HYPERVERALENT IODINE COMPOUNDS WITH HALOGEN-CONTAINING AND PHOSPHINATE LIGANDS

yakun cao
yakunc@smu.edu

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HYPERVALENT IODINE COMPOUNDS WITH HALOGEN-CONTAINING AND PHOSPHINATE LIGANDS

Approved by:

Prof. Nicolay V. Tsarevsky
Associate Professor of Chemistry

Prof. Isaac Garcia-Bosch
Assistant Professor of Chemistry

Prof. David Y. Son
Professor of Chemistry

Prof. Brian Zoltowski
Associate Professor of Chemistry

Prof. Mihaela C. Stefan
Eugene McDermott Professor of Chemistry
(University of Texas at Dallas)
HYPERVALENT IODINE COMPOUNDS WITH HALOGEN-CONTAINING AND
PHOSPHINATE LIGANDS

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Partial Fulfillment of the Requirements
for the degree of
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with a
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by
Yakun Cao

B.A., Applied Chemistry, Shandong University, China

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In modern organic chemistry, hypervalent (HV) iodine(III) compounds have been used widely as oxidizing agents but applications of \( \lambda^3 \)-iodanes in polymer and material chemistry is still underexplored. In the first project, a new series of heterocyclic HV iodine(III) compounds with I–Cl bonds and various substituents at the N atom were synthesized and successfully employed in the synthesis of highly branched polymers when added to mixtures of styrene and 1,4-divinylbenzene containing 10–80 mol% of the divinyl crosslinker, or even pure crosslinker. HV iodine(III) also can be utilized for polymer modification. HV iodine(III) compounds with fluorine-containing ligands (F, CF\(_3\), C\(_6\)F\(_5\)CO\(_2\), or CF\(_3\)(CF\(_2\))\(_8\)CO\(_2\) (\(n\)-C\(_9\)F\(_{19}\)CO\(_2\))) reacted, in the presence of iodine or copper salts, with the double bonds in cis-1,4-polyisoprene (polyIP) to afford fluorine-containing polymers. The modified polymers showed relatively good thermal stability and high hydrophobicity, with contact angles toward water in the range of 89–116°. HV iodine(III) compound with phosphate ligand was also utilized for the modification of polyIP to prepare the phosphorus-containing material, which is promising as flame retardant.
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LIST OF ABBREVIATION

AIBN  $\alpha,\alpha'$-azoisobutyronitrile

DAIB  (diacetoxyiodo)benzene

DMAc  dimethylacetamide

DVB  divinylbenzene

HB  Hyperbranched

HV  Hypervalent

$M_{n,\text{app}}$  apparent number-average molecular weight
PHIB  [(diphenylphosphoryloxy)(hydroxy)iodo]benzene

PhIO  iodosylbenzene

SEC  size exclusion chromatography

Sty  styrene

THF  tetrahydrofuran

Togni reagent I  3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole

Togni reagent II  1-trifluoromethyl-1,2-benziodoxol-3-(1H)-one

$T_g$  glass-transition temperature
CHAPTER 1

1.1 History of Hypervalent Iodine(III) Compounds

In 1811, iodine was discovered by French chemist Bernard Courtois. Courtois was extracting sodium and potassium compounds from seaweed ash. But too much sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) was accidentally added to process the ash, and a violet-colored cloud erupted from the mass and condensed on metal objects in the room. Courtois suspected it might be a new element but lacked the laboratory equipment to establish this. He gave specimens of the new products to other scientists to continue the study, including J. L. Gay Lussac, the most distinguished French chemist of his day. Lussac suggested the name “iode”, meaning "violet-colored,” reflecting the characteristic lustrous, deep purple color of resublimed crystalline iodine as well as the color of its vapor.\textsuperscript{1} In 1813, the British chemist Sir Humphry Davy recognized it as an element analogous to chlorine and anglicized the name “iodine”.\textsuperscript{2} Today, iodine is mainly obtained from deposits of sodium iodate (NaIO\textsubscript{3}) and sodium periodate (NaIO\textsubscript{4}) in Chile and Bolivia. It is well known that iodine plays an important role in thyroid hormone production in humans as well as in all vertebrates. Iodine deficiency can lead to serious health problems, such as goiter (enlarged thyroid gland), intellectual disability, and cretinism.\textsuperscript{3}
The organic iodine compounds have been developed and used in various reactions since the mid 1800's, such as Hofmann’s alkylation of amines, the Williamson ether synthesis, and the Wurtz coupling reactions. Iodine is classified as a halogen—a subset of very chemically reactive elements (Group 17 on the periodic table) that exist in the environment as compounds rather than as pure elements. The other halogens include fluorine (F), chlorine (Cl), bromine (Br), and astatine (At). In contrast with the F, Cl, Br, iodine possess higher polarity and less electronegativity that make the formation of stable polyvalent organic iodine compound possible.

In 1886, German chemist Willgerodt prepared the first stable polyvalent organic iodine compound, (dichloroiodo)benzene (PhICl₂). After that, a variety of polyvalent iodine compounds, such as (diacetoxyiodo)benzene (PhI(OAc)₂), iodosylbenzene (PhIO) and diaryliodonium salts, were prepared in a short time. As Figure 1-1 shown, PhIO was synthesized by the hydrolysis of PhICl₂ with basic solutions. The most important and well investigated organic polyvalent iodine compound, PhI(OAc)₂, was synthesized by reacting PhIO with a mixture of acetic acid and peracetic acid.
By 1914, Willgerodt prepared various polyvalent iodine(III) and iodine(V) compounds and investigated their chemical and physical properties. Up to today, the preparation, physicochemical characterization, chemical reactivity, and application of polyvalent iodine compounds, have been well summarized.\textsuperscript{4,8-13}

### 1.2 General Structural Aspects

In 1916, Kössel\textsuperscript{14} and Lewis\textsuperscript{15} developed an important theory of chemical combination between atoms known as the electronic theory of chemical bonding. They demonstrated that main group elements tend to bond either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons to have eight electrons in its valence shell, which is known as “octet rule”. However, the existence of polyvalent iodine(III), iodine(V) and iodine(VII) compounds seemed to contradict the octet rule. The exceeded valence numbers in polyvalent iodine compounds was initially described as “promotion” of one or more p- or even s-
electrons (total number of n) to one or more vacant d-orbitals, followed by the formation of hybrid sp³dⁿ orbitals.¹⁶ In 1951, the idea of a three-center-four-electron (3c-4e) bond was independently proposed to explain the bonding by G. C. Pimentel¹⁷ and R. E. Rundle.¹⁸ According to the fundamental description of the 3c-4e bond for L–X–L, one pair of bonding electrons is delocalized to the two ligands L that resulted in the charge distribution of almost −0.5 on each ligand and +1.0 on the central atom X. In 1969, the term “hypervalent (HV) bonds” was introduced by Musher¹⁹ to describe those bonds formed by using doubly-occupied lone-pair orbitals, which was later supported by theoretical studies from Kutzelnigg²⁰ in 1984 and Reed²¹ in 1990. The σ-bonding in higher main group elements (those beyond period 2) is significantly ionic and that d-orbitals are not directly involved in bonding. As Figure 1-2 shown, the formation of 3c-4e HV bonds involves a main-group atom X having at least one lone pair and two atoms or groups, namely ligands, each possessing a single electron on a p-orbital (L¹ and L²).⁴

![Figure 1-2. Hypervalent bonds between a central atom X and ligands L¹ and L².](image)

A 5p orbital of iodine atom overlaps with the two orbital of each X atom to give a bonding (Ψ₁), a nonbonding (Ψ₂, HOMO), and an antibonding (Ψ₃, LUMO) (Figure 1-2). The four available bonding electrons populate the first two molecular orbitals and the net result is that the two ligands L receive a partial negative charge, while the central atom X becomes electrophilic due to partial positive charge. Because of the polarized nature of the 3c-4e bond, ligands with
higher electronegativity, such as F, Cl, O, N and so on, tend to bond to the central HV atom and form stable hypervalent compounds.\textsuperscript{20, 22}

Hypervalent (HV) iodine compounds are commonly named according to N-X-L nomenclature,\textsuperscript{23} where “N” represents the number of electrons formally assigned to the central atom (X), and “L” represents the number of ligands bonded to it. Most of the HV iodine compounds can be therefore classified as 10-I-3 (iodine(III)) and 12-I-5 (iodine(V)), but representatives of other groups are also shown in Figure 1-3. Iodanes are designated as \(\lambda^3\)- and \(\lambda^5\)-iodanes based on the lambda convention set forth by the 1983 IUPAC recommendations\textsuperscript{24} that state that heteroatoms with nonstandard valence states (n) are named with \(\lambda^n\) notation. For example, 10-I-3 compounds are referred to as \(\lambda^3\)-iodanes.

![Figure 1-3. Most common classes of HV iodine compounds.](image)

1.3. Reactivity of HV Iodine(III) Reagents

HV iodine(III) compounds participate in three main types of reactions, i.e., ligand exchange, reductive elimination, and ligand coupling. Ligand exchange reactions of \(\lambda^3\)-iodanes are mostly affected by the nature of substrates and solvents, but the general rule of “the better leaving group” similar to \(S_N\) reactivity at carbon centers is always observed in the ligand transfer process. Two possible reactions patterns, i.e., associative and dissociative pathways, were proposed based on mechanisms similar to \(S_N1\) and \(S_N2\) reactions, as shown in Figure 1-4.\textsuperscript{25, 26} In the dissociative
pathway, a nucleophile first adds to the electrophilic iodine center affords the 8-I-2 cationic intermediates [ArIL]^+, followed by isomerization and elimination process. The formation of low stability of di-coordinated iodonium ion [ArIL]^+ indicated the dissociative pathway is less likely to occur. The associative pathway of ligand exchange starts from the addition of a nucleophile to the positively charged iodine atom of a λ3-iodane with the initial formation of a trans HV 12-I-4 square-planar species, which then isomerizes to generate the cis 12-I-4 square-planar intermediate and eliminates the ligand to afford the new HV species. In general, the 3c-4e HV iodine(III) bonds are longer and less stable in comparison with the regular covalent bonds. The homolytic dissociation can be triggered by heating, irradiation, or sonication.26

![Figure 1-4. Two pathways of ligand exchange reactions of HV compounds.](image)

1.4. Applications of HV Iodine Compounds for Polymer Synthesis and Modification

1.4.1. Synthesis of Polymers by HV Iodine(III) Compounds

HV iodine(III) compounds, which have been extensively utilized as oxidants and electrophilic reagents in organic synthesis,9 are increasingly used in the polymer chemistry. In 1977, Crivello and Lam27 investigated the utilization of iodonium salts with complex metal halide
anions (BF\textsubscript{4}\textsuperscript{−}, PF\textsubscript{6}\textsuperscript{−}, AsF\textsubscript{6}\textsuperscript{−}, or SbF\textsubscript{6}\textsuperscript{−}) as efficient photoinitiators in the cationic polymerization of a wide variety of monomers among which are included olefins (styrene, α-methylstyrene, vinyl ethers), cyclic ethers (epoxides, tetrahydrofuran, 1,3,5-trioxane), cyclic sulfides, cyclic acetals, and lactones, as shown in Figure 1-5.

![Figure 1-5](image)

**Figure 1-5.** (a) Structures of diaryliodonium salts that have been used as photoinitiators, (b) various monomers used for polymerization.

As Scheme 1-1 shown, the mechanism for the photolysis of diaryliodonium salts was also proposed. The major pathway involves the facile decomposition of the excited iodonium compound I to aryliodo radical cation II, aryl radical III, and anion IV. Interaction of the aryliodo radical cation II with the solvent (S–H) generates a protonated iodoaromatic compound V that rapidly deprotonates, and a radical S• derived from the solvent. They also found that the BF\textsubscript{4}\textsuperscript{−}, PF\textsubscript{6}\textsuperscript{−}, AsF\textsubscript{6}\textsuperscript{−}, or SbF\textsubscript{6}\textsuperscript{−} counter ions associated with the diaryliodonium salts remain unchanged during the photolysis process, and appear in the products as the corresponding Brønsted acids that work as real photoinitiators when diaryliodonium salts are utilized in the cationic photopolymerization of various monomers.
The effects of different anions on the photolysis rates of two diaryliodonium salts with same cations were also been investigated. The analogous BF$_4^-$, PF$_6^-$, AsF$_6^-$ or SbF$_6^-$ salts showed the same photolysis rates, i.e., the anion plays no role in determining the photosensitivity of the iodonium salts. The effect of variations in cation structure on their relative photolysis rates was also studied. Only minor variations in the rates of photolysis of these compounds were observed. In contrast to this, Park and co-workers have demonstrated that both anionic and cationic portions of iodonium salts may play an important role in the overall effectiveness of the photoinitiator.$^{28}$

As Scheme 1-2 shown, they investigated the photo-initiated cationic polymerization of epoxides using diaryliodonium salt bearing alkyl groups and anions. The alkyl-substituted diphenyliodonium cations, such as bis(4-tert-butyl-phenyl)iodonium and 4-cumenyl-4'-tolyliodonium salts, showed higher protic acid generation efficiency in comparison with the unsubstituted diphenyliodonium salts. The lower nucleophilicity and huge volume size of the anions were found to influence the propagation period and final conversion in the polymerization, i.e., 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. Consequently, the cationic polymerization rate follows the following order, PF$_6^-$ $<$ AsF$_6^-$ $<$ B(C$_6$F$_5$)$_4^-$.
Scheme 1-2. Photo-initiated cationic chain polymerization of epoxides.

