PERSPECTIVE

Emerging Concepts in Iodine Transfer Polymerization

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Controlled radical polymerization corresponds to variety of synthetic strategies that aim the generation of precise macromolecular architectures. Iodine transfer polymerization (ITP) is one of the oldest methods to conduct controlled radical polymerization; however, it seems to have lost visibility compared to other popular techniques. It relies on utilization of iodine species in reversible deactivation kinetics, and it has some significant advantages compared to other methods. Its simplicity, minimized toxicity, metal-free nature, no coloring on final product, and ease of purification provide widespread applicability, even in industry. In this perspective, the basics of ITP are re-introduced, and emerging technologies (heterophase polymerization, photoinitiation, and sustainability) in ITP are discussed.

1. Introduction

Iodine is the heaviest stable halogen with appealing properties. It is deeply involved in biological functions and it is an essential nutrient for a well-functioning body.[1] Iodine deficiency in childhood is related to impaired neurodevelopment,[2] and iodine plays a key role in thyroid activities.[3] Potassium iodide is part of an effective protection mechanism applied in nuclear accidents which prevents radioactive iodine species to be absorbed by thyroid.[4] In atmospheric science, silver iodide is known as a most effective ice nucleation agent applied in cloud seeding technologies to enhance precipitation.[5] In aerospace science, ionized molecular iodine has a potential to be used as a propellant at in-orbit levels.[6] Also chemistry enjoys the utilization of iodine in some key applications. The van Arkel–de Boer process enables production of high-purity titanium, vanadium, hafnium, and zirconium via formation of iodine salts followed by decomposition to attain pure metals.[7] Due to ease of molecular iodine

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solubility in organic solvents, iodine mediated catalytic transformations are widely applied.[8] In energy devices, sodium-iodine[9,10] and lithium-iodine[11] batteries are being popularized. Hence, chemical properties of iodine address variety of fields with a growing interest.

Radical polymerization is one of the most common polymerization routes which is applied in industry-scale including bulk, solution, and heterophase polymerization.[12,13] In research, radical polymerization remains the technological workhorse mainly due to its simplicity and efficiency toward vinyl monomers.[14,15] Soluble polymers in this case possess high polydispersity, hence for polymer molecular architecting controlled molecular weights and polydispersities are required.[16] Controlled radical polymerization broke new grounds and brought synthetic chemistry closer to natural systems.[17] From synthetic perspective, polymers made via controlled radical polymerization exhibit narrow molecular weight distributions while its largely "living" character can be employed to fabricate block copolymers.[18,19] Common approaches for reversible-deactivation radical polymerization (RDRP) are identified as atom transfer radical polymerization (ATRP),[20–22] nitroxide-mediated polymerization (NMP),[23,24] reversible addition fragmentation chain transfer (RAFT) polymerization,[25,26] and telluride mediated polymerization.[27,28] All these systems rely on addition of a control agent which tunes the interplay of polymerization rate, monomer reactivity, concentration of chain carriers, termination, and concentration of initiating species.[29] Molecular weights are controlled through equilibrium reactions, and active living chain ends could be used to form block copolymers.[30] Iodine transfer polymerization (ITP) is one of the oldest controlled radical polymerization methodology, and iodine is used to mediate kinetics and manufacture polymer materials.

In this short perspective, the re-discovery and emerging trends in ITP are covered. The electronic structure of elemental iodine enables unprecedented reaction mechanisms to conduct controlled polymerization of various monomers. Articles on heterophase polymerization and sustainable ITP systems will be reviewed, and readers will be introduced into iodine-based controlled polymerization mechanisms, to some extend unlocking novel features of polymer materials.

