

HYPERVALENT IODINE COMPOUNDS AS POLYMERIZATION INITIATORS

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Abstract. This review summarizes general features of iodonium salts and [bis(acyloxy)iodo]arenes as polymerization initiators and promoters. In particular, diaryliodonium salts are widely used in industry as photoinitiators for cationic photopolymerizations. Recent developments in the application of [bis(acyloxy)iodo]arenes and iodobenzene/pseudohalide-based initiators for radical polymerization are also presented.

Keywords: polymers, iodonium salts, iodine, polymerization, hypervalent iodine.

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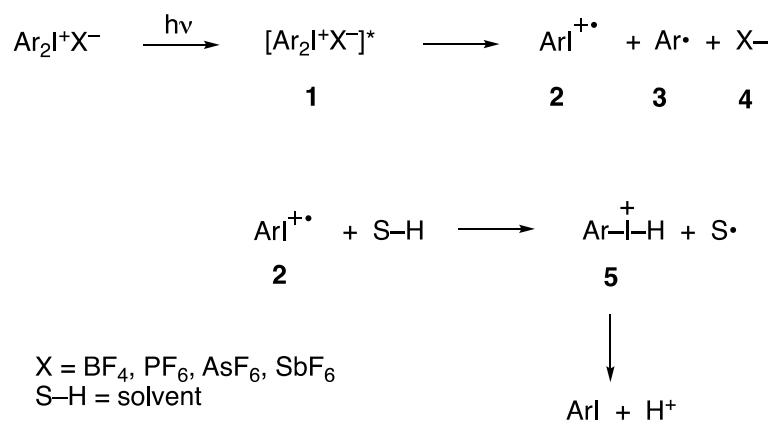
1. Introduction

Hypervalent iodine compounds have recently emerged as versatile, efficient and environmentally friendly synthetic reagents with numerous applications in academic and industrial research (Zhdankin, 2014; Yoshimura & Zhdankin, 2016; Yoshimura *et al.*, 2018; Yusubov *et al.*, 2016). In particular, diaryliodonium salts are widely used in industry as photoinitiators for cationic photopolymerizations (Crivello *et al.*, 1984, 1989, 1998; Roffey, 1997). Photoinitiated cationic polymerization is of great practical interest due to its applicability for the curing of coatings and printing inks, and for photoresist technology used in lithography (Crivello *et al.*, 1998; Roffey, 1997). General synthetic methods, properties, and photochemistry of diaryliodonium salts as photoinitiators were reviewed by Crivello in 1984 (Crivello *et al.*, 1984). Several aspects of applications of hypervalent iodine compounds in polymer science were discussed in a recently published book chapter (Vaish & Tsarevsky, 2018). In the present review, general features of iodonium salts and other hypervalent iodine compounds as polymerization initiators and promoters are discussed, and recent developments in their applications are summarized.

2. Iodonium salts as polymerization initiators

Crivello and co-workers have first discovered that iodonium salts having BF_4^- , PF_6^- , AsF_6^- or SbF_6^- counter ions are efficient photoinitiators for the polymerization of a variety of cationically polymerizable monomers (Crivello & Lam, 1977). The study of the mechanism of photolysis of iodonium salts confirmed a pathway, involving radical-cations and aryl radicals as key intermediates. The major pathway involves the facile

decomposition of the excited iodonium compound **1** to arylido radical-cation **2**, aryl radical **3**, and anion **4** (Scheme 1). This process should be highly efficient due to the very low bond energy of the C–I bond (26–27 kcal/mol). Interaction of the arylido radical-cation with the solvent (S–H) generates a protonated iodoaromatic compound **5**, which rapidly deprotonates, and a radical S• derived from the solvent. During the photolysis, the BF₄[−], PF₆[−], AsF₆[−] or SbF₆[−] counter ions associated with the diaryliodonium salts remain unchanged and appear in the products as the corresponding Brønsted acids. These acids (HX) are credited as the true initiators of cationic polymerization when diaryliodonium salts are employed in the cationic photopolymerization of various monomers. According to this mechanism of action, diaryliodonium salts belong to an important class of photoacid generators (PAGs), which find broad applications in the manufacturing of protective coatings, smart cards, 3D rapid prototyping, UV adhesives, semiconductor devices, anti-reflective coatings, holograms, etc.



Scheme 1.