The development of more efficient photoinitiators based on iodonium salts has attracted much attention. As Figure 1-6a shown, a series of substituted diaryliodonium hexafluorophosphates aiming at improved solubility and lower toxicity of the photoinitiators were also prepared.\(^\text{29}\) The alkyl substituted iodonium salts that combined with 2-ethyl-9,10-dimethoxyanthracene as the photosensitizer showed especially high photocuring ability. As Figure 1-6b shown, Neckers and co-workers\(^\text{30}\) developed a variety of diaryliodonium butyltriphenylborate salts, which were found to be more efficient photoinitiators for the polymerization of acrylates than iodonium tetrphenylborate salts, Ar₂IBPh₄. In addition, iodonium borate salts exhibit strong absorption below 300 nm with tail absorption above 400 nm, which indicates that these salts can be used as efficient photoinitiators under visible light.

Figure 1-6. Photoinitiators based on (a) diaryliodonium hexafluorophosphates, and (b) diaryliodonium butyltriphenylborate salts.
$\lambda^3$-iodanes can also be used as a photo- and thermal- initiator for cationic and (mostly) radical polymerization. In 1985, Georgiev and coworkers firstly demonstrated the application of PhI(OAc)$_2$ and PhI(OCOCF$_3$)$_2$ as photoinitiators for cationic polymerization of butyl vinyl ether in presence of UV light.$^{31}$ In 1992, Georgiev and coworkers further investigated the homo- and copolymerization of methyl methacrylate, 2-(dimethylaminoethyl)methacrylate, and styrene by using PhI(OAc)$_2$ and PhI(OCOCF$_3$)$_2$ as efficient photoinitiators.$^{32}$ The proposed mechanism for the photoinitiation involves initial homolytic decomposition of PhI(OAc)$_2$, producing iodanyl radical 1 and acyl radical 2 (Scheme 1-3). The actual initiators of radical polymerization are methyl radical 3 generated by the decarboxylation of acyl radical 2, which has been proved by the radical scavenger method. The iodanyl radical 1 can further undergo both homolytic and heterolytic decomposition. The homolytic fragmentation produces additional acyl radical 1 and methyl radical III, while heterolytic fragmentation generates phenyliodide cation 4, which is a precursor of the true cationic initiator.

**Scheme 1-3.** Photodecomposition of PhI(OAc)$_2$.
Recently, the iodosylbenzene-pseudohalide based initiators and utilized them for radical polymerizations of various vinyl monomers was also reported. The unstable HV iodine compounds, which generated in situ by the reaction of iodosylbenzene (PhIO) and various (pseudo)-halides (trimethylsilyl azide or isocyanate or potassium azide, cyanate, and bromide), were easily dissociated to form the (pseudo)halide radicals that initiated the polymerization of styrene, (meth)acrylates and vinyl esters. As Scheme 1-4 shown, depending on the termination mechanism and the occurrence of transfer of (pseudo)halide groups from the initiator to the propagating radicals, (pseudo)halide functionalities can be introduced at α-chain ends and ω-chain ends.

Scheme 1-4. Polymerization of vinyl monomers initiated by the iodosylbenzene-pseudohalide system and formation of pseudohalide-capped polymers.
Most reactions of $\lambda^3$-iodanes with general formula PhIL$_2$, where L represents a ligand attached to central iodine atom, involve the initial exchange of ligands on the iodine atom with an external nucleophile. As Scheme 1-5a shown, by taking advantage of this reaction, Ph(IOAc)$_2$ was used to exchange with methacrylic acid in various solvents to yield the products, [(acetoxy methacryloyloxy)iodo]benzene and (dimethacryloyloxy)iodobenzene. These two in situ formed HV iodine(III) compounds that containing both polymerizable and initiating moieties acted as inimers for self-polymerization as shown in Scheme 1-5b. Branched and transiently crosslinked polymers were prepared by heating a mixture of PhI(OAc)$_2$, methacrylic acid, and methyl methacrylate.

Scheme 1-5. (a) Exchange of acetoxy groups in PhI(OAc)$_2$ with methacrylic acid. (b) Branched and transiently crosslinked polymers prepared by HV iodine based inimers.
Our group also developed a new approach to azide-containing linear and branched polymers by using exchange reaction of PhI(OAc)$_2$ with NaN$_3$. The in situ generated unstable azide containing HV iodine(III) compounds, PhI(N$_3$)(O$_2$CCH$_3$) and PhI(N$_3$)$_2$, decomposed rapidly event at ambient temperature to form monovalent iodobenzene and azide radicals. The radical polymerization of methyl methacrylate was initiated by the azide radicals to yield the polymers with azide functionalities at the $\alpha$-terminus (Scheme 1-6). In the presence of divinyl compounds, namely crosslinker, azide-containing highly branched polymers were prepared successfully and further functionalized by “click” coupling reaction with pyrenyl 4-pentynoate to afford polymers with multiple fluorescent pyrene moieties at chain ends.

**Scheme 1-6.** Ligand exchange of PhI(OAc)$_2$ with NaN$_3$. Formation of highly branched multiazidated polymers and further functionalized by “click” coupling reaction.
Recently, our group prepared network polymers with (diacyloxy)iodoarene-type crosslinks by employing ligand-exchange reaction of PhI(OAc)$_2$ and linear polymers bearing multiple carboxylate pendant groups (copolymers of styrene and acrylic acid), as shown in Scheme 1-7. The obtained polymer materials showed dynamic and self-healing properties due to the presence of unreacted carboxylate groups in the polymers that can participate in further ligand-exchange reactions with the HV iodine(III) centers at the crosslinks. Under light or heat conditions, the dynamic network converted to permanent due to the homolytic cleavage of the weak HV I–O bonds present at the crosslinks, followed by irreversible radical coupling of adjacent polymer-bound C- and/or O-centered radicals.

**Scheme 1-7.** Preparation of dynamic network polymers by ligand-exchange reactions with PhI(OAc)$_2$, curing of the gels using light or heat, and conversion of the dynamic to permanent network.
HV iodine(III) compounds were not only used as initiators but also crosslinkers for preparing polymers. Recently, our group synthesized an HV iodine(III)-containing crosslinker, (diacyloyloxyiodo)benzene (PhI(OAcr)₂),\(^{36}\) and copolymerized it with tert-butyl acrylate to yield the soluble highly branched polymers under reversible deactivation radical polymerization conditions (Scheme 1-8). The obtained branched polymers were responsive and react with monocarboxylic acids due to the (diacyloyloxyiodo)benzene-type linkers. In addition, by reaction with reducing agents, for instance, tributylphosphine, iodine(III) were converted to iodine(I), and polymer degraded with the formation of random linear copolymers of tert-butyl acrylate and acrylic acid.

**Scheme 1-8.** Synthesis of branched polymers with HV iodine(III) groups at the branching points. Degradation of branched polymers with HV iodine(III)-based crosslinks in the presence of reducing agents or carboxylic acids.
1.4.2. Post-Polymerization Modifications of Polymers by HV Iodine(III) Compounds

HV iodine(III) compounds are mainly used as oxidizing agents in organic synthesis or initiators for radical or cationic polymerizations. The application of HV iodine(III) compounds in the post-modification of polymers also have attracted more attention. In 2010, Tsarevsky\textsuperscript{37} reported a new approach to azidated polystyrene by employing the reaction of polystyrene with a combination of PhI(OAc)\textsubscript{2} and TMSN\textsubscript{3}. It was found that approximately 1 in every 11 styrene units could be successfully modified under the optimized conditions. The azidated polystyrene was further used in copper-catalyzed click-type grafting-onto reactions using poly(ethylene oxide) monomethyl ether 4-pentyanoate as the functional alkyne to afford polymeric brushes with hydrophilic side chains (Scheme 1-9).

\textbf{Scheme 1-9.} Direct azidation of polystyrene using ligand-exchange reaction between PhI(OAc)\textsubscript{2} and TMSN\textsubscript{3} and preparation of graft copolymers using click reaction between the multiazidated product and poly(ethylene oxide) monomethyl ether 4-pentyanoate.
Bielawski and Liu\textsuperscript{38} reported the direct C-H azidation of polypropylene by using a stable azidoiodinane. The addition of imidazole or benzimidazole promoted the reaction at elevated temperatures. The high-molecular-weight ($M_w > 100$ kDa) functionalized polypropylene containing up to 3 mol\% of azido groups were afforded. Recently, Lim and coworkers\textsuperscript{39} utilized Zhdankin reagent generated in situ from iodosobenzoic acid and TMSN\textsubscript{3} with an iron catalyst to prepare azidated phenyl-terminated polybutadienes (PtPBs), as Scheme 1-10 shown. By adjusting the amount of reagents, azidated PtPBs with various azide contents (5 \%, 10 \%, and 15 \%) were prepared readily.

Scheme 1-10. Iron-catalyzed direct azidation of PtPB using the Zhdankin reagent.

Recently, we prepared the HV iodine(III) compounds with tetrazole ligands $C_6H_5I(N_4CR)_2$ (R = CH\textsubscript{3}, C\textsubscript{6}H\textsubscript{5}, and 4-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}) and utilized them in the modification of cis-1,4-polyisoprene (polyIP) with iodine to afford iodo-tetrazolylated polymers (Scheme 1-11). The alkyl-iodide groups in the products were either utilized as macro chain-transfer agents for the iodine-transfer polymerization of methyl methacrylate, which yielded brush polymers with well-defined poly(methyl methacrylate) side chains or substituted with NaN\textsubscript{3}, followed by functionalization with poly(ethylene oxide) by click chemistry. The thermal decomposition of both iodo-tetrazolylated and azidotetrazolylated polymers was exothermic, especially for the latter materials.
In conclusion, various HV iodine(III) compounds have been developed and utilized into polymer synthesis and modification. However, some of them have poor stability and/or solubility, which limit their applications into polymer field. In some cases, the modifications of polymers by HV iodine(III) are suffered from the degradation and/or crosslinking. Herein, we developed new HV iodine(III) and used them into polymer synthesis and modifications without significant degradation and/or crosslinking, as seen in the following chapters.

1.5 References


CHAPTER 2

2.1. Introduction

2.1.1. Hyperbranched Polymers

Hyperbranched (HB) polymers are a class of branched polymers where the branching repeat units have a possibility of secondary branching leading to random and highly dense polymer structures. HB polymers, compared to the linear polymers, possess various advantages, such as highly branched topological structures, abundant functional groups, intramolecular cavities, and low viscosity.\textsuperscript{1-3} The applications of HB polymers have been explored in various fields including drug delivery, bioimaging, photoelectric materials, membranes, and coatings.\textsuperscript{4-6} To date, polycondensation of AB\textsubscript{n}-type monomers remains the predominate synthetic approach in the preparation of HB polymers (Figure 2-1a).\textsuperscript{7-14} Another widely used method for the synthesis of HB polymers is chain-growth reaction that includes the homo- or copolymerization of the compound, namely inimer, which contains both initiating and polymerizable groups in the same molecule (a process dubbed self-condensing polymerization) (Figure 2-2b).\textsuperscript{15-18} The self-condensing polymerization approach has the important advantage that crosslinked gels are not formed even at high conversion, but it always required multi-steps to synthesize the inimer, which is costly and time-consuming.
Another well-developed approach is home- or copolymerization of monomers containing more than one polymerizable functionality, namely crosslinker, in the presence of agents mediating controlled/“living” polymerization,\textsuperscript{19, 20} efficient chain transfer agent (CTA),\textsuperscript{21-26} or large concentration of initiator.\textsuperscript{27-29} The addition of these reagents limits the molecular weights of the chains, i.e., the average number of polymerizable groups per chain, which finally leads to the formation of soluble HB polymers prior to the significantly delayed formation of gels. The (co)polymerization of crosslinker in the presence of CTA, which has been known for a long time,\textsuperscript{22, 30} is very attractive due to the low cost and easy preparation. The widely used CTAs include conventional transfer agents such thiols,\textsuperscript{31-33} CBr$_4$,\textsuperscript{22, 24, 34, 35} or controlling group that also imparts pseudo-livingness to the polymerization system (Scheme 2-1).\textsuperscript{36} By employing CTA to prepare the HB polymers, the functionalities originating from CTAs are incorporated at the multiple chain ends of the obtained polymers and can be easily used for further functionalization reactions.
Scheme 2-1. Copolymerization of vinyl monomers with di-vinyl crosslinker in the presence of CBr₄ as CTA, yielding multi-brominated HB polymers.²⁴

2.1.2. Development of Chlorine-Containing Hypervalent Iodine(III) Compounds

Among various functional groups, chlorine is often found in natural products and bioactive compounds, and organochlorine compounds have also been utilized as useful building blocks. Up to today, a variety of chlorine-containing HV iodine(III) compounds have been developed and utilized as chlorinating reagents.³⁷-³⁹ Among HV iodine(III) reagents with chlorine ligand, PhICl₂ is a representative reagent for chloro-functionalization of alkenes. For instance, Nicolaou and coworkers⁴⁰ reported the asymmetric dichlorination of allylic alcohols using a dimeric cinchona alkaloid derivative as a catalyst, as Figure 2-2a shown. Du and coworkers recently investigated the oxychlorination of alkenes by employing PhICl₂ in DMF,⁴¹ as seen in Figure 2-2b.
However, the cyclic chlorine-containing HV iodine(III) compound, 1-chloro-1,2-benziodoxol-3-(1H)-one (CBIO), which is more stable, has not been thoroughly studied. The reactivity of the compound toward organo-functional groups has not been examined, except in a few cases. For example, it was used as a terminal oxidant in alcohol oxidation with 2,2,6,6-tetramethylpyrrolidine N-oxide (TEMPO), as shown in Figure 2-3a. It also can be used as electrophilic chlorination reagents for chlorination of 1,2,4,5-tetramethylbenzene (durene) in acetic acid and β-dicarbonyl compounds (Figure 2-3b). In the presence of nucleophile X, CBIO would undergo rapid ligand exchange reactions to form various types of reactive species (Figure 2-3c). For example, substitution by an electronically neutral Lewis base would give a more Lewis-acidic HV iodine(III), and ligand exchange reaction followed by reductive elimination would give Cl−X species. Thus, the nature of the added nucleophile may influence the reaction pathway, opening up the possibility of obtaining unique difunctionalization products. Recently, Hamashima and coworkers reported the utilization of CBIO for difunctionalization of alkenes in the presence of various nucleophiles, such as oxy-chlorination, dichlorination, azido-chlorination, as well as chloro-thiocyanation (Figure 2-3c).
Figure 2-3. Examples of reactions of CBIO.

