des polymères. *Actua. Chim.*, *12*, 31 – 43.

Moulay, S. (2014). Molecular iodine in monomer and polymer designing. *Des. Monom. Polym.*, *17*, 501 – 527.

Moulay, S. (2015a). Review: poly(vinyl alcohol) functionalizations and applications. *Polym. Plast. Technol. Eng.*, *54,* 1289 – 1319.

Moulay, S. (2015b). Covalent functionalizations of poly(vinyl chloride) in tune with applications: an update. *J. Res. Updates Polym. Sci.*, *4*, 79 – 122.

Mutlu, H., Montero de Espinosa, L. & Meier, M.A.R. (2011). Acyclic diene metathesis: a versatile tool for the construction of defined polymer architectures. *Chem. Soc. Rev.*, *40*, 1404 – 1445.

Nicolas, J., Guillaneuf, Y., Lefay, C., Bertin, D., Gigmes, D. & Charleux, B. (2013). Nitroxide-mediated polymerization. *Progr. Polym. Sci.*, *38*, 63 – 235.

Odian, G. (2004). *Principles of polymerization.* Hoboken: John Wiley & Sons.

Ogawa, K.A., Goetz, A.E. & Boydston, A.J. (2015). Metal-free ring-opening metathesis polymerization. *J. Amer. Chem. Soc.*, *137*, 1400 – 1403.

Otsu, T. & Yoshida, M. (1982). Role of initiator-transfer agent-terminator (iniferter) in radical polymerizations: polymer design by organic disulfides as iniferters. *Makromol. Chem. Rapid Commun*., *3*, 127 – 132.

Qin, A.-J., Lam, J.W.Y. & Tang, B.Z. (2010a). Click polymerization. *Chem. Soc. Rev.*, *39*, 2522 – 2544.

Qin, A.-J., Lam, J.W.Y. & Tang, B.Z. (2010b). Click polymerization: progresses, challenges, and opportunities. *Macromolecules*, *43*, 8693 – 8702.

Rogers, E.M. & Timothy, E.L. (2003). *Synthetic methods in step-growth polymerization*. Hoboken: John Wiley & Sons.

Rostovtsev, V.V., Green, L.G., Fokin, V.V. & Sharpless, K.B. (2002). A stepwise Huisgen cycloaddition process: copper(I)-catalyzed regioselective ligation of azides and terminal alkynes. *Angew. Chem. Int. Ed.*, *41*, 2596 – 2599.

Sauty, N.F., Caire da Silva, L., Schulz, M.D., Few, C.S & Wagener, K.B.(2014). Acyclic diene metathesis polymerization and precision polymers. *Appl. Petrochem. Res.*, *4*, 225 – 233.

Schrock, R.R. (1990). Living ring-opening metathesis polymerization catalyzed by well-characterized transition-metal alkylidene complexes. *Acc. Chem. Res.*, *23*, 158 – 165.

Sheina, E.E., Liu, J., Iovu, M.C., Laird, D.W. & McCullough, R.D. (2004). Chain growth mechanism for regioregular nickel-initiated cross-coupling polymerizations. *Macromolecules*, *37*, 3526 – 3528.

Smith, J.A., Brzezinska, K.R., Valenti, D.J. & Wagener, K.B. (2000). Precisely controlled methyl branching in polyethylene via acyclic diene metathesis (ADMET) polymerization. *Macromolecules*, *33*, 3781 – 3794.

Sui, A., Shi, X., Wang, Y., Geng, Y. & Wang, F. (2015). Kumada catalyst transfer polycondensation for controlled synthesis of polyfluorenes using 1,3-bis(diarylphosphino)propanes as ligands. *Polym. Chem.*, *6*, 4819 – 4827.

Sutthasupa, S., Shiotsuki M. & Sanda, F. (2010). Recent advances in ring-opening metathesis polymerization, and application to synthesis of functional materials. *Polym. J.*, *42*, 905 – 915.

Vega-Rios, A. & Licea-Claveríe, A. (2011). Controlled synthesis of block copolymers containing *N*-isopropylacrylamide by reversible addition-fragmentation chain-transfer (RAFT) polymerization. *J. Mex. Chem. Soc.*, *55,* 21 – 32.

Wagener, K.B., Boncella, J.M. & Nel, J.G. (1991). Acyclic diene metathesis (ADMET) polymerization. *Macromolecules*, *24*, 2649 – 2657.

Wagener, K.B., Valenti D. & Hahn, S.F. (1997). ADMET modeling of branching in polyethylene: the effect of a perfectly-spaced methyl group. *Macromolecules*, *30*, 6688 – 6690.

Wang, S.Y. (2004). Molecular iodine. *Synlett.*, *14*, 2642 – 2643.

Wang, J.-S. & Matyjaszewski, K. (1995a). Controlled/living radical polymerization: atom transfer radical polymerization in the presence of transition-metal complexes. *J. Amer. Chem. Soc.*, *117,* 5614 – 5615.

Wang, J.-S. & Matyjaszewski, K. (1995b). Controlled/Living radical polymerization: halogenatom transfer radical polymerization promoted by a Cu(I)/Cu(II) redox process. *Macromolecules*, *28*, 7901 – 7910.

Yamago, S. & Nakamura, Y. (2013). Recent progress in the use of photoirradiation in living radical polymerization. *Polymer*, *54*, 981 – 994.

Yao, B.-C., Sun, J.-Z., Qin, A.-J. & Tang, B.Z. (2013). Thiol-yne click polymerization. *Chin. Sci. Bull., 58*, 2711 – 2718.

Yao, B.-C., Mei, J., Li, J., Wang, J., Wu, H., Sun, J.Z., Qin, A.-J. & Tang, B.Z. (2014). Catalyst-free thiol-yne click polymerization: a powerful and facile tool for preparation of functional poly(vinylene sulfide)s. *Macromolecules*, *47*, 1325 – 1333.

Yokoyama, A., Miyakoshi, R. & Yokozawa, T. (2004). Chain-growth polymerization for poly(3-hexylthiophene) with a defined molecular weight and a low polydispersity. *Macromolecules*, *37*, 1169 – 1171.

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