2. A Short Summary on Iodine Transfer Polymerization

Even though RDRP research was massive, its industrial application is rather rare, even when compared to controlled ionic

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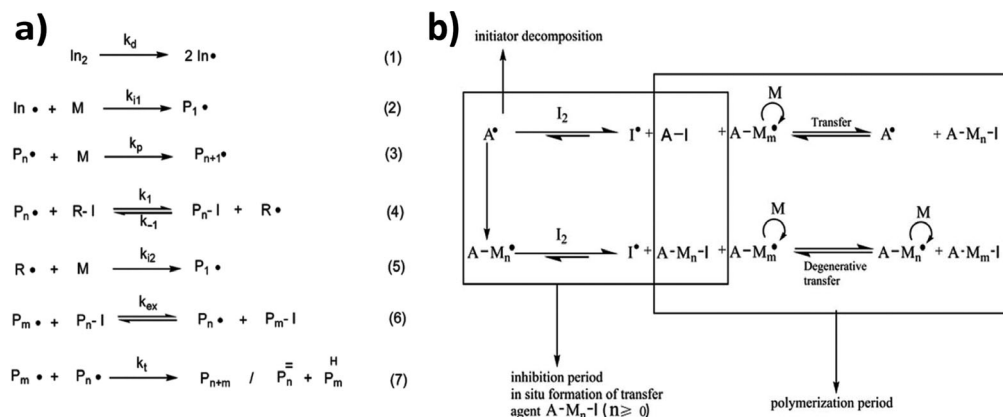www.mcp-journal.de

Figure 1. a) Radical formation steps in ITP. Adapted with permission.[37] Copyright 2003, American Chemical Society. b) Elementary steps in reverse ITP. Adapted with permission.[39] Copyright 2015, Royal Society of Chemistry.

polymerization. Typical chain transfer agents (CTAs) for RDRP include metal-based salts (for ATRP and tellurium-based systems), thioester-based organic molecules (RAFT), and nitroxide-containing organic molecules (NMP). Many of these CTAs results in undesired coloring in final polymer products, high efforts for purification, high cost, possible toxicity based on leaching, and purity issues in industrial production which hinder practical applications. Employing iodine species to conduct RDRP might bring advantages mainly on cost, robustness, and purification processes. However, it is important to note that ITP suffers from moderate polydispersity control compared to other RDRP techniques, while the monomer library in this scenario is restricted. Yet, a few commercialization attempts based on ITP were successfully implemented, mainly for fluoroelastomers with iodine curing units, some commercial fluoropolymers, and acrylic acid-based superabsorbent polymers.[31]

ITP was originally proposed in 1979 before ATRP,[32,33] while the use of iodine as initiating species in cationic polymerization has been investigated in 1977–1984.[34,35] ITP relies on degenerative chain transfer process, that alkyl iodide reacts with propagating radicals to generate R• and terminal iodine-containing polymers (Pn–I). R• can react to promote a new propagating species (**Figure 1**a). In reverse ITP (RITP), active iodide species are generated in situ by using elemental iodine as a CTA. (Figure 1b).[36] Alternatively, in situ halogen exchange forms iodine-based RDRP as well. For this strategy, one can use an alkyl bromide with iodide salts, which undergo halogen-exchange to produce iodine-based CTA. It is important to note that iodine-amine species to run ITP proceed via reversible complexation mechanism. ITP has been successfully applied to many monomers spanning from styrene,[37] vinyl acetate,[38] methyl methacrylate (MME),[39] chloroprene,[40] ethylene,[41] and highly halogen substituted monomers,[42] just to name few. Livingness of the polymers made via ITP was harnessed to manufacture advanced block copolymers with low polydispersities.[43] Majority of the research focuses on solution-based homogeneous ITP,[43] but our focus in this perspective is to discuss the more contemporary, emerging trends in ITP.