In the same groundbreaking paper (Crivello & Lam, 1977), Crivello has also demonstrated that the anion plays no significant role in determining the photosensitivity of the iodonium salt, and the photolysis rates of diaryliodonium salts having the same cations but different nonnucleophilic counter ions (BF₄[−], PF₆[−], AsF₆[−] or SbF₆[−]) are identical. Likewise, the cation structure has little effect on the photodecomposition of diaryliodonium salts. The utility of iodonium salts as photoinitiators has been demonstrated on several cationic polymerizations using olefins, epoxides, cyclic ethers, lactones, and cyclic sulfides as the monomers.

More recently, iodonium salts have been widely utilized as photoinitiators in the polymerization studies of various monomeric precursors, such as: copolymerization of butyl vinyl ether and methyl methacrylate by combination of radical and radical promoted cationic mechanisms (Braun *et al.*, 2001), thermal and photopolymerization of divinyl ethers (Chen *et al.*, 2007), photopolymerization of vinyl ether networks using an iodonium initiator (Chen *et al.*, 2009; Cook *et al.*, 2009), dual photo- and thermally initiated cationic polymerization of epoxy monomers (Crivello & Bulut, 2006), preparation and properties of elastomers based on a cycloaliphatic diepoxide and poly(tetrahydrofuran) (Hartwig & Sebald, 2003), photo-induced crosslinking of divinyl ethers (Kahveci *et al.*, 2008), cationic photopolymerization of 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane (Lazauskaite *et al.*, 1998), preparation of interpenetrating polymer network hydrogels based on 2-hydroxyethyl methacrylate and *N*-vinyl-2-

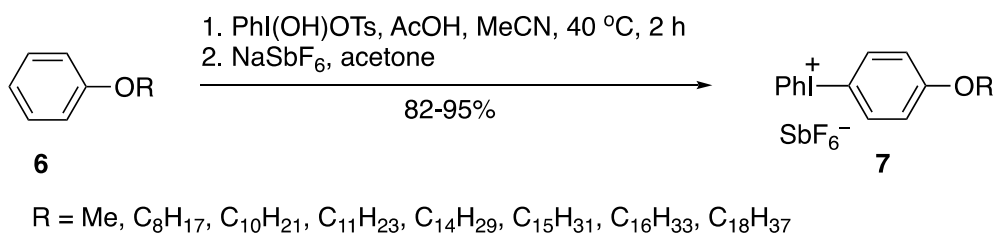
pyrrolidone (Wang *et al.*, 2010), photopolymerization of unsaturated cyclic ethers (Zhu & Schnabel, 1998), and many other works.

Different initiation techniques have been investigated in the polymerizations induced by iodonium salts, such as: visible laser irradiation (Fouassier & Chesneau, 1991), dual photo- and thermally initiated cationic polymerization (Chen *et al.*, 2007; Crivello & Bulut, 2006), and two-photon photopolymerization initiation system (Li *et al.*, 2001, 2009). For example, the dual photo- and thermal initiation systems based on selective inhibition of the photoinitiated cationic ring-opening polymerization of epoxides by dialkyl sulfides have been developed (Crivello & Bulut, 2006). Such a dual system, iodonium salt/dialkyl sulfide, in the presence of a monomer can be activated by UV irradiation and then subsequently be polymerized by the application of heat. It is proposed that dialkyl sulfides terminate the initial or growing polyether chains at an early stage to form stable trialkylsulfonium salts. These systems are dormant at room temperature but on heating, the sulfonium salts are capable of reinitiating ring-opening polymerization. These dual photo- and thermal cure systems have potential applications in adhesives, potting resins, and composites (Crivello & Bulut, 2006). Another initiation system, the two-photon photopolymerization initiation system, consists of a photosensitizer dye and the photoinitiator diaryliodonium salt encapsulated by methylated- β -cyclodextrin (Li *et al.*, 2009). Such a complex can be used as an effective photoinitiator for two-photon photopolymerization in an aqueous system.