The analogous iodine-nitrogen heterocycles, benziodazoles, have received much less attention. In 1970, Henderson and coworkers\(^4\) first developed new chlorine-containing benziodazole-based HV iodine(III) compounds by chlorination of iodobenzenamines with chlorine gas (Scheme 2-2). Those compounds were tested against a range of viral, bacterial, fungal, protozoal, and helminth organisms but none showed an interesting level or type of activity. Thus, work in this series was discontinued.

Scheme 2-2. Examples of heterocyclic HV iodine(III) compounds (benziodazoles).
HV iodine(III) compounds of the type ArIL$_2$ (Ar = aryl, L = ligand, such as (pseudo)halide or carboxylate), under heating or irradiation, decompose to generate iodoarene ArI and the radicals L$^\cdot$ that can initiate radical polymerization of various monomers. In addition, some ArIL$_2$ compounds, i.e., those with (pseudo)halide ligands, can participate in radical transfer reactions with C-centered radicals leading to the (irreversible) formation of C-L bonds. In other words, the mentioned HV iodine(III) compounds can not only serve as initiators of polymerization but also very efficient CTAs, and can potentially be useful for the synthesis of chain-end functionalized HB polymers. However, the applications are limited due to their poor stability. Although the benziodoxols or benziodazoles based HV iodine(III) reagents have been prepared long ago and are known to be much stable and easy to store for a prolonged time, these compounds have not received enough attention, especially in polymer chemistry. The presence of the exocyclic I-L (exocyclic) and the endocyclic I-O (in benziodoxols) or I-N (in benziodazoles) HV bonds indicates their potential to serve as efficient initiators and CTAs. However, to our knowledge, the applications of these stable HV iodine(III) compounds as radical initiators or CTAs have not yet been studied. In addition, benziodazoles are more attractive in comparison with benziodoxols due to the ease with which their solubility can be fine tuned (via selection of the substituents at the N atom).

In this chapter, we report the synthesis of benziodazoles based HV iodine(III) compounds with the easy to cleave I-Cl bonds and various substituents at the N atom. We utilized the benziodazoles as both radical initiators and very efficient CTAs for preparing highly branched polystyrene(polySty) by co- and even homopolymerization of divinylbenzene (crosslinker). We also proposed the mechanism.
2.2. Results and Discussion

2.2.1. Synthesis of Heterocyclic HV Iodine(III) Compounds (benziodazoles) with I-Cl bonds

![Scheme 2-3](image)

**Scheme 2-3.** Synthesis of heterocyclic HV iodine(III) compounds (benziodazoles) with I-Cl bonds employed as polymerization initiators and CTAs.

As mentioned above (Scheme 2-2), the benziodazoles (3a-b) were previously prepared by passing chlorine gas to the corresponding iodobenzamides (2a-b) and followed by the spontaneous dehydrochlorination in the solid-state.\(^6\) In this chapter, we developed a convenient and safer approach to 3a-d, in which instead of chlorine, sodium chlorite and concentrated HCl were used to generate chlorine\(^{51}\) in situ. Using this modified method (Scheme II-3), the targeted N-substituted benziodazolones (3a-d) were obtained in very good yields (62-70%).

2.2.2 Chain Transfer Coefficients

PhICl\(_2\) can easily transfer Cl atoms to carbon-centered radicals, and some rate constants have been reported.\(^{52}\) Here, to examine the ability of compounds 3a-d to participate in efficient
chlorine transfer reactions with propagating radicals in the polymerization process, we firstly focused on determining chain transfer coefficients (C_{CTA}) and transfer rate coefficients (k_tr) of the newly synthesized HV iodine(III) compounds 3a-d in the polymerization of styrene (Sty). The classical Mayo equation (1)\textsuperscript{53} was employed.

\[
\frac{1}{DP_{n}} = \frac{1}{DP_{n,0}} + k_{p} \frac{[CTA]}{k_{p} [M]} = \frac{1}{DP_{n,0}} + C_{CTA} \frac{[CTA]}{[M]}
\]  

(Equation 1)

DP_{n,0} and DP_{n} are respectively the number-average degrees of polymerization of a polymer obtained at low monomer (M) conversion in the absence and the presence of a CTA (at concentration [CTA]). To optimize the polymerization conditions, the polymerizations of Sty have been done at 60 °C and 80 °C. As Figure 2-4 shown, the radical polymerization of Sty at 80 °C showed an acceptable rate, while less than 10 % conversion was observed after 100 h at 60 °C due to the thermal lability of compounds 3a-d. Thus, the experiments aimed at determination of the values of C_{CTA} were conducted at 60 °C, at which no appreciable initiation by 3a-d took place, especially during short (< 20 min) periods.

![Figure 2-4. Polymerization of Sty in presence of 3d ([Sty]:[3d] = 100:1) at 60 °C and 80 °C: (a) kinetics; (b) evolution of molecular weights and dispersities.](image-url)
In all cases, azoisobutyronitrile (AIBN) was used as the thermal initiator. As Figure 2-5 shown, the transfer coefficients of 3a, 3c, and 3d were determined readily. However, the measurement of 3b could not be done due to poor solubility in pure Sty. The well-known efficient CTA, CCl₄, was also determined for comparison purposes, under identical reaction conditions.

![Mayo plots for the bulk polymerization of Sty in the presence of different CTAs at 60 °C. In all cases, the monomer conversions were below 5 %.](image)

As summarized in Table II-1, the rate coefficients for Cl transfer from HV iodine compounds 3a, 3c, and 3d, to the propagating polySty radicals, were determined as 4417, 435, and 887 M⁻¹.s⁻¹, i.e., 2-3 orders of magnitude higher than the corresponding transfer rate coefficient for CCl₄, which was found to be 3.4 M⁻¹.s⁻¹. The transfer rate coefficients were determined by using the value of the propagation rate coefficient for Sty at 60 °C (kₚ = 340 M⁻¹.s⁻¹), which was, in turn, calculated using the Arrhenius equation with the reported pre-exponential factor (A = 4.27×10⁷ L mol⁻¹ s⁻¹) and activation energy (Eₑact = 32.5 kJ mol⁻¹) for the polymerization of Sty.
The compound 3d was used in all further experiments due to its efficiency as a CTA in addition to relatively high solubility in common organic solvents.

**Table 2-1.** The chain transfer coefficients (Cₜₐ) and transfer rate coefficients (kₜₑ) of new synthesized HV iodine(III) compounds.

<table>
<thead>
<tr>
<th>#</th>
<th>CTA</th>
<th>Cₜₐ (60 °C)</th>
<th>kₜₑ (60 °C) [M⁻¹·s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CCl₄</td>
<td>0.012</td>
<td>3.4</td>
</tr>
<tr>
<td>2</td>
<td>3a</td>
<td>12.99</td>
<td>4417</td>
</tr>
<tr>
<td>3</td>
<td>3c</td>
<td>1.28</td>
<td>435</td>
</tr>
<tr>
<td>4</td>
<td>3d</td>
<td>2.61</td>
<td>887</td>
</tr>
</tbody>
</table>

### 2.2.3 Synthesis and Analysis of Linear PolySty

As Scheme 2-4 shown, under heating conditions, the benziodazoles 3a-d with thermally labile HV I-Cl bond degrade homolytically to produce Cl’ and I-centered radicals. The latter can also further degrade to yield an N-centered radical and a monovalent iodine species. The polymerization can be initiated by Cl’ and/or N-centered radicals. On the other hand, Cl’ and the N-centered radicals also participate in termination reactions by coupling with the growing polymeric radicals. Thus, the formed polymers containing alkyl chloride and amide groups, both at the α- (from initiation) and at the ω-ends (termination by coupling reaction), were expected to be observed. In addition, the formation of chlorine capped (at the ω-ends) polymers also can be attributed to the above-mentioned Cl transfer reactions.
Scheme 2-4. Proposed mechanism for the formation of linear and branched polymers in radical (co)polymerizations initiated by HV iodine(III) compounds 3, in which the same compounds served also as CTAs.

Homopolymerization of Sty was conducted in bulk at 80 °C (at which these HV iodine compounds degraded sufficiently fast) in the presence of 3d ([Sty]₀ / [3d]₀ = 25). The polymerization was terminated in 12 h (20 % conversion) to afford the low-molecular-weight linear polymer (Mₙ = 2,500 g mol⁻¹), which was characterized by ¹H NMR and IR spectroscopy.
Figure 2-6. $^1$H NMR spectra of 3d and linear polySty synthesized by using 3d as the initiator and CTA.

In the $^1$H NMR spectrum (Figure 2-6), the signals at 7.9-7.7 ppm were assigned to the aromatic protons present in the amide group (originating from radical II in Scheme 2-4) at the α- or ω-chain ends, while the aromatic protons from the pendant phenyl groups in polySty were seen in the spectral region 7.2-6.4 ppm. The resonances of benzylic proton on carbon attached to Cl at the ω-chain ends were observed at 4.6-4.3 ppm. The signals that appeared at 3.8-3.5 ppm corresponded to the methylene protons next at the Cl-capped α-terminus or amide groups (originating from radical II in Scheme 2-4). The signals observed at 1.0-0.5 ppm were related to the protons from the hexyl groups attached to the N atoms in the amide functionalities at the α- or ω-chain ends.
The FT-IR spectrum of polySty synthesized in the presence of 3d is displayed in Figure 2-7. The absorption at 1633 cm\(^{-1}\) can be assigned to the stretching vibrations of the C=O bonds (amide I band),\(^{56}\) which was absent in the spectrum of standard polySty. The C-Cl vibrations could not be discerned in the spectrum due to overlap with other bands., which are normally observed around 750-620 cm\(^{-1}\).\(^{57}\)

![FT-IR spectra of films cast on KBr plates from (top to bottom) standard, Cl-, and azide-terminated polySty (prepared at 30 °C and 60 °C).](image)

**Figure 2-7.** FT-IR spectra of films cast on KBr plates from (top to bottom) standard, Cl-, and azide-terminated polySty (prepared at 30 °C and 60 °C).

### 2.2.4. Synthesis of Azide-Terminated Linear PolySty

To gather further proof of the existence of alkyl chloride terminal groups in the linear polySty prepared by using 3d, the polySty was reacted with NaN\(_3\) in DMF at 60 °C. In the \(^1\)HNMR spectrum, the signal at 4.6-4.3 ppm that belonged to benzylidene protons at the ω-terminal carbon
atom attached to Cl, disappeared after substitution reaction and a new peak at 4.0 ppm appeared, which proved the formation of ω-azide-capped polySty (Figure 2-8). A film cast from the polymer onto a KBr plate was analyzed by IR spectroscopy (Figure 2-7). The observed absorbance at 2,100 cm⁻¹ was assigned to the asymmetric stretching vibration of azide groups, which confirmed that the nucleophilic substitution reaction was successful.

![Figure 2-8](image)

**Figure 2-8.** ¹H NMR spectra of Cl- and azide-terminated polySty (the latter being synthesized at 30 and 60 °C).

### 2.2.5. Chain Extension Reaction Under ICAR ATRP Conditions

Chain extension reactions, under initiators for continuous activator regeneration atom transfer radical polymerization (ICAR ATRP) conditions, were also carried out as another important approach to prove the presence of alkyl chloride terminal groups. The Cl-capped linear polySty (Mₙ, app = 2,500 g mol⁻¹, Mₘ/Mₙ = 1.62) was used as macroinitiator for chain extension.
reaction with Sty in the presence of CuCl₂ and TPMA as the catalyst components, and AIBN as the precursor of the reducing radicals (needed to continuously regenerate the activating Cu(I) complex). The kinetics are shown in Figure 2-9. The first-order kinetic plot of Sty consumption was linear up to moderate conversion (58 %), and that, along with the linear increase of the apparent molecular weights (Mₙ, app) with monomer conversion, accompanied with decrease in Mₙ/Mₚ, confirmed that the chain extension had the characteristics of controlled/“living” radical polymerization.

As shown in Figure 2-10, Mₙ, app increased gradually from 2,500 g mol⁻¹ to 11,300 g mol⁻¹ at 58 % conversion in 11 h. The above-mentioned azidation reaction prove the presence of alkyl chloride groups at the chain ends but failed to distinguish the alkyl chloride groups at the α- or the ω-terminus. The successful ATRP chain extension reaction proved the existence of alkyl chloride
groups specifically at the ω-chain-ends, further validating the mechanism proposed in Scheme 2-4.

![Figure 2-10](image)

**Figure 2-10.** SEC traces for the successful chain extension polymerization of the macroinitiator polySty-Cl with Sty under ICAR ATRP conditions. The numbers from left to right are chain extension time, conversion, and $M_n$.