3. Heterophase Polymerization Based on Iodine Transfer Polymerization

Heterophase polymerizations to architect colloidal objects can take special profit from ITP, using some adaptions to the multiphase character of reactant distribution and growth processes.[44] Microsuspension polymerization of methyl acrylate via ITP using CHI_3 as CTA was demonstrated.[45] The reaction setup was based on vortex stirring organic phase (consisting of methyl acrylate, benzoyl peroxide as initiator, and CHI_3 with altered ratios) in aqueous poly(vinyl alcohol) solution, where polymerization was carried out at 80 °C in 6 h. Controlled (with Đ: 1.5) living polymerization with high conversion (up to 92%, M_w 90 000 g mol^{-1}) was obtained for micrometer-sized polymer particles, while no submicrometer-sized byproducts were observed. Recently, the same group optimized methyl acrylate ITP to follow industrial recipes.[46] A similar reaction was conducted to form poly(methyl methacrylate) micrometer-sized particles as well (90% conversion, Đ: 1.7) (**Figure 2**a).[47] ITP in microsuspension eliminates a possible emulsion polymerization as a side reaction which leads to uncontrolled renucleation from the water phase. As the authors mention, benzoyl peroxide-based radicals possess a significant hydrophilicity and escape from the emulsion droplet, the loci of organic polymerization loci, whereas iodine-based propagating radicals are hydrophobic and stay exclusively in the organic phase. Furthermore, Okubo and his team investigated ITP of MMA in microsuspension using similar recipe in presence of N-iodosuccinimide as a control agent, and good control and high reactivity was found as the particle size decreases.[48] ITP of vinyl acetate, a challenging monomer for radical polymerization, was attempted in microsuspension system using iodoform as CTA.[49] Using high temperatures for polymerization led to undesired hydrolysis of poly(vinyl acetate), thus the 2,2′-azobis(4-methoxy-2.4-dimethyl valeronitrile) (V-70) initiator at 30 °C was employed for optimum polymerization condition. Average particle size was 22.3 µm with Đ: 2.0 and a molecular weight of 26 000 g mol^{-1} was obtained. Higher temperatures led to cross-linking due to aldol reaction, while low temperature polymerization where water hy-
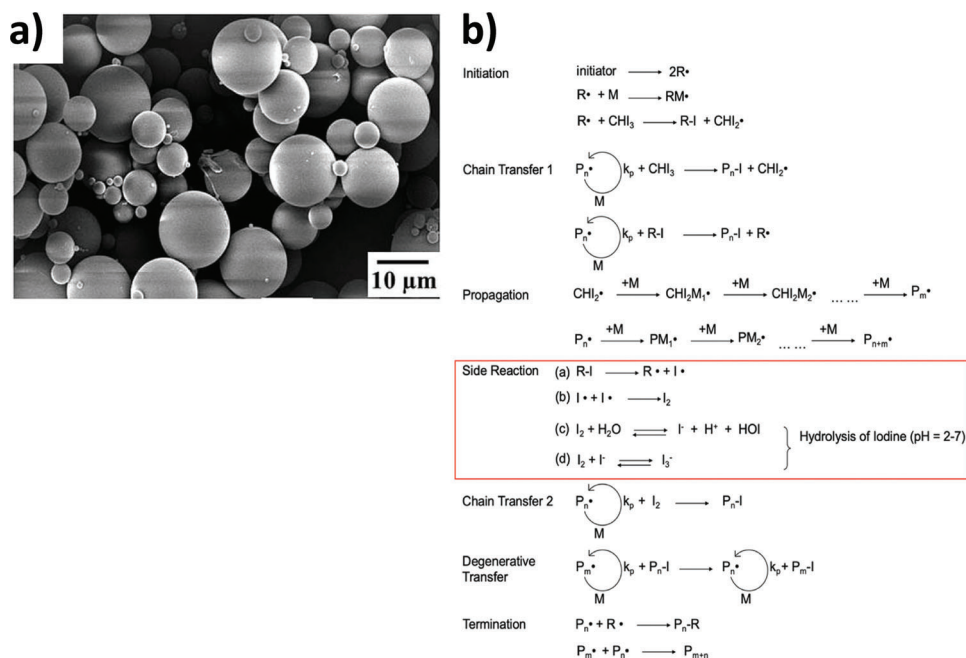
Figure 2. a) SEM images of dried PMMA particles prepared by ITP. Adapted with permission.[46] Copyright 2016, Royal Society of Chemistry. b) Typical reaction mechanism of ITP in aqueous system. Adapted with permission.[48] Copyright 2022, Royal Society of Chemistry.

drolyses in situ formed iodine generates well-defined polymer particles (Figure 2b). From an application perspective, microencapsulation of an essential oil methyl anthranilate by microsuspension ITP of MMA and ethylene glycol dimethacrylate copolymer using iodoform as CTA was performed, and polymer shells or capsules could be manufactured.[50] Particle size, uniformity, and shape could be varied by the stabilizer. Methyl anthranilate loading was determined via thermogravimetric analysis, and the slowed down release kinetics indicated effective and structurally perfect encapsulation.