Numerous publications have been devoted to the development of the more efficient photoinitiators based on iodonium salts. In contrast to the original observations of Crivello that neither cationic part of iodonium salt, nor the counter ions have effect on the photodecomposition of diaryliodonium salts (Crivello & Lam, 1977), it has been demonstrated that both anionic and cationic portions of iodonium salts may play an important role in the overall effectiveness of the photoinitiator. Park and co-workers have published a detailed study on the participation of the anion and alkyl substituent of diaryliodonium salts in photo-initiated cationic polymerization reaction of epoxides (Park *et al.*, 2006). It was found that the alkyl substituted diphenyliodonium cations, such as bis(4-*tert*-butyl-phenyl)iodonium and 4-cumenyl-4'-tolyliodonium salts, have higher photoacid generation efficiency compared to the unsubstituted diphenyliodonium salts. The lower nucleophilicity and large volume size of the anions plays a decisive role in enhancing the rate of polymerization, with the general order of reactivity found to be $\text{PF}_6^- < \text{AsF}_6^- < \text{B}(\text{C}_6\text{F}_5)_4^-$ (Park *et al.*, 2006). In general, the larger the anion is, the more loosely it is bound to the end of the growing cationic chain, and the more active the propagating cationic species is in the polymerization. For this series, $\text{B}(\text{C}_6\text{F}_5)_4^-$ is the largest anion and the most loosely bound, while PF_6^- is the smallest and, therefore, the most tightly bound anion. For comparison, in the case of the most nucleophilic trifluoromethanesulfonate anion, cationic polymerization of epoxides was not observed (Park *et al.*, 2006).

Crivello and Lee described the synthesis and characterization of a series of (4-alkoxyphenyl)phenyliodonium salts **7**, which are excellent photo- and thermal initiators for the cationic polymerization of vinyl and heterocyclic monomers (Crivello & Lee, 1989). Iodonium salts **7** are conveniently prepared by the reaction of alkoxyphenols **6** with [hydroxy(tosyloxy)iodo]benzene followed by the anion exchange with sodium hexafluoroantimonate (Scheme 2). Products **7** have very good solubility and photoresponse characteristics, which make them especially attractive for use in UV curing applications. Compounds **7** with alkoxy chains of eight carbons and longer are

essentially nontoxic, compared to diphenyliodonium hexafluoroantimonate, which has an oral LD₅₀ of 40 mg/kg (rats) (Crivello & Lee, 1989).



Scheme 2.

Shirai, Kubo, and Takahashi have prepared and examined a series of new substituted diaryliodonium hexafluorophosphates aiming at improved solubility and lower toxicity of the photoinitiators (Shirai *et al.*, 2002). The alkyl substituted iodonium salts **8** -**13** (Fig.1) in combination with 2-ethyl-9,10-dimethoxyanthracene as the photosensitizer demonstrated especially high photocuring ability.

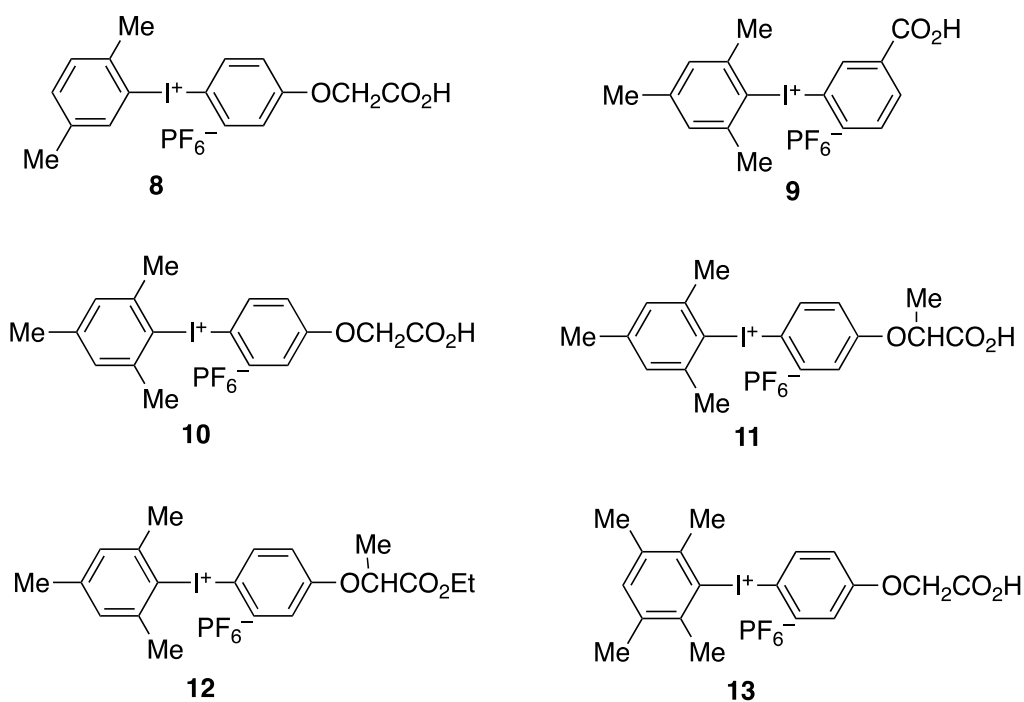
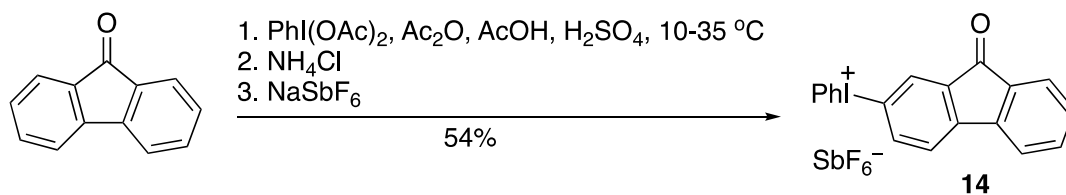