### 2.2.6. Synthesis of Hyperbranched PolySty Using 3d as the Initiator and CTA

When divinyl crosslinkers are used to prepare HB polymers in the absence of CTAs, insoluble gels are instead produced usually extremely fast at low monomer conversion. The gelation can be significantly delayed by adding an efficient CTA to the reaction mixture; the extent, to which gelation is delayed depends upon the amount of both the crosslinker and the CTA, as well as the transfer efficiency of the latter. When the concentrate of CTA is fixed, the increase of concentration of crosslinker resulted in the increased degree of branching and macroscopic
gelation at lower conversion. Very highly branched polymers can be prepared by employing high fraction of crosslinker (relative to the total monomer amount) and may even by homopolymerization of crosslinker but the CTA must be very efficient and/or used at high concentrations. As discussed above, the new synthesized chlorine-containing benziodazoles with high transfer coefficients could be very useful as efficient CTAs, even when pure crosslinkers are polymerized. In particular, 3d, which showed high transfer coefficient and excellent solubility in non-polar media, is suitable as additive in the copolymerization of Sty and divinylbenzene (DVB) to prepare HB polymers. The compound decomposes sufficiently fast at 80 °C and its decomposition products (Cl• and the amide radical II) can initiate copolymerization of Sty and DVB to afford Cl-capped HB polymers, which, in analogy with alkyl bromide-capped HB polymers, can be further functionalized (e.g., substitution with azide followed by click reaction with alkynes or chain extension reactions under ATRP conditions to afford star polymers with branched cores).

The effect of crosslinker amount on the degree of branching was firstly examined (Table 2-3 and Figures 2-11). In one set of experiments, the concentration of 3d ([vinyl groups]₀ / [3d]₀ = 100) was fixed while the amount of DVB was varied from 10, 20, 40, 60, 80, to 100 mol% of the total vinyl groups (Sty and DVB).
Figure 2-11. Copolymerization of Sty and DVB at 80 °C with 3d as initiator and CTA ([vinyl groups]₀ / [3d]₀ = 100) and using 10, 20, 40, 60, 80 or 100 mol% DVB with respect to vinyl groups: (a) kinetics; (b) evolution of molecular weights and $M_w/M_n$.

As Figure 2-11a shown, the polymerization rates were independent of the amount of DVB. The apparent number average molecular weights ($M_{n,app}$) increased in an almost linear fashion with conversion and the molecular weight distributions (MWD) were broad, with the width increasing as the amount of DVB increased (Figure 2-11b), in accordance with the expected increase in the degree of branching. As shown in Table 2-2, at almost the same vinyl group conversion (in the range 9-12 %), the value of the MWD dispersity ($D = M_w/M_n$) of the polymers formed in the reactions containing 10, 20, 40, 60, 80, and 100 mol% of DVB were 2.3, 2.7, 3.3, 5.4, 14.9, and 15.2, respectively. When DVB was homopolymerized (no Sty), gelation only occurred at 9 %, up to which point, soluble highly branched (and with high content of pendant vinyl groups$^{24}$) were formed (entry 6 in Table 2-3).
Table 2-2. Characteristics of HB polymers prepared using 3d as initiator and CTA in the copolymerization of Sty with DVB (at various amounts of DVB) at 80 °C.

<table>
<thead>
<tr>
<th>#</th>
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<th>$M_w/M_n$ b)</th>
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a) Relative to the vinyl groups.

b) Determined by SEC calibrated using linear polySty standards and equipped with an RI detector.

Next, the effect of the amount of 3d on the outcome of the polymerization was examined systematically (Figure 2-12). In the set of experiments summarized in Table 2-3, the amount of DVB was fixed at 40 mol% relative to all vinyl groups, but the concentration of 3d was varied ($[\text{vinyl groups}]_0 / [3d]_0 = 25, 50, 100, 200$ or $400$).
Figure 2-12. Copolymerization of Sty and DVB (40 mol%) at 80 °C with various amounts of 3d: (a) kinetics; (b) evolution of molecular weights and MWD dispersities.

The polymerization rates were virtually unaffected by the amount of 3d (Figure 2-12a). However, the amount of 3d impacted the MWD (Figure 2-12b), i.e., as the concentration of 3d increased, the MWDs became narrower. For example, for the experiments where [vinyl groups]₀ / [3d]₀ = 100, the value of Δ was 6.3 (at 14 % conversion) but as the concentration of 3d was doubled, the HB polymers had a narrower MWD (Δ = 5.5 at 15 % conversion), and when it was quadrupled the MWD was narrower still (Δ = 3.8 at the same conversion), as seen in Table 2-3 (entries 1–3).

As expected, with higher concentrations of 3d, the gelation was delayed to higher monomer conversions. Thus, at [vinyl groups]₀ / [3d] = 400, macroscopic gelation was observed in less than 4 h at 10 % conversion but a 16-fold increase of the amount of 3d ([vinyl groups]₀ / [3d] = 25) made it possible to produce soluble HB polymers up to 30 % monomer conversion, which occurred in more than 12 h (entries 1–5 in Table 2-4).
Table 2-3. Characteristics of HB polymers prepared by the copolymerization of Sty and DVB (40 mol% of DVB) at 80 °C using various amounts of 3d.

<table>
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<th>#</th>
<th>[vinyl groups]₀ / [3d]₀</th>
<th>Time [h]</th>
<th>Conversion</th>
<th>Mₙ, app [g mol⁻¹] b)</th>
<th>Mₓ/Mₙ b)</th>
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<td>6,800</td>
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<tr>
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<td>0.14</td>
<td>9,500</td>
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<td>0.18</td>
<td>14,000</td>
<td>16.5</td>
</tr>
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<td>7.5</td>
<td>gel</td>
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<tr>
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<td>4</td>
<td>0.11</td>
<td>15,800</td>
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<td>0.13</td>
<td>16,800</td>
<td>12.2</td>
</tr>
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<td>gel</td>
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<tr>
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<td>gel</td>
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</table>

a) Relative to the total vinyl groups.

b) Determined by SEC calibrated using linear polySty standards and equipped with an RI detector.

In conclusion, these observations are consistent with the fact that at higher concentrations of 3d, shorter chains containing smaller number of pendant vinyl groups are formed, and thus the probability of each chain to serve as crosslinker connecting many other chains decreases, thus delaying gelation.
2.3. Experimental

2.3.1. Materials

Styrene (Sty, 99 %, Acros) was purified before the experiments by passing the neat monomer through a column filled with basic alumina. 1,4-divinylbenzene (DVB) was synthesized according to a literature procedure by a Wittig reaction of (4-vinylbenzyl)triphenylphosphonium chloride with formaldehyde. All other reagents, including 4-vinylbenzyl chloride (98 %, Aldrich), triphenylphosphine (Ph₃P, 98 %, Aldrich), aqueous solution of formaldehyde (37 %, Aldrich), 2-iodobenzonic acid (98 %, Aldrich), oxalyl chloride (99 %, Aldrich), triethylamine (Et₃N, 98 %, Aldrich), methylamine hydrochloride (98 %, Aldrich), i-propylamine (99 %, Aldrich), hexylamine (99 %, Aldrich), ammonia (28 %, aqueous solution, Aldrich), concentrated hydrochloric acid (37 %, Aldrich), NaClO₂ (80 %, technical grade, Aldrich), NaOH (99 %, Aldrich), azobisisobutyronitrile (AIBN, 98 %, Aldrich), anhydrous MgSO₄ (97 %, Fisher), NaN₃ (99 %, Aldrich), CuCl₂ (97 %, Aldrich), tris(2-pyridylmethyl)amine (TPMA, 98 %, Aldrich), and the solvents, namely acetonitrile (>99.8 %, Aldrich), anisole (99 %, Aldrich), dichloromethane (98 %, Aldrich), N,N-dimethylformamide (DMF, 99.8 %, Aldrich), dioxane (>99.8 %, Aldrich), methanol (98 %, Aldrich), and tetrahydrofuran (THF, 99 %, Fisher), were used as received. CDCl₃ (99.8 % D, Cambridge Isotope Laboratories) used in the NMR analyses contained a small amount of tetramethylsilane as a chemical shift reference.

2.3.2. Analyses

To monitor the progress of the polymerization reactions, samples were withdrawn periodically using a nitrogen-purged syringe equipped with a Teflon-coated needle. Part of each sample was diluted with CDCl₃ for NMR analysis (determination of conversion), which was carried out on a
Bruker Avance DRX (400 MHz) spectrometer. Another part of the sample was diluted with THF and filtered through an Acrodisc 0.2 μm PTFE syringe filter, and the solution was subjected to size exclusion chromatography (SEC) analysis. Molecular weights (number-average (M_n) and weight-average (M_w)) and molecular weight distribution dispersities (Đ = M_w/M_n) were determined by SEC on a Tosoh EcoSEC system equipped with a series of 4 columns (TSK gel guard Super HZ-L, Super HZM-M, Super HZM-N, and Super HZ2000) and using THF as the eluent (flow rate 0.35 mL min⁻¹, 40 °C) and a refractive index detector. The SEC instrument was calibrated using a series of linear polySty standards. Infrared (IR) spectra were collected on a Thermo Scientific Nicolet iS10 FT-IR Spectrometer. The samples were prepared by dissolving 10 mg of polymer in 0.5 mL of THF, followed by casting a film on a KBr plate.

2.3.3. Synthetic Procedures

General Procedures for the Synthesis of Substituted 2-Iodobenzamides (2a-d) sixty-six

2-Iodobenzoic acid (10.0 g, 40 mmol, 1 eq.) was added into a round bottom flask charged with a magnetic stir bar. Then, dry CH₂Cl₂ (100 mL) was added with a few drops of DMF as a catalyst. Oxalyl chloride (5.2 mL, 60 mmol, 1.5 eq.) was added dropwise into the round bottom flask while stirring at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 2 h. The mixture was concentrated in vacuum and the crude product was directly used in the next step.

To a stirred, cold (ice-bath) mixture of 2-iodobenzoyl chloride (10.6 g, 40 mmol) in CH₂Cl₂ (50 mL), primary amine R-NH₂ (48 mmol, 1.2 eq.) and Et₃N (80 mmol, 2.0 eq.) were slowly added. After 16 h of additional stirring, water (50 mL) was added and the organic layer was separated and washed sequentially with 10 % aqueous HCl (50 mL), 5 % aqueous NaOH (2×25 mL), distilled
water (2×25 mL), and finally dried over anhydrous MgSO₄. The solvent was evaporated, and the resulting white solid was recrystallized from hexane and dried in a vacuum desiccator.

2-Iodobenzamide (2a). In the above procedure, aqueous solution of ammonia was used as the primary amine. The mixture in this case was heterogeneous. Yield: 6.42 g (65 %). ¹H NMR (400 MHz, CDCl₃, δ [ppm]): 7.90 (d, J = 8.0 Hz, 1H), 7.48 (dd, J = 7.7, 1.9 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.13 (td, J = 7.9, 2.0 Hz, 1H), 5.86 (s, 2H). ¹³C NMR (101 MHz, CDCl₃, δ [ppm]): 170.8, 141.1, 140.2, 131.4, 128.4, 128.2, 92.0.

2-Iodo-N-methylbenzamide (2b). Methylamine hydrochloride was used as the reactant. Yield: 7.32 g (70 %). ¹H NMR (400 MHz, CDCl₃, δ [ppm]): 7.90 (d, J = 8.0 Hz, 1H), 7.48 (dd, J = 7.7, 1.9 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.13 (td, J = 7.9, 2.0 Hz, 1H), 5.86 (s, 2H). ¹³C NMR (101 MHz, CDCl₃, δ [ppm]): 170.1, 142.3, 139.8, 131.0, 128.2, 128.1, 92.5, 26.8.

2-Iodo-N-isopropylbenzamide (2c). The reactant used in the general procedure described above was i-propylamine. Yield: 8.33 g (72 %). ¹H NMR (400 MHz, CDCl₃, δ [ppm]): 7.78 (d, J = 7.9 Hz, 1H), 7.36 – 7.25 (m, 2H), 7.09 – 6.97 (m, 1H), 5.92 (s, 1H), 4.27 – 3.99 (m, 1H), 1.23 (d, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃, δ [ppm]): 168.5, 142.5, 139.6, 130.8, 128.1, 128.1, 92.5, 42.1, 22.6.

2-Iodo-N-hexylbenzamide (2d). Hexylamine was employed as the reactant. Yield: 8.28 g (62 %). ¹H NMR (400 MHz, CDCl₃, δ [ppm]): 8.19 (dd, J = 7.5, 1.5 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.63 (t, J = 7.4 Hz, 1H), 3.44 (t, J = 7.4 Hz, 2H), 1.72 – 1.50 (m, 2H), 1.44 – 1.16 (m, 6H), 0.84 (m, 3H). ¹³C NMR (101 MHz, CDCl₃, δ [ppm]) 169.4, 142.6, 139.8, 130.9, 128.2, 128.1, 92.5, 40.1, 31.5, 29.4, 26.7, 22.6, 14.1.
General Procedures for the Synthesis of Benziodazolones

Concentrated HCl (50 mL) was added dropwise over 1 h to a stirred suspension of the amide (26 mmol, 1 eq.) and NaClO₂ (30 mmol, 1.2 eq.) in distilled water (150 mL) at room temperature. After the complete addition of HCl, the solution was stirred for another 16 h in dark at room temperature. The off-white precipitate was filtered and washed with excess of water (500 mL) and dried in vacuum to afford the crude product. The crude product was recrystallized from methanol to afford yellow needle-like crystals.