Emulsion polymerization of styrene via ITP employing methyl-2-iodopropionate as transfer agent, 2,2′-azobis[N-(2-carboxyethyl)-2-methylpropionamidine]tetrahydrate (VA-057) as initiator and dodecyl sulfate sodium salt (SDS) as surfactant showed the formation of rather unusual latexes.[51] PS particles with only 30 nm average diameter and a molecular weight of 8400 g mol^{-1} ($Đ$: 1.82) were obtained and could be subjected for chain extension to fabricate block copolymer nanoparticles with n-butyl acrylate. An ab initio emulsion strategy was exhibited for reverse ITP using I_2 and potassium persulfate acting as radical initiator and oxidant to generate n-butyl acrylate polymer particles.[52] Polymerization was conducted at 85 °C using sodium 1-hexadecanesulfonate as surfactant, which yielded almost quantitative conversion with 83 nm average particle size ($Đ$: 1.8, M_n: 9800 g mol^{-1}). Livingness of the system was proven via seeded emulsion for chain extension, and persulfate prevented disproportionation of iodide species in aqueous media by continuous regeneration of I_2 in organic phase. Both recipes were highlighted as being applicable to industrial synthetic conditions. Chaiyasat and colleagues prepared poly(methacrylic acid)-I (PMA-I) via solution ITP which can be used as an active emulsifier in emulsion polymerization. PMA-I macroCTA was prepared via ITP of methacrylic acid using iodoform as

CTA, germanium iodide as catalyst, and 2,2-azobis(4-methoxy-2,4-dimethylvaleronitrile) as an initiator in dioxane in 40 °C.[53] By using PMA-I, emulsion ITP of styrene to obtain monodisperse particles were reported.[54] Miniemulsion reverse ITP of styrene was conducted via bis(4-$tert$-butylcyclohexyl) peroxydicarbonate initiator with dodecyl SDS as surfactant and hexadecane as hydrophobe at 60 °C in the presence of I_2.[55] Continuous addition of oxidant (hydrogen peroxide) in acidic conditions controlled iodine regeneration by preventing hydrogen iodide formation, and highly stable, color-free latexes ($Đ$: 1.4, M_n: 7900 g mol^{-1}) could be obtained that are industrially interesting.