Figure 1. Efficient photoinitiators with high solubility and low toxicity.

Preparation and properties of (9-oxo-9H-fluoren-2-yl)-phenyliodonium hexafluoroantimonate **14** as a new photoinitiator for the cationic polymerization of epoxides have been reported (Hartwig *et al.*, 2001). Compound **14** was prepared by the reaction of (diacetoxyiodo)benzene with fluorenone followed by treatment with sodium hexafluoroantimonate (Scheme 3). Photoinitiator **14** has the advantage of intramolecular photosensitization, and it is a more effective initiator compared to the conventional iodonium salts.



Scheme 3.

An alkynyliodonium salt, namely phenyl(phenylethynyl)iodonium hexafluorophosphate, has been tested for application as cationic photoinitiator (Hoefer & Liska, 2009). High activity of phenyl(phenylethynyl)iodonium salt as a photoinitiator was verified by photo-DSC experiments in direct irradiation and in photosensitized initiation using 9,10-dibutylanthracene, 2-isopropylthioxanthone, and benzophenone as sensitizers.

Neckers and co-workers have prepared diaryliodonium butyltriphenylborate salts **15** - **18** (Fig.2) by the anion exchange of respective diaryliodonium halides with tetramethylammonium butyltriphenylborate and investigated their reactivity as photoinitiators for the polymerization of acrylates (Feng *et al.*, 1998). Butyltriphenylborate salts **15** - **18** were found to be more efficient photoinitiators than iodonium tetraphenylborate salts, Ar_2IBPh_4 . It was found from a study of the photoreaction of iodonium borate salts with a model monomer, methyl methacrylate, that iodonium butyltriphenylborate salts **15** - **18** simultaneously produce a butyl radical from the borate anion and an aryl radical from the iodoniumcation upon irradiation. Both radicals initiate polymerization. Iodonium tetraphenylborate salts, Ar_2IBPh_4 , were found to release an aryl radical, but only from the iodoniumcation. Iodonium borate salts exhibit strong absorption below 300 nm with tail absorption above 400 nm. Thus, iodoniumbutyltriphenyl borate salts **15** - **18** are efficient photoinitiators even when used with visible light (Feng *et al.*, 1998).

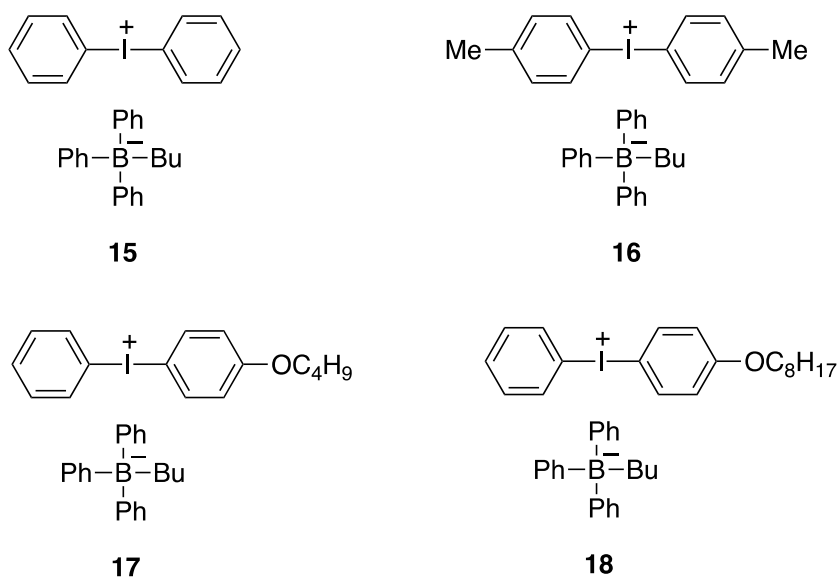
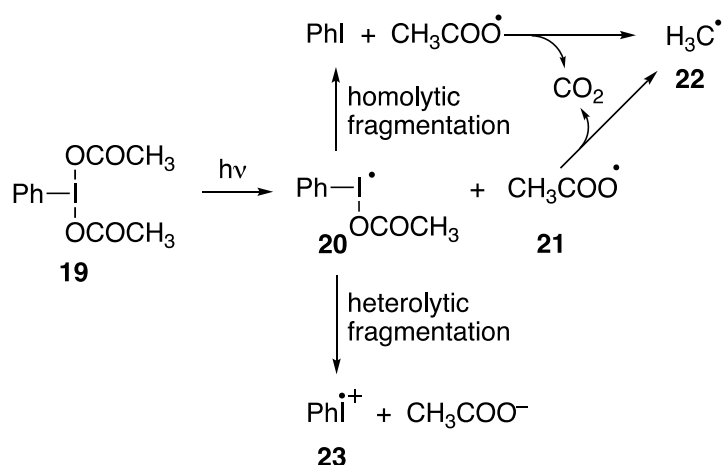