1,2-Dichloro-1,2-benziodazole-3(2H)-one (3a). The amide 2a was used as the reactant. Yield: 5.16 g (63 %). ¹H NMR (400 MHz, CDCl₃, δ [ppm]): 8.33 (dt, J = 8.5, 1.1 Hz, 1H), 8.28 (dt, J = 7.5, 1.5 Hz, 1H), 7.91 (ddt, J = 8.6, 7.3, 1.5 Hz, 1H), 7.77 (tt, J = 7.4, 1.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃, δ [ppm]): 164.7, 135.8, 132.0, 131.7, 129.8, 127.2, 116.3.

1-Chloro-2-methyl-1,8-benziodazol-3(2H)-one (3b). The reactant was the amide 2b. Yield: 5.21 g (68 %). ¹H NMR (400 MHz, CDCl₃, δ [ppm]): 8.49 (d, J = 8.4 Hz, 1H), 8.22 (dd, J = 7.3, 1.8 Hz, 1H), 7.88 (td, J = 9.9, 8.3, 1.9 Hz, 1H), 7.78 (t, J = 7.4 Hz, 1H), 3.33 (s, 1H). ¹³C NMR (101 MHz, CDCl₃, δ [ppm]): 166.3, 135.1, 131.9, 131.5, 131.3, 127.5, 116.3, 29.6.

1-Chloro-2-isopropyl-1,8-benziodazol-3(2H)-one (3c). This compound was synthesized using the amide 2c as the precursor. Yield: 5.89 g (70 %). ¹H NMR (400 MHz, CDCl₃, δ [ppm]): 8.45 (dd, J = 8.4, 1.0 Hz, 1H), 8.14 (dd, J = 7.4, 1.8 Hz, 1H), 7.89 – 7.59 (m, 2H), 4.54 (hept, J = 6.6 Hz, 1H), 1.44 (d, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃, δ [ppm]): 165.1, 134.7, 133.0, 131.8, 131.4, 127.7, 116.2, 47.1, 24.6.

1-Chloro-2-hexyl-1,8-benziodazol-3(2H)-one (3d). The reactant employed in the above general procedure was the amide 2d. Yield: 5.88 g (62 %). ¹H NMR (400 MHz, CDCl₃, δ [ppm]):
8.45 (d, $J = 8.3$ Hz, 1H), 8.16 (d, $J = 7.1$ Hz, 1H), 7.78 (dt, $J = 36.7$, 7.3 Hz, 2H), 3.76 (t, $J = 7.1$ Hz, 2H), 1.97 – 1.59 (m, 2H), 1.54 – 1.15 (m, 7H), 0.87 (d, $J = 6.4$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$, δ [ppm]): 166.2, 134.9, 132.1, 131.8, 131.4, 127.7, 116.6, 43.8, 31.5, 31.2, 26.7, 22.5, 14.1.

**Determination of Chain Transfer Coefficients**

To a 10 mL reaction test tube equipped with a magnetic stir bar, Sty (2.0 mL, 17.3 mmol, 2000 eq.), AIBN (1.4 mg, 8.65 μmol, 1 eq.) and 3d (6.3 mg, 17.3 μmol, 2 eq.) were added followed by the addition of dioxane (30 μL, as internal standard). The tube was capped with rubber septum (pre-washed with acetone and dried), secured with electric tape, and wrapped with aluminum foil to prevent the exposure of the contents to light, and was then placed in an ice-water cooling bath (in order to minimize evaporation of the reaction components). After deoxygenation of the reaction mixture by purging with nitrogen using a teflon-coated needle for 10 min, the reaction tube was transferred to a preheated oil bath at 60 °C. The polymerization was stopped after 10 min by opening the reaction tube to air. The conversion was determined by $^1$H NMR spectroscopy and the molecular weight of the produced polymer was determined by SEC. Similar experiments were carried out with varying amounts of 3d (4 eq., 6 eq., and 8 eq. vs AIBN) in addition to an experiment where no 3d was added to the reaction mixture. Another set of similar experiments were performed with chain transfer reagents 3a, 3e, and CCl$_4$. All other reaction conditions were identical. In all experiments, the monomer conversions were below 5 % after 10 min of polymerization.
Synthesis of Linear PolySty for Chain End Analysis and Functionalization

In a 10-mL dry reaction tube, a magnetic stir bar was added, followed by Sty (1 mL, 8.73 mmol), 3d (0.127 g, 0.35 mmol), and 30 µL dioxane as internal standard. The tube was capped with a rubber septum, (pre-washed with acetone and dried), which was secured with electric tape. The reaction tube was then wrapped with aluminum foil to prevent the exposure of the contents to light and was placed in an ice-water cooling bath. The reaction mixture was deoxygenated by purging with nitrogen (using a teflon-coated needle) for 10 min, after which the reaction tube was transferred to an oil bath preheated to 80 °C. At timed intervals, samples (ca. 0.04 mL) were withdrawn from the mixture with a nitrogen-purged syringe, part of which were then diluted with CDCl₃ (for NMR analysis) and part-with THF (for SEC analysis). The reaction was stopped after 12 h at 20 % conversion by opening the tube to air. The polymer was dissolved in DCM (10 mL) and purified by precipitation into methanol and dried in a vacuum desiccator for 2 days. \( M_n = 2,500 \text{ g mol}^{-1} \), \( M_w/M_n = 1.62 \).

Synthesis of Azide-Terminated PolySty

A dry 50 mL round-bottom flask was charged with Cl-terminated polySty described above (1.0 g), NaN₃ (0.13 g, 2 mmol), and DMF (20 mL). The mixture was stirred at 60 °C and the reaction was monitored using \(^1\text{H}\) NMR spectroscopy for the disappearance of the \( \omega \)-terminal CH(Ph)-Cl methine protons (4.6-4.3 ppm). After 16 h, the reaction mixture was poured into methanol. The white precipitate was dissolved in CH₂Cl₂ and reprecipitated in methanol, this purification procedure was repeated three times. The obtained white powder was washed with
water (200 mL) and methanol (200 mL) and then dried in vacuum for 2 days to obtain 0.8 g of azide-terminated polySty.

**Chain Extension Under ICAR ATRP Conditions**

A stock solution of CuCl$_2$ (0.039 g, 0.29 mmol), TPMA (0.084 g, 0.29 mmol), and AIBN (0.190 g, 1.16 mmol) in DMF (10 mL) was prepared. Linear Cl-terminated polySty described above ($M_n = 2,500$ g mol$^{-1}$, $M_w/M_n = 1.62$, 0.145 g, 0.12 mmol) was weighed in a 10 mL reaction tube and Sty (1.0 mL, 8.7 mmol) was added, followed by a fraction of the stock solution of catalyst and AIBN (100 µL, containing 2.9 µmol of CuCl$_2$ and TPMA, and 11.6 µmol of AIBN). A magnetic stir bar was added and the tube was capped with a rubber septum (pre-washed with acetone and dried), secured with electric tape. The tube was placed in an ice-water cooling bath and the reaction mixture was deoxygenated by purging with nitrogen for 10 min. The reaction tube was then placed in an oil bath preheated to 80 °C. At timed intervals, samples (ca. 0.04 mL) were withdrawn from the mixture with a nitrogen-purged syringe for NMR and SEC analysis.

**Synthesis of HB Polymers by Copolymerization of Sty and DVB in the Presence of HV Iodine(III)-Based CTAs**

In the following procedure, 40 mol% of DVB of the total vinyl groups and 3d (1 mol% vs. the total vinyl groups) were used. In a 10 mL reaction tube, a magnetic stir bar was added, followed by Sty (0.66 mL, 5.76 mmol), DVB (0.250 g, 1.92 mmol), and 3d (0.035 g, 9.59 mmol). The tube was capped with a rubber septum (pre-washed with acetone and dried), which was secured with electric tape, and the contents were protected from light by wrapping the tube with aluminum foil.
Dry dioxane (1.34 mL) was then injected and the tube was placed in an ice-water cooling bath, and the reaction mixture was deoxygenated by purging with nitrogen using a teflon-coated needle for 10 min. The reaction tube was then placed in an oil bath preheated to 80 °C. At timed intervals, samples (ca. 0.04 mL) were withdrawn from the reaction mixture with a nitrogen-purged syringe equipped with a teflon-coated needle to determine the monomer conversion (by NMR) and the molecular weights (SEC) of the polymers.

Similar experiments were conducted using the same amount of 3d ([vinyl groups]₀ / [3d]₀ = 100), but varying amounts of DVB. The Sty and DVB amounts were: Sty (1 mL, 8.64 mmol) and DVB (0.063 g, 0.48 mmol) for [DVB]₀ = 10 mol% of the total vinyl groups; Sty (0.88 mL, 7.64 mmol) and DVB (0.125 g, 0.96 mmol) for [DVB]₀ = 20 mol% of the total vinyl groups; Sty (0.44 mL, 3.74 mmol) and DVB (0.374 g, 2.88 mmol) for [DVB]₀ = 60 mol% of the total vinyl groups; Sty (0.22 mL, 1.92 mmol) and DVB (0.499 g, 3.84 mmol) for [DVB]₀ = 80 mol% of the total vinyl groups; and pure DVB (0.624 g, 4.80 mmol, corresponding to 9.6 mmol of vinyl groups). In each case, the amount of dioxane used was changed so that the total volume of the reaction mixture was 2 mL.

When varying amounts of 3d relative to vinyl groups were used, the amounts of Sty (1 mL, 8.64 mmol), DVB (0.374 g, 2.88 mmol), and dioxane (1 mL) were kept constant while the amount of 3d was changed to 0.2102 g (0.576 mmol for [vinyl groups]₀ / [3d]₀ = 25), 0.1051 g (0.288 mmol for [vinyl groups]₀ / [3d]₀ = 50), 0.053 g (0.144 mmol for [vinyl groups]₀ / [3d]₀ = 100), 0.026 g (0.072 mmol for [vinyl groups]₀ / [3d]₀ = 200), or 0.013 g (0.036 mmol for [vinyl groups]₀ / [3d]₀ = 400).
2.4. Conclusions

A series of heterocyclic HV iodine(III) compounds (benziodazoles) with I-Cl bonds and various substituents at the N atom were synthesized and were found to be very efficient chain transfer agents (CTAs) in the polymerization of styrene (Sty). The chain transfer coefficients and transfer rate coefficients were found to be higher than those of a traditionally used CTA, CCl₄. The presence of alkyl chloride end groups at the ω-terminus of the produced chains was demonstrated by spectroscopy and further chain-end functionalization reactions (e.g., nucleophilic substitution with azide and chain extension under low-catalyst-concentration ATRP conditions). At high temperatures, the HV iodine(III) compounds served simultaneously as efficient radical initiators and CTAs, which made them very suitable reactants for the synthesis of highly branched and chain-end functionalized (mostly Cl-capped) polymers when added to mixtures of Sty and a divinyl crosslinker, 1,4-divinylbenzene. Due to the significant values of the chain transfer coefficients, the HV iodine(III) compounds could be used at relatively low concentrations (in some cases, less than 1 mol% vs. vinyl groups), even in copolymerizations in the presence of large concentrations of crosslinker, and still efficiently delay gelation up to moderate to high conversions and yield soluble highly branched end-functional polymers.

2.5 Acknowledgements

We gratefully acknowledge financial support by the National Science Foundation through a CAREER grant (CHE1455200) to NVT.
2.6 References


2.7 Appendix

Figure 2.7.1. $^1$H NMR spectrum of 2a in CDCl$_3$.

Figure 2.7.2. $^{13}$C NMR spectrum of 2a in CDCl$_3$. 
Figure 2.7.3. $^1$H NMR spectrum of 2b in CDCl$_3$.

Figure 2.7.4. $^{13}$C NMR spectrum of 2b in CDCl$_3$. 
Figure 2.7.5. $^1$H NMR spectrum of $2c$ in CDCl$_3$.

Figure 2.7.6. $^{13}$C NMR spectrum of $2c$ in CDCl$_3$. 
Figure 2.7.7. $^1$H NMR spectrum of 2d in CDCl$_3$.

Figure 2.7.8. $^{13}$C NMR spectrum of 2d in CDCl$_3$. 
Figure 2.7.9. $^1$H NMR spectrum of 3a in CDCl$_3$.

Figure 2.7.10. $^{13}$C NMR spectrum of 3a in CDCl$_3$.  

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.33 (dd, $J$ = 8.5, 1.1 Hz, 1H), 8.28 (dd, $J$ = 7.5, 1.5 Hz, 1H), 7.91 (dd, $J$ = 8.6, 7.3, 1.5 Hz, 1H), 7.77 (d, $J$ = 7.4, 1.1 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.71, 135.79, 132.05, 131.74, 129.82, 127.23, 116.31.
Figure 2.7.11. $^1$H NMR spectrum of 3b in CDCl$_3$.

Figure 2.7.12. $^{13}$C NMR spectrum of 3b in CDCl$_3$. 
Figure 2.7.13. $^{1}$H NMR spectrum of 3c in CDCl$_3$.

Figure 2.7.14. $^{13}$C NMR spectrum of 3c in CDCl$_3$. 
Figure 2.7.15. $^1$H NMR spectrum of 3d in CDCl$_3$.

Figure 2.7.16. $^{13}$C NMR spectrum of 3d in CDCl$_3$. 