4. Improved Sustainability and Photoinitiation in Iodine Transfer Polymerization

ITP was also used to improve the sustainability of polymers and processes. And ITP of partially sustainable molecules is a starting point. Vanillin methacrylate (obtained via methacrylation of biomass derived vanillin) was polymerized via RITP using I_2 and AIBN in various solvents (**Figure 3**a).[56] Polymer was successfully obtained with low dispersity ($Đ$: 1.4) and high conversion (73% concluded via ^{1}H NMR). Livingness of polymer was elucidated via block copolymer formation with MMA as confirmed via SEC (increase from 8060 to 57 780 g mol^{-1}). Thorough mechanistic investigation, especially the role of solvent in CTA formation, was presented. A more green ITP has been designed using metabolizable choline iodide in bulk or in green solvents encompassing ethyl lactate, water, and ethanol.[57] A variety of monomers such as MMA, butyl acrylate, 2-hydroxylethyl methacrylate, poly(ethylene glycol) methyl ether methacrylate, 2-methoxyethyl acrylate, poly(ethylene glycol) methyl ether acrylate, 2-methacryloyloxyethyl phosphorylcholine, and [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)
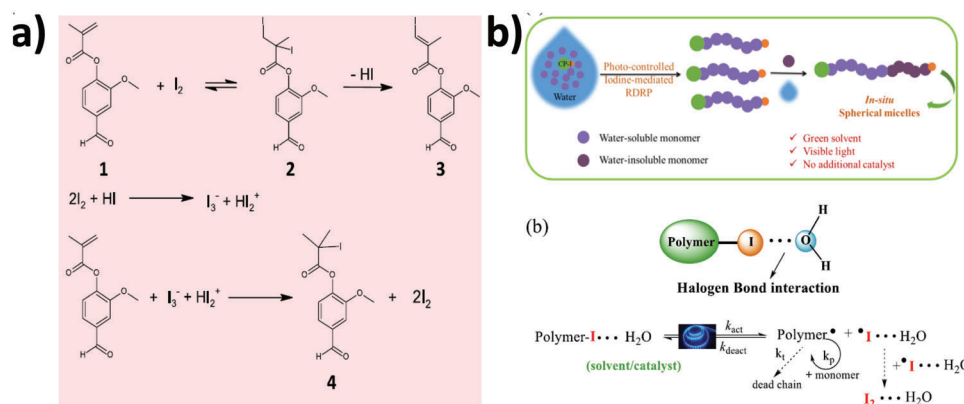
Figure 3. a) Reaction mechanism of reverse ITP for vanillin methacrylate. Adapted with permission.[55] Copyright 2021, American Chemical Society. b) Schematic description of ITP-based block copolymer formation (top) and water promoting ITP by acting as catalyst (bottom). Adapted with permission.[58] Copyright 2019, American Chemical Society.

ammonium hydroxide (sulfobetaine methacrylate) were polymerized with choline iodides. For all cases, authors have proven effective polymerization with good conversion and low dispersity, which naturally differs in each case. Furthermore, successful block copolymer formation clarified the livingness of polymer chains thanks to active iodide end groups. This article highlighted again that green and simplified conditions can be set to conduct RDRP based on ITP.

Photomediated ITP offers an attractive synthetic strategy using light as a trigger. Wolpers and Vana investigated the effect of UV irradiation on ITP of butyl methacrylate using 2-methyl-4′-(methylthio)-2-morpholinopropiophenone photoinitiator with either phenylethyl iodide (PE−I) or cyanopropyl iodide (CP−I) CTAs.[58] They observed a remarkable effect of UV light on polymerization kinetics, so that a polymer with 1.1 dispersity could be obtained whereas a reference sample with thermal initiation possessed Đ: 1.5. Based on detailed kinetic investigations, it was observed that nanomolar formation of iodine promotes reversible termination mechanism coexisting to degenerative chain-transfer which allows precise molecular weight control. Water soluble methacrylic monomers were subjected to visible light induced RDRP by using 2-iodo-2-methylpropionitrile (CP-I) as the initiator.[59] The authors established the suitability of methacrylic monomers compared to acrylic ones, as the C−I bond in acrylic polymers is stronger than methacrylic analogues which leads to no polymerization under visible light. Altered synthetic conditions based on a varied monomer–initiator–water ratio have been reported, and well-controlled polymers were obtained in each case. For the initiation mechanism, water was found out to be an active catalyst to accelerate polymerization as it contributes to activation-deactivation equilibrium (Figure 3b).

A highly simplified photoinitiated ITP, which does not require additional photocatalyst nor iodide salts, was achieved by employing tosyl iodide in dimethyl acetamide solvent to conduct polymerization of methacrylic monomers.[60] Under light irradiation, tosyl iodide produces p-toluenesulfonyl radicals that can add to double bonds and fabricates iodinated derivatives. The authors reported well-controlled polymer synthesis (Đ: 1.1–1.3, depending on monomer and reaction conditions), and the polymerization shows a decent response to light on–off cycles.