Figure 2. Photoinitiators based on diaryliodonium butyltriphenylborate salts.

3. [Bis(acyloxy)iodo]arenes as radical initiators

In 1985, Georgiev, Spyroudis, and Varvoglis have first reported that [bis(acyloxy)iodo]arenes, such as $\text{PhI}(\text{OAc})_2$ and $\text{PhI}(\text{OCOCF}_3)_2$, are effective photoinitiators of cationic and radical polymerization (Georgiev *et al.*, 1985). In particular, under photochemical conditions $\text{PhI}(\text{OAc})_2$ and $\text{PhI}(\text{OCOCF}_3)_2$ are efficient initiators for the homopolymerizations of 2-(dimethylaminoethyl)methacrylate (DMAEM) and methyl methacrylate (MMA) and also for the copolymerizations of DMAEM with MMA or styrene (Georgiev *et al.*, 1985, 1992). The proposed mechanism for the photoinitiation involves initial homolytic decomposition of [bis(acyloxy)iodo]arene, e.g., $\text{PhI}(\text{OAc})_2$ **19**, producing acyl **21** and iodanyl **20** radicals (Scheme 4) (Georgiev *et al.*, 1987, 1992, 1999, 2001; Khristov *et al.*, 1991). The actual initiators of radical polymerization are methyl radicals **22** generated by the decarboxylation of acyl radical **21**, as has been proved by the radical scavenger method (Alberti *et al.*, 1989). It was proposed that the iodanyl radical **20** can further undergo both homolytic and heterolytic decomposition; homolytic fragmentation produces additional acyl and methyl radicals, while the phenyliodidecation–radical **23**, which is a precursor of the true cationic initiator (Georgiev, 1999).



Scheme 4.

Georgiev has reported a photoiniferter ability for [bis(acyloxy)iodo]arenes during the bulk polymerization of methyl methacrylate, styrene and *N*-vinylpyrrolidone (Georgiev, 1999). The term "photoiniferter" refers to a chemical compound that has a combined function of being a free radical initiator, transfer agent, and terminator in photolytically induced polymerization (Otsu *et al.*, 1982). Under visible light [bis(acyloxy)iodo]arenes initiate the "pseudoliving" radical polymerization, while a conventional radical or cationic polymerization are the consequences of the iodane decomposition under UV irradiation. It is suggested that the spectral selectivity of the iodanyl radical **20** (Scheme 4) decomposition and the relative instability of the ends of the iodane macromolecule are the reasons of this unusual iodane ability (Georgiev, 1999).

The acetoxy groups in (diacetoxyiodo)benzene can exchange with methacrylic acid in various solvents yielding [acetoxy(methacryloyloxy)iodo]benzene or

(dimethacryloyloxyiodo)benzene. These two iodanes can serve as inimers due to the presence of polymerizable moiety and the easy generation of radicals upon thermal or light-induced homolysis of the I–O bonds (Han & Tsarevsky, 2012). When $\text{PhI}(\text{OAc})_2$ is added to mixtures of methacrylic acid and methyl methacrylate, and upon heating to 80°C , branched or transiently crosslinked polymers are formed. In contrast, when homopolymerization of methyl methacrylate is initiated by $\text{PhI}(\text{OAc})_2$ in the absence of the monomer with carboxylic acid group, no branching or gelation is observed (Han & Tsarevsky, 2012).