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CHAPTER 3

3.1. Introduction

3.1.1. Modifications of Natural Rubber (cis-Polyisoprene)

Natural rubber (NR), which is mainly produced in the form of latex by the tree *Hevea brasiliensis*, has been used widely as raw material for manufacturing various industrial products, such as tires, adhesives, water-impermeable materials, etc., as it possesses excellent physical properties including high elasticity, high tensile strength, and low heat build-up.\(^1,2\) The backbone structure of NR comprises of a *cis*-1,4-polyisoprene (polyIP) with two or three *trans*-isoprene units at the ω-terminus.\(^3,4\) Various functionalization reactions (typically electrophilic or radical addition) with reactive double bonds in the backbone of NR have been successfully employed to synthesize polymers with improved characteristics\(^5\) and/or with new desired properties, i.e., materials with high added value for specialty applications.\(^5,6\) To date, NR has been modified and utilized as self-healing materials,\(^7\) drug delivery systems,\(^8,9\) as well as optical and electrochemical devices.\(^10\)
Fluorine-containing polymers have attracted much attention owing to their excellent chemical and physical properties including inertness, ultralow surface energy, and thermal stability. Numerous practical applications of fluorine-containing polymers such as self-cleaning coatings, in automotive and aerospace parts, optics and sensor,11-16 have been reported. One of the most important routes for the synthesis of fluorinated polymers is incorporating the fluorine-containing moieties into a non-fluorinated parent polymer. Recently, the synthesis of fluorine-containing polymers derived from NR or polydienes has attracted growing attention.17 For example, Hillmyer and coworkers18 investigated the synthesis of fluoropolymers by the reaction of polydienes with difluorocarbene (:CF₂) generated in situ by the thermolysis of hexafluoropropylene oxide (Scheme 3-1a). The perfluoroalkylation of polybutadiene by addition of perfluoroalkyl iodides (RfI) to the reactive double bonds in the backbone was also reported (Scheme 3-1b).¹⁹ N-fluoroalkyl and fluoroaryl triazolinediones were prepared and successfully grafted onto the backbones of unsaturated polymers (Scheme 3-1c).²⁰ Recently, Yusoff et al.²¹ developped an approach to perfluoroalkylated NR by hydroxylation and subsequent esterification with fluorine-containing acyl chlorides (Scheme 3-1d). Although various methodologies have been reported, they are suffered from many drawbacks, such as low yields, loss of pendant functionalities, degradation (reflected by a decrease of molecular weights), and/or crosslinking. Thus, alternative efficient protocols for the introduction of fluorine-containing functional groups in unsaturated polymers are still highly desired.
3.1.2. Fluorine-Containing HV Iodine(III) Compounds

Up to today, fluorine chemistry has been developed as a major multidiscipline area of research due to the remarkable properties of fluorinated compounds in comparison with those of non-fluorinated analogues. Since the naturally occurring organofluorides are exceedingly sparse, almost all of the known fluorine-containing compounds have to be manually synthetic. Therefore, developing efficient methods for the construction of fluorine-containing compounds is highly desirable. Fluorination and fluoroalkylation with diverse F, CF₃, CF₂R, CR₁R₂F, CH₂CF₃, CₙF₂n+1, and XRᵣᵣ (X = O, S or Se; Rᵣᵣ = CF₃, CₙF₂n+1, CF₂H, CH₂F or CH₂CF₃) transfer reagents has become one of the most efficient means to the straightforward synthesis of functional fluorine-containing compounds.

Hypervalent (HV) iodine reagents, which have already proven their versatility as synthetic tools in organic and polymer chemistry, are increasingly used in the preparation of fluorine-containing compounds. To date, various fluorine-containing HV iodine(III) compounds have

Scheme 3-1. Synthesis of fluorine-containing polymers derived from NR or polydienes.
been developed (Figure 3-1a) and some are commercially available, including benziodoxoles with trifluoromethyl ligands, known as the Togni reagents.43-45 The family of HV iodine compounds is divided into different subgroups: the linear and cyclic λ3-iodoarenes (Figure 3-a and b), the aryliodonium salts (Figure 3-1c).

Figure 3-1. Examples of fluorine-containing HV iodine(III) reagents.

The HV iodine(III) reagent, 4-(difluoroiodo)toluene (4-TolIF2),46 has been used as a stable, solid surrogate for elemental fluorine. It has found great success as a source of 'electrophilic' fluorine or as a fluorine transfer agent, and its many applications include the difluorination,47 phenylselenofluorination48 and iodo fluorination49,50 of alkenes and alkynes. For example, Tingoli and co-worke48 investigated the utilization of 4-TolIF2 in the 1,2-phenylselenofluorination of alkenes (Scheme 3-2a). The highly reactive phenyl selenyl fluoride species were generated in situ, by the oxidative cleavage of the Se–Se bond of Ph2Se2 by 4-TolIF2. The reactions proceeded efficiently, using a range of substrates bearing both terminal and vicinal disubstituted olefins as starting materials. All transformations proceeded regio- and diastereoselectively, yielding

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exclusively the anti-addition Markovnikov products in moderate to good yields (58–78%). Even protected glycals were converted successfully (67–81 % yield) with Ph₂Se₂/pTolF₂ as reagents into the trans-diaxial products. In 2006, the same group expanded the scope of this reaction to iodofluorination by simply replacing the diphenyldiselenide with I₂ (Scheme 3-2b). Through this methodology, the corresponding iodofluorination products were obtained in moderate to good yields (58–91%).

Scheme 3-2. Modifications of alkenes promoted by 4-TolIF₂: (a) phenylselenofluorination, (b) iodofluorination.

As Scheme 3-3 shown, HV iodine(III) reagents for trifluoromethylation, in particular compounds based on the benziodoxolone and benziodoxole scaffold, named Togni reagent I and II, respectively, have been known reported in 2006 by Togni.⁴³
In recent years, the trifluoromethylation of alkenes using Togni reagents as electrophilic trifluoromethylation reagents, has become a research hotspot and many effective methods have been studied intensively. For example, the groups of Buchwald, Wang have independently explored the copper-catalyzed electrophilic allylic trifluoromethylation of unactivated olefins. Furthermore, a variety of alkene difunctionalizations involving trifluoromethylation, such as 2-iodobenzoate, amino, azido, cyano, halo-containing trifluoromethylation, and thiocyanate have also been developed (Figure 3-4).
Reactions of Togni reagents and alkenes: (a) allylic trifluoromethylation, (b) 2-iodobenzoate-trifluoromethylation, (c) amino-trifluoromethylation, (d) azido-trifluoromethylation, (e) cyano-trifluoromethylation, (f) chloro or bromo-trifluoromethylation, (g) thiocyanate-trifluoromethylation.

Furthermore, HV iodine(III) compounds with more complex perfluoroalkyl groups have been synthesized and utilized in the perfluoroalkylation of alkenes. Umemoto and coworkers developed the (perfluoroalkyl)phenyliodonium trifluoromethanesulfonates (FITS reagents) as highly reactive electrophilic perfluoroalkylating agents (Scheme 3-5a). FITS reacted with alkenes or alkadienes to form a cationic intermediate which then gave substitution products, nucleophile addition products, cyclization products, or hydride shift deprotonation or cyclization products, depending on the reaction (Scheme 3-5b).
Scheme 3.5. Synthesis and application of perfluoroalkylation reagents: (a) synthesis of (perfluoroalkyl)phenyliodonium trifluoromethanesulfonates (FITS), (b) reactions of FITS with alkenes and alkadienes.

Various efficient and reliable methods for the introduction of fluorine-containing groups in small organic molecules have been reported, but their potential in macromolecular chemistry has not been explored. Encouraged by our recent finding that polyIP can be functionalized efficiently and without apparent degradation or crosslinking with HV iodine(III) compounds of the type PhI(N₄CR)₂ (R = aryl or alkyl, Ph = C₆H₅) in the presence of iodine,⁷¹,⁷² we attempted several simple and efficient synthetic approaches to fluorine-containing polymers derived from polyIP, based on reactions of the unsaturated polymer with both cyclic and acyclic HV iodine(III) reagents with fluorine-based ligands.

3.2. Results and Discussion

3.2.1. Synthetic Methodologies and Spectral Characterization

In this work, polyIP (Mₙ,app = 10,000 g mol⁻¹, Mₙ/Mₚ = 2.8) was used as a low molar mass model for NR in all chemical transformations. The modified polymers are designated using a “poly(A, B)” nomenclature, where A and B represent the newly introduced functional groups that
are attached to the carbon atoms that had formerly been linked through a double bond in the polyIP backbone. For example, poly(F, I) is used for a polymer with fluoro and alkyl iodide pendant groups, while poly(CF₃, =) is used for a polymer containing trifluoromethyl pendant groups in addition to extra double bonds (formed due to elimination). In addition, the symbols “xi” (i = 1, 2, 3,...) are used to designate the total number of units with specific structure in each of the copolymers produced as a result of the chemical modifications of polyIP. In the discussions concerning NMR spectra, the H and F atoms are numbered with Arabic and Roman numerals, respectively. For simplicity, the labeling of the atoms is valid only within a section describing a specific modification.

**Iodo-Fluorinated polyIP (poly(F, I)).** Tingoli and coworkers developed the approach to iodo-fluorinated alkenes and alkynes by employing of 4-TolIF₂ and I₂.²⁵⁰ The reaction took place regioselectively and, in the cases when it was applied to terminal alkenes, it produced exclusively the isomers predicted by the Markovnikov rule for the addition of electrophilic iodine. This methodology was utilized here for the iodo-fluorination of polyIP. The fluorine-containing HV iodine(III) reagent, 4-TolIF₂, was mixed with I₂ in CHCl₃ and solution of polyIP was added. The reaction was monitored by ¹HNMR spectroscopy, and the polymer was precipitated, purified, and characterized by NMR and IR spectrum.
As Figure 3-2a shown, the reactive double bonds in the backbone of polyIP were completely consumed, which indicated by the disappearance of the signals of vinyl protons at 5.1 ppm. The new appearing peaks at 4.4 ppm and 3.8 ppm were assigned to –CHI (H-7 in Figure 3-2a) and –CHF (H-11), respectively. The presence of alkyl fluoride pendant groups was also confirmed by the $^{19}$F NMR spectroscopy. As Figure 3-2b shown, the signals around at –134.0 to –146.0 ppm corresponded to tertiary alkyl fluoride (F-i), while secondary alkyl fluoride (F-ii) groups were seen at around –174.0 ppm.\(^73\) Several peaks were observed for the tertiary alkyl fluoride F atom (F-i) over a relatively broad spectral region (–134.0 to –146.0 ppm), which was plausibly owing to the formation of repeat units with different configurations at the newly formed asymmetric carbon atoms and the coexistence of several stereosequences. The complexity in the
\(^{19}\text{F}\) NMR spectra of fluoropolymers with random stereochemistry has been well documented.\(^{74-76}\) Based on the integration of the signals in the NMR spectra, it was determined that the repeat units with the secondary alkyl fluoride groups were less than 5 mol\% of the total.

As Figure 3-2c shown, polyIP and poly(F, I) were also characterized by IR spectroscopy. The main peaks in the spectrum of polyIP are located at 3050 (C(sp\(^2\))–H stretching vibration), 3000-2850 (C(sp\(^3\))–H stretching), and 1660 cm\(^{-1}\) (C=C stretching).\(^{77, 78}\) The intensity of the absorption bands corresponding to the C(sp\(^2\))–H and the C=C stretching vibrations decreased very markedly upon iodo-fluorination and new peaks appeared at 1250 cm\(^{-1}\) (C–F stretching), which was consistent with the formation of alkyl fluoride groups.\(^{79}\)

2-Iodobenzoyloxylation-trifluoromethylated PolyIP (poly(CF\(_3\), 2-IC\(_6\)H\(_4\)CO\(_2\))) and Unsaturated Polymer with Pendant Trifluoromethyl Groups (poly(CF\(_3\), =)). Sodeoka and coworkers\(^{55}\) achieved the 2-iodobenzoyloxylation-trifluoromethylation of styrene derivatives under mild conditions by using Togni reagent II and copper(I) salts. The 2-iodobenzoyloxy groups could be readily removed upon addition of triflic acid to afford the product of elimination, namely the vinyl-trifluoromethyl derivative. This methodology was applied to modify polyIP by using Togni reagent II in the presence of CuI (20 mol\%) as the catalyst, and the reaction yielded poly(CF\(_3\), 2-IC\(_6\)H\(_4\)CO\(_2\)), as shown in Figure 3-3.
In the $^1$H NMR spectrum (Figure 3-3a), the signals at 7.8-7.2 ppm (H-7-10) confirmed the presence of 2-iodobenzoyloxy groups in poly(CF$_3$, 2-IC$_6$H$_4$CO$_2$), while at the same time the broad signals at 6.1-5.1 ppm (H-16 and H-21) indicated the presence of repeat units, in which elimination had occurred. Based on the integration, it can be determined that 22 mol% of units contain 2-iodobenzoyloxy groups after modification. The degree of functionalization was found to be lower than that of styrene derivatives used in previous work,$^{59}$ due to the lower reactivity of the double bonds in polyIP. The $^{19}$F NMR spectrum analysis also suggested the formation of elimination products, i.e., the signals observed in the region from −65.0 to −70.0 ppm corresponded to CF$_3$.
groups attached to allylic carbon atoms (F-iii and F-iv), as seen in Figure 3-5b. The signals in the spectral region between −63.5 and −64.0 ppm were assigned to F-i and F-ii. The precise assignment of the two signals is difficult due to the very closed chemical shifts. Based on the integration of $^1$H NMR and $^{19}$F NMR, the ratio of $x_3:x_4:(x_5 + x_6)$ in poly(CF$_3$, 2-IC$_6$H$_4$CO$_2$) was determined as 22:57:21.

The 2-iodobenzoyloxy groups in poly(CF$_3$, 2-IC$_6$H$_4$CO$_2$) can be removed under acid conditions. In this work, TfOH was added to poly(CF$_3$, 2-IC$_6$H$_4$CO$_2$) to afford the unsaturated polymer, poly(CF$_3$, =). As Figure 3-5a shown, the intensities of the characteristic signals of 2-iodobenzoyloxy groups in the $^1$H NMR spectrum of poly(CF$_3$, =) decreased substantially, indicating that elimination took place. In the $^{19}$F NMR spectrum of poly(CF$_3$, =), the intensity of the signal centered at −63.5 ppm in the starting material decreased, relative to the signal centered at −64.0 ppm. This not only proved the successful elimination reaction but also allowed the precise assignment of the two signals at −63.5 and −64.0 ppm to F-i and F-ii, respectively. The CF$_3$ groups of type i in poly(CF$_3$, =) belonging to unreacted repeat units with 2-iodobenzoyloxy pendant groups could still be discerned, suggesting that the elimination was not complete (a fact that could also be ascertained by examining the $^1$H spectrum of poly(CF$_3$, =), in which low-intensity signals of aromatic protons were still seen). Based on the integration in the $^1$H NMR spectrum, it was ascertained that one out of 25.5 units (ca. 4 mol%) in poly(CF$_3$, =) was not modified upon the treatment of poly(CF$_3$, 2-IC$_6$H$_4$CO$_2$) with TfOH. In other words, ca. 82 % of the originally present 2-iodobenzoyloxy groups (1 in 4.5 units) were eliminated. By analysis of the $^{19}$F NMR spectrum of poly(CF$_3$, =), it was determined that 77 % of F atoms belonged to F-i and F-v. Taking into account that the remaining F-i was ca. 4 % of the repeat units, the ratio $x_3:x_7:(x_8 + x_9)$ in poly(CF$_3$, =) was determined as 4:73:23. The elimination of 2-iodobenzoyloxy groups resulted in the
formation of tetrasubstituted alkene backbone groups, which increased from 57 mol% in poly(CF₃, 2-IC₆H₄CO₂) to 73 mol% in poly(CF₃, =).

As Figure 3-3c shown, the IR spectrum of poly(CF₃, 2-IC₆H₄CO₂) contained several important absorption bands, namely 1728 cm⁻¹ (C=O stretching of the 2-iodobenzoate groups), as well as 1134 and 1255 cm⁻¹ (vibrations of C−F bonds in the CF₃ groups). The intensity of the C=O stretching peak at 1728 cm⁻¹ decreased very substantially in the spectra of poly(CF₃, =), formed after treatment of poly(CF₃, 2-IC₆H₄CO₂) with TfOH.

Chloro-Trifluoromethylated PolyIP (poly(CF₃, Cl)) and Bromo-Trifluoromethylated PolyIP (poly(CF₃, Br)). Fu and coworkers⁶² developed a copper-catalyzed intermolecular chloro- and bromotrifluoromethylation of electron-deficient alkenes and unactivated alkenes with Togni reagent II and thionyl chloride or bromide under mild reaction conditions. The reactions were catalyzed by a copper(II) catalyst to give the Cl-/Br-containing trifluoromethyl derivatives in high yields. The procedure is also capable of tolerating a relatively wide range of substrates for the bromotrifluoromethylation, and good results can also be obtained. This report prompted us to explore the utility of the method in halo-trifluoromethylation of polyIP. The use of CuBr₂ as catalyst in the reaction of polyIP with Togni reagent II and thionyl halides allowed the incorporation of alkyl halide and CF₃ pendant groups under mild conditions (Figure 3-4), without any chain degradation or crosslinking, as ascertained by SEC analysis.
As Figure 3-4 shown, the yielded polymers were characterized by $^1$H and $^{19}$F NMR, as well as IR spectroscopy. In the $^1$H NMR spectrum of poly(CF$_3$, Cl), the new appearing broad signals at 2.6-2.2 ppm were attributed to the protons of methine groups attached to CF$_3$ groups, i.e., –CHCF$_3$ (H-7, H-14, and H-18 in Figure 3-4a) and allylic protons (H-9, H-11, and H-16 in Figure 4a). In the $^{19}$F NMR spectrum of poly(CF$_3$, Cl), the signals between −62.7 and −63.7 ppm corresponded to F-i and F-ii. Elimination reaction was also observed, indicated by the signals at −68.2 to −70.0 ppm belonging to CF$_3$ groups attached to allylic moieties (F-iii and F-iv). Based on integration of
the signals in the $^{19}$F NMR spectrum of poly(CF$_3$, Cl), x10, x11, and (x12 + x13) were estimated as ca. 40 %, 57 % and 3 % of the total, respectively. The degree of chloro-trifluoromethylation of polyIP was determined as 40 %, which is consistent with Fu’s observation$^{62}$ that lower yield (39-45 %) could be afforded when trisubstituted alkenes were used as starting materials under the same conditions. Similar conclusions could be drawn from the $^1$H and $^{19}$F NMR spectra of poly(CF$_3$, Br), but the ratio x14:x15:(x16 + x17) was 37:41:22, i.e., 37 mol% of repeat units contained both alkyl bromide and trifluoromethyl groups.

The IR spectra of polyIP, poly(CF$_3$, Cl), and poly(CF$_3$, Br) are displayed in Figure III-4c. The absorption bands at 1254 and 1139 cm$^{-1}$ in the spectrum of poly(CF$_3$, Cl) can be assigned to C–F stretching vibrations, which indicated that the CF$_3$ groups were successfully introduced. Similar results were also observed in the IR spectrum of poly(CF$_3$, Br).

Azide-Containing PolyIP-Derived Polymers and Their Subsequent Use in Click Reactions.

The presence of alkyl halide pendant groups in the poly(CF$_3$, Cl ) and poly(CF$_3$, Br) made them suitable substrates for nucleophilic substitution reactions. For instance, poly(CF$_3$, Cl) was used to react with NaN$_3$ in DMF to afford polymers with multiple azide pendant groups (Figure 3-5). Since the alkyl chloride groups are tertiary, no apparent difference was observed in the $^1$H NMR spectra of poly(CF$_3$, Cl) and the product, poly(CF$_3$, N$_3$), as shown in Figure 3-5a. But the absorption at 2103 cm$^{-1}$ (corresponding to the asymmetric azide stretching vibration)$^{81}$ was clearly visible in the IR spectrum of the poly(CF$_3$, N$_3$), suggesting the presence of azide functionalities, as seen in Figure 3-5c.
Figure 3-5. (a) $^1$H NMR spectra of poly(CF$_3$, Cl), poly(CF$_3$, N$_3$) and poly(CF$_3$, pyrene) in CDCl$_3$, (b) $^{19}$F NMR spectra of films of poly(CF$_3$, Cl) and poly(CF$_3$, N$_3$), (c) FT-IR spectra of films of poly(CF$_3$, Cl), poly(CF$_3$, N$_3$) and poly(CF$_3$, pyrene).

In the $^{19}$F NMR spectrum of poly(CF$_3$, N$_3$), the intensity of the signal centered at –62.7 ppm in the starting material decreased relative to the signal centered at –63.7 ppm. This allowed the assignment of the resonances in the starting material, poly(CF$_3$, Cl), discussed above, to F-i and F-ii, respectively (Figure 3-5b). Elimination, which typically occurs in competition with substitution when tertiary alkyl halides react with bases and nucleophiles was also observed, which was indicated by the increased intensity of the signals in the range from –68 to –70 ppm. In addition, the emergence of new resonances at –56.4 to –58.3 ppm suggested that cycloaddition took place between azide and the electron deficient (due to the presence of CF$_3$ groups) olefin, which is well documented.$^{82-87}$ The precise structure of the product of this side reaction is unknown (and the
newly-formed functionality is represented with Z in the reaction scheme in Figure 3-5), but azide functionalities were clearly present in the poly(CF₃, N₃), which was supported both by the spectral evidence and the ability of the polymer to participate in azide-alkyne click reactions.

A functional alkyne containing the fluorescent pyrenyl group, namely propargyl 4-(1-pyrenyl)butyrate, was chosen for the click reaction. The formation of poly(CF₃, pyrene) was proved by ¹H NMR (Figure 3-5a) and IR spectroscopy (Figure 3-5c). In the ¹H NMR spectrum of poly(CF₃, pyrene), the resonances at 8.3-7.6 ppm were assigned to the pyrene protons (collectively marked Hₚyr) and the linker triazole groups (H-1). The disappearance of the azide stretching band at 2103 cm⁻¹ and the appearance of the carbonyl stretching at 1735 cm⁻¹ in the IR spectrum of the reaction product further proved the successful “click” coupling functionalization (Figure 3-5c). Due to the fact that the precise structures of all units formed after reaction of poly(CF₃, Cl) with azide is unknown, the amount of introduced pyrene groups could not be estimated but their presence could be established by studying the fluorescence properties of poly(CF₃, pyrene). Somewhat brittle films could be cast from CHCl₃ solutions of the polymer, which showed blue fluorescence upon irradiation with UV light, as shown in Scheme 3-6.

**Iodo-Pentafluorobenzoyloxylated PolyIP (poly(C₆F₅CO₂, I)) and Iodo-Perfluorodecanoyloxylated PolyIP (poly(n-C₉F₁₉CO₂, I)).** Perfluoroalkyliodonium salts have been developed and used as electrophilic perfluoroalkylating agents in various reactions. However, the reaction of perfluoroalkyliodonium salts with alkenes or dienes always gives byproducts caused by substitution and cyclization, which makes these reactions less than ideal for the post-polymerization modifications of unsaturated polymers. A series of new HV iodine(III) reagents based on the 1,3-dihydro-3,3-dimethyl-1,2-benziodoxole and 1,2-benziodoxol-3-(1H)-
one scaffolds, which contain various perfluoroalkyl groups as the ligands attached to the iodine atom, have been prepared and used in electrophilic perfluoroalkylation reactions\textsuperscript{67, 88} but the synthesis of those reagents is time-consuming and costly. Herein, we demonstrate an easy procedure to introduce pentafluorobenzoyloxy and perfluorodecanoyloxy groups in polymers by modification of polyIP with \( \text{PhI(O}_2\text{CR})_2 \) \((R_f = \text{C}_6\text{F}_5 \text{ or } n-\text{C}_9\text{F}_{19})\) in the presence of \( \text{I}_2 \).

The synthesis of \( \text{PhI(O}_2\text{CR}_f)_2 \) was first achieved by reacting \( \text{PhIO} \) with fluorinated carboxylic acids, namely pentafluorobenzoic and perfluorodecanoic acid. The reactions were initially conducted on a small scale and monitored by \( ^1\text{H} \) NMR spectroscopy, as shown in Figure 3-6.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3-6.png}
\caption{\( ^1\text{H} \) NMR spectra of (a) solution of \( \text{PhIO} \) (0.1 mmol) and \( \text{C}_6\text{F}_5\text{CO}_2\text{H} \) (0.22 mmol) in CDCl\(_3\) (1 mL) and (b) solution of \( \text{PhIO} \) (0.1 mmol) and \( n-\text{C}_9\text{F}_{19}\text{CO}_2\text{H} \) (0.22 mmol) in CD\(_3\)CN (1 mL). Both spectra were collected ca. 5 min after mixing of the reagents at 30 °C.}
\end{figure}
In a scaled-up procedure, PhI(O_2CC_6F_5)_2 was successfully isolated in 90% yield and its identity was confirmed by NMR spectroscopy and comparison with published spectral data. Attempts to isolate PhI(O_2C(n-)_C_9F_19)_2 were unsuccessful due to its instability but the compound could be easily generated and used *in situ*.

Trifluoroacetyl hypoiodite (CF_3CO_2I) can be readily formed *in situ* via oxidation of I_2 by PhI(O_2CCF_3)_2 and then it can be employed directly to react with a variety of alkenes to afford the corresponding iodo-trifluoroacetoxylated derivatives. We explored the applications of (diacyloxyiodo)benzenes with perfluorinated carboxylate ligands in the iodo-pentafluorobenzoyloxylation and iodo-perfluorodecanoyloxylation of polyIP. First, PhI(O_2CC_6F_5)_2 (1.0 eq.) was mixed with I_2 (0.5 eq.) to produce C_6F_5CO_2I, which then quickly reacted (within 10 min at ambient temperature) with the double bonds of polyIP. The less stable HV iodine(III) compound, PhI(O_2C(n-)_C_9F_19)_2 was generated *in situ* by mixing PhIO (1.0 eq.) and C_9F_19CO_2H (2.05 eq.) in CH_3CN. Then, I_2 (1.0 eq.) was added to generate the reactive intermediate. As expected, the reactions yielded random copolymers with both secondary and tertiary alkyl iodide and pentafluorobenzoyloxy or perfluorodecanoyloxyl pendant groups.

The structures of poly(C_6F_5CO_2, I) and poly(n-C_9F_19CO_2, I) were confirmed by NMR spectroscopy (Figure 3-7a, b). In the ^1H NMR spectrum of poly(C_6F_5CO_2, I), new signals appeared at 5.4-5.0 ppm (H-11) and 4.9-4.5 ppm (H-7), which corresponded to the methine protons −CHO_2CC_6F_5 and −CHI, respectively. In the ^19F NMR spectrum of poly(C_6F_5CO_2, I), the characteristic peaks of pentafluorobenzoyloxy groups were seen at −134.5 ppm, −148.1 ppm, and −160.2 ppm. The two isomeric fluorine-containing repeat units in the modified polymer, poly(C_6F_5CO_2, I), shown in Figure 3-7, were present in virtually equal amounts. Similar results
were observed in the $^1$H and $^{19}$F NMR spectra of poly($n$-C$_9$F$_{19}$CO$_2$, I) but the ratio of $x_{32}$ to $x_{33}$ was calculated as 1.5:1.

![Chemical Structures and Spectra](image)

**Figure 3-7.** (a) $^1$H NMR spectra of polyIP, poly(C$_6$F$_5$CO$_2$, I) and poly($n$-C$_9$F$_{19}$CO$_2$, I) in CDCl$_3$. (b) $^{19}$F NMR spectra of poly(C$_6$F$_5$CO$_2$, I) and poly($n$-C$_9$F$_{19}$CO$_2$, I) in CDCl$_3$. (c) IR spectra of films of polyIP, poly(C$_6$F$_5$CO$_2$, I) and poly($n$-C$_9$F$_{19}$CO$_2$, I).

The structures of poly(C$_6$F$_5$CO$_2$, I) and poly($n$-C$_9$F$_{19}$CO$_2$, I) were also confirmed by IR spectroscopy (Figure 3-7c). In the IR spectrum of poly(C$_6$F$_5$CO$_2$, I), new absorption peaks at 1233 cm$^{-1}$ and 1740 cm$^{-1}$, corresponding to C−F and C=O stretching vibrations, respectively, were seen. Similar features were seen in the IR spectrum of poly($n$-C$_9$F$_{19}$CO$_2$, I).
All functionalizations of polyIP with fluorine-containing HV iodine(III) reagents described above are presented in Scheme 3-6. For simplicity, only repeat units that were present at more than 5 mol% are shown.

Scheme 3-6. Functionalizations of polyIP with fluorine-containing HV iodine(III) reagents.

3.2.2. Molecular Weight Analysis by SEC

Modifications of unsaturated polymers such as polyIP, often lead to chain-scission or crosslinking reactions that can affect the physical properties of the material. SEC measurements were thus performed to examine if any changes in the molecular weight distributions occurred upon the modifications. The polymer with the highest fluorine contents, poly(n-C₉F₁₉CO₂, I), was only slightly soluble in THF, which led to an SEC trace with relatively low intensity. The data revealed that the modifications were accompanied with minor increase of $M_n$ and decrease of $M_w/M_n$, without any significant changes in the shapes of the molecular weight distributions,
proving that no significant chain degradation or crosslinking occurred. The molecular weight distributions of the modified polymers were typically narrower than the starting polyIP, likely due to the loss of the low molecular weight “tail” in the distribution during the purification by repeated reprecipitations. The SEC traces are presented in Figure 3-8.

![SEC traces](image)

**Figure 3-8.** SEC traces and molar mass distribution characteristics of (a) poly(F, I), (b) poly(CF₃, 2-IC₆H₄CO₂) and poly(CF₃, =), (c) poly(CF₃, Cl) and poly(CF₃, Br), and (d) poly(C₆F₅CO₂, I) and poly(n-C₅F₁₀CO₂, I). The SEC trace of the starting material, polyIP, is added to each of the plots for easy comparison.

### 3.2.3. Thermal analysis

To examine the thermal stability and degradation behavior of the modified polymers, TGA was carried out (Figure 3-9a). In the starting material, polyIP, only a single mass loss step was observed, while the degradation of all modified polymers was more complex. For instance, the thermogram of poly(CF₃, Cl) exhibited two degradation steps. The decomposition began (plausibly...
with dehydrochlorination) at ca. 170 °C and the maximum rate was reached at 262 °C. At the end of this first stage, the polymer lost 35 % of its weight. The second step commenced at ca. 320 °C and the maximum rate of decomposition occurred at 385 °C. At the end of that second stage of degradation when the temperature reached ca. 450 °C, the polymer lost additional 60 % of its original weight. The polymers containing alkyl bromide groups (poly(CF₃, Br)) and especially alkyl iodide groups (poly(F, I), poly(C₆F₅CO₂, I), and poly(n-C₉F₁₉CO₂, I)) degraded at the lowest temperatures, due to the relatively low stability of the C-Br and C-I bonds. For instance, the bond dissociation energies of the C-Br bonds in sec- and tert-butyl bromide are respectively ca. 300 and 293 kJ mol⁻¹, while those of the C-I bonds in the iodine-containing analogues, sec- and tert-butyl iodide, are as low as, respectively, 238 and 227 kJ mol⁻¹. The lability of alkyl iodide pendant groups makes the corresponding polymers suitable as macro chain transfer agents for chain extensions reactions, i.e., in the synthesis of graft copolymers. All results are summarized in Table 3-1, where \( T_i \) is the temperature where the degradation starts and \( T_{n, \text{max}} \) is the temperature of the maximum rate of decomposition during the \( n \)-th step.

![Figure 3-9](image-url)  
**Figure 3-9.** (a) TGA traces of polyIP and modified polymers. (b) DSC thermograms of modified polymers
Table 3-1. Thermal properties of polyIP and modified polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Degradation temperatures [°C]</th>
<th>Tg [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$</td>
<td>$T_{1,\text{max}}$</td>
</tr>
<tr>
<td>polyIP</td>
<td>250</td>
<td>364</td>
</tr>
<tr>
<td>poly(F, I)</td>
<td>116</td>
<td>116</td>
</tr>
<tr>
<td>poly(CF$_3$, 2-IC$_6$H$_4$CO$_2$)</td>
<td>144</td>
<td>184</td>
</tr>
<tr>
<td>poly(CF$_3$, Cl)</td>
<td>193</td>
<td>335</td>
</tr>
<tr>
<td>poly(CF$_3$, Br)</td>
<td>170</td>
<td>262</td>
</tr>
<tr>
<td>poly(C$_6$F$_3$CO$_2$, I)</td>
<td>100</td>
<td>149</td>
</tr>
<tr>
<td>poly(n-C$<em>9$F$</em>{19}$CO$_2$, I)</td>
<td>120</td>
<td>128</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>136</td>
</tr>
</tbody>
</table>

Differential scanning calorimetry (DSC) was applied to determine the glass transition temperatures of the polymers, and the DSC curves are shown in Figure 3-9b. The measurements were performed in heat-cool-heat cycles, in the temperature range from −30 °C to about 10-15 °C below the degradation temperature of the particular sample. No thermal transitions were observed for polyIP and poly(CF$_3$, Br) in the studied thermal region. The thermograms of all other modifier polymers showed the existence of one glass transition, except for poly(n-C$_9$F$_{19}$CO$_2$, I), in the DSC trace of which two endothermic transitions were seen. Such transitions have already been observed for other fluorine-containing polymers with similar structures and interpreted as solid-mesophase and mesophase-isotropic transitions.$^{94, 95}$

3.2.4. Contact Angles and Surface Free Energies

The surface properties of polymers can be described in terms of hydrophobicity and the sliding behavior of liquid droplets. The hydrophobicity of polymer surfaces is commonly estimated
by measuring the water dynamic contact angles (Figure 3-10a), which varied from 89° to 116° in the modified polymers. The presence of polar groups attached to the modified polymer chains, such as Cl, Br, I and iodobenzoate groups, led to decreased hydrophobicity. However, with the introduction of long perfluoroalkyl chains (poly(n-C9F19CO2, I)), the water contact angle increased to 116°, which is higher than that of Teflon-type materials (112°).96, 97

Figure 3-10. (a) Water droplets on polymer films. (b) Owens–Wendt plots for polyIP and modified polymers.

The contact angles of polyIP and the modified polymers against glycerol and ethylene glycol were also measured, and the results are summarized in Table III-2. The surface energy was calculated using the Owens and Wendt equation:98

$$\gamma_l \left(1 + \cos \theta \right) = 2 \left(\gamma^d_s \gamma^d_l \right)^{1/2} + 2 \left(\gamma^p_s \gamma^p_l \right)^{1/2} \quad (1),$$
where $\gamma_l$ is the surface tension of the liquids, $\gamma_{lp}^p$ and $\gamma_{ld}^d$ are the surface tensions of the polar and dispersion components of the liquids, and $\gamma_s^p$ and $\gamma_s^d$ are surface tensions of the polar and dispersion components of the solids. After rearrangement, the following linear dependence was obtained:

$$\frac{\gamma_l(1 + \cos \theta)}{2 (\gamma_d)^{1/2}} = \left(\gamma_s^p \right)^{1/2} \left(\frac{\gamma_{lp}^p}{(\gamma_{ld}^d)^{1/2}} \right) + \left(\gamma_s^d \right)^{1/2}$$  \hspace{1cm} (2)

Equation 2 can be employed for direct evaluation of the surface energy with $\frac{\gamma_l(1 + \cos \theta)}{2 (\gamma_d)^{1/2}}$ as the dependent variable and $\left(\frac{\gamma_{lp}^p}{(\gamma_{ld}^d)^{1/2}} \right)$ is the independent variable. Accordingly, the square of the slope of the linearized Owens–Wendt plot is $\gamma_s^d$ and the square of the intercept is equal to $\gamma_s^p$.

Contact angle values for water, glycerol, and ethylene glycol, of which the dispersion and polar components are known, were measured and the Owens–Wendt plots for all studied polymers are shown in Figure 3-10b. The surface energies of polymer films were calculated, and the results are collected in Table 3-2. Most of the modified polymers showed higher surface energy than unmodified polyIP (11.9 mN/m), but they were still competitive with Teflon-type materials (19.0 mN/m). As long perfluoroalkyl groups were introduced, the resulting polymer, poly($n$-C$_9$F$_{19}$CO$_2$, I), showed surface free energy as low as 8.8 mN/m.
Table 3-2. Wetting properties of the polymer films from polyIP and modified polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Static contact angle (θ)</th>
<th>Surface free energy [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>Glycerol</td>
</tr>
<tr>
<td>polyIP</td>
<td>104°</td>
<td>97°</td>
</tr>
<tr>
<td>poly(F, I)</td>
<td>94°</td>
<td>86°</td>
</tr>
<tr>
<td>poly(CF₃, 2-IC₆H₄CO₂)</td>
<td>95°</td>
<td>88°</td>
</tr>
<tr>
<td>poly(CF₃, =)</td>
<td>94°</td>
<td>88°</td>
</tr>
<tr>
<td>poly(CF₃, Cl)</td>
<td>95°</td>
<td>93°</td>
</tr>
<tr>
<td>poly(CF₃, Br)</td>
<td>89°</td>
<td>86°</td>
</tr>
<tr>
<td>poly(C₆F₅CO₂, I)</td>
<td>92°</td>
<td>89°</td>
</tr>
<tr>
<td>poly(n-C₉F₁₉CO₂, I)</td>
<td>116°</td>
<td>108°</td>
</tr>
</tbody>
</table>

II.3. Experimental Section

III.3.1. Materials

4-(difluoriodo)toluene (4-TolIF₂), Togni reagent II, propargyl 4-(1-pyrenyl)butyrate, iodosylbenzene (PhIO), and [bis(pentafluorobenzoylxy)iodo]benzene (PhI(O₂CC₆F₅)₂) were prepared by previously reported procedures. PolyIP (97 %, Mₙ = 10,000 g mol⁻¹, Mₘ/Mₙ = 2.8, Aldrich), I₂ (98 %, Aldrich), CuI (98 %, Aldrich), CuBr (97 %, Aldrich), CuBr₂ (97 %, Aldrich), SOCl₂ (98 %, Fisher), SOBr₂ (98 %, Oakwood), trifluoromethanesulfonic (triflic) acid (TfOH, 99 %, Aldrich), NaN₃ (99 %, Aldrich), perfluorodecanoic acid (n-C₉F₁₉CO₂H, 98 %, Oakwood), pentafluorobenzoic acid (98 %, Fisher) and the solvents, namely CHCl₃ (99 %, Aldrich), CH₂Cl₂ (99 %, Aldrich), 1,2-dichloroethane (DCE, 99 %, Fisher), ethylene glycol (99 %, Fisher), glycerol (99 %, Fisher), methanol (99 %, Aldrich), tetrahydrofuran (THF, 99 %, Fisher), N,N-dimethylformamide (DMF, 99 %, Fisher), and α,α,α-trifluorotoluene (PhCF₃, 99 %, Aldrich), were
used as received. The deuterated solvents used in the NMR analyses, CDCl₃ and CD₃CN (99.8 % D, Cambridge Isotope Laboratories), contained a small amount of tetramethylsilane as the chemical shift reference.

III.3.2. Analytical Techniques.

Molecular weights (number-average (Mₙ) and weight-average (Mₘ)) and molecular weight distribution dispersities (D = Mₘ/Mₙ) were determined by size exclusion chromatography (SEC) on a Tosoh EcoSEC system equipped with a series of 4 columns (TSK gel guard Super HZ-L, Super HZM-M, Super HZM-N, and Super HZ2000), and using THF as the eluent (flow rate 0.35 mL min⁻¹, 40 °C) and a refractive index detector. The SEC instrument was calibrated using a series of linear polystyrene standards. Infrared (IR) spectra were collected on a Thermo Scientific Nicolet iS10 FT-IR Spectrometer. Each sample was prepared by dissolving ca. 10 mg of polymer in 0.5 mL of CH₂Cl₂ or PhCF₃, followed by casting a film on a KBr or NaCl plate. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG 209 F3 Tarsus instrument at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere at a flow rate of 50 mL min⁻¹, with samples that were weighed in alumina crucibles. ¹H and ¹⁹F NMR spectra of the