Furthermore, the effect of irradiation wavelength on dispersity was reported for methyl methacrylate (violet light [Đ: 1.28] and sunlight [Đ: 1.23]). Using milder irradiation based on near-IR can trigger ITP once special yet simple conditions are set. 2-iodo-2-methylpropionitrile was used as the initiator at room temperature together with carbonyl-containing solvents (i.e., 1,3-dimethyl-2-imidazolidinone) acting as catalysts to promote ITP of methacrylates under near infrared (NIR) irradiation.[61] Very high conversions (up to 97% calculated gravimetrically) with high control (Đ: 1.04–1.1) were attained. It was noted that the halogen bond interaction between carbonyl unit and iodine controls the balance of dormant and propagating species, which is enhanced in high-polar solvents. Successful block copolymer formation was exhibited to affirm living character, and polymerization under a mask (i.e., thick pork skin) confirms penetrability and efficacy of NIR-assisted ITP for potential future applications. As a last example, in situ formation of iodine CTA based on bromine–iodine exchange to conduct photoassisted ITP was elucidated for the synthesis of hydrophilic polymers.[62] Ethyl α-bromophenylacetate was converted to an iodo-type initiator in the presence of NaI which afforded high poly(poly(ethylene glycol) methyl ether methacrylate) conversion (up to 99.4%, as concluded via ¹H-NMR) with good control on Đ (1.11). The so-formed hydrophilic macroinitiator was chain extended via hydrophobic benzyl methacrylate under light irradiation to attain photopolymerization induced self-assembly-based spherical nanoparticles.

5. Conclusions and Perspectives

RDRP is a well-researched technique of polymer synthesis to conduct polymerization reactions with higher, partly very high control. ITP is amongst the oldest RDRP techniques and uses iodine-based equilibria to generate controlled and living polymers. A variety of techniques can be employed to achieve iodine-based dynamic radical processes for reversible deactivation mechanisms, and the literature is rich enough to reveal rather unexpected influencing factors (such as solvent, catalyst, presence of heterophases, and iodine specific molecular interactions) to create a
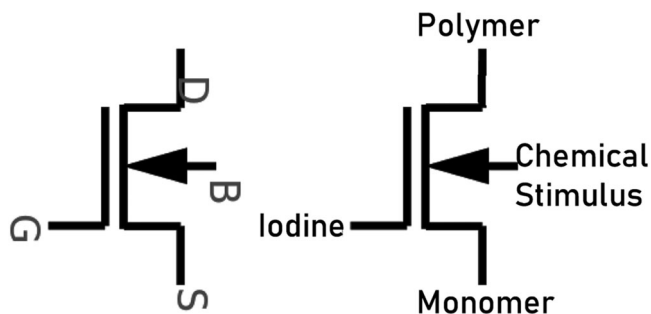
Figure 4. Functional similarity of a FET and the control of ITP by external effects, such as added solvents, interfaces, or metal salts.

higher level of complexity in polymerization processes with close-to bio-like regulation cycles.

We believe for instance that adaptation of ITP to the specific needs of heterophase polymerization is very powerful, as shown by delicate articles who report on the on–off control of side reactions both on the level of polymers and the colloidal scale, and more attention should be paid in near future for industrialization of controlled polymer latexes with expanded structure and performance profile. Especially the synthesis of polymer amphiphiles and block copolymers can progress with great ease. ITP of sustainable vinyl monomers is promising since it allows straightforward reactions with possible higher sustainability metrics compared to other RDRP methods but further improvement of sustainability in ITP design by the means of using sustainable solvents and photoassisted mechanisms are certainly needed.

The most important and appealing point however is that the ITP works with the very polarizable and interactive iodine as the transfer agent. It was already stated that livingness can be controlled and improved by amidic solvents or the presence of water, that is, the temporal termination equilibrium is sensitive to secondary factors stabilizing or destabilizing the free iodine radical, which are in the hand of chemists.

As that, this living polymerization is not only controllable, but adaptive, and the scheme is similar to a field effect transistor (**Figure 4**).

The outer stimulus is controlled speed and dispersity of the ITP, and chemists could use it for temporal polymerization control (such as boosting reactions at the end to reduce free monomer) or also spatial polymerization control (e.g., by applying spatial functionality patterns to create a "polymerization contrast," or by running polymerization only at specific nanoscopic sites by a polymerization enhancer).

Just thinking about the option of such control illustrates the new potential of one of the oldest controlled polymerization technique, involving iodine.

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Conflict of Interest

The authors declare no conflict of interest.

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