Tsarevsky has found that hypervalent iodine compounds can be used for direct azidation of polystyrene and consecutive click-type functionalization (Tsarevsky, 2010). In particular, polystyrene can be directly azidated in 1,2-dichloroethane or chlorobenzene using a combination of trimethylsilylazide and (diacetoxyiodo)benzene. 2D NMR HMBC spectra indicate that the azido groups are attached to the polymer backbone and also possibly to the aryl pendant groups. Approximately one in every 11 styrene units can be modified by using a ratio of $\text{PhI}(\text{OAc})_2$ to trimethylsilylazide to styrene units of 1 : 2.1 : 1 at 0°C for 4 hours followed by heating to 50°C for 2 hours in chlorobenzene. The azidated polymers have been further used as backbone precursors in the synthesis of polymeric brushes with hydrophilic side chains via a copper-catalyzed click reaction with poly(ethyleneoxide) monomethyl ether 4-pentynoate (Tsarevsky, 2010).

4. Iodosylbenzene/Pseudohalide-Based Initiators for Radical Polymerization

Tsarevsky and Han have utilized exchange reactions involving hypervalent iodine compounds for the direct synthesis of azide-containing linear and branched polymers (Han & Tsarevsky, 2014). Specifically, a method for the preparation of azide-containing linear and branched polymers was developed based on the efficient exchange of the acetoxy ligands in (diacetoxyiodo)benzene with azide in the presence of sodium azide. The in situ generated azide-containing hypervalent iodine(III) compounds, $\text{PhI}(\text{N}_3)\text{OAc}$ and $\text{PhI}(\text{N}_3)_2$ rapidly decompose at temperatures close to ambient, to iodobenzene and azide (and also acetoxy and/or methyl) radicals. The reactive azide radicals initiate the polymerization of methyl methacrylate at $40\text{--}100^\circ\text{C}$, yielding polymers with an azide functionality at the α -terminus. Fast termination by coupling of the propagating radicals with azide radicals and possibly azide transfer from hypervalent iodine azides are responsible for the formation of low-molecular-weight linear polymers with an azide group at the ω -end. If the polymerization is carried out in the presence of divinyl compounds (crosslinkers), highly branched polymers are produced prior to gelation. The use of the hypervalent iodine azide initiating system proved to be an efficient one-pot route to mono- and diazide-capped linear or multi-azidated branched polymers that could be easily functionalized, for example, under azide-alkyne 'click' coupling conditions with alkynes, such as propargyl 4-(1-pyrenyl)butyrate.

Very recently, this methodology was extended to various other (pseudo)halides (Kumar *et al.*, 2018). It has been found that iodosylbenzene reacts with various (pseudo)halides, such as: (trimethylsilylazide or isocyanate or potassium azide, cyanate, and bromide) to yield unstable hypervalent iodine (III) compounds, PhIX_2 (X = azide, isocyanate, cyanate, or bromide), which undergo rapid homolysis of the hypervalent

I–X bonds and generate pseudohalide radicals initiating the polymerization of styrene, (meth)acrylates, and vinyl esters. Polymers are formed containing (pseudo)halide functionalities at the α -chain end but, depending on the termination mechanism and the occurrence of transfer of (pseudo)halide groups from the initiator to the propagating radicals, also at the ω -chain end. With slowly polymerizing monomers (styrene and methyl methacrylate) and initiators that were generated rapidly at high concentrations and were especially unstable, the reactions proceed via a “dead-end” polymerization mechanism, and only low to moderate monomer conversions are attained. When the initiator is generated more slowly and continuously throughout the polymerization (using the combination of iodosylbenzene with the poorly soluble potassium (pseudo)halide salts), typically higher conversions and higher molecular weights are reached.

5. Conclusion

Summarized in this review publications demonstrate a great potential of hypervalent iodine compounds as polymerization initiators and promoters of various types. In particular, diaryliodonium salts are useful industrial photoinitiators for cationic photopolymerizations. [Bis(acyloxy)iodo]arenes can be used as efficient initiators for radical polymerization of alkenes. And finally, the recent study of the iodosylbenzene/pseudohalide-based systems has demonstrated that these systems are valuable initiators for the direct synthesis of various pseudohalide-containing linear and branched polymers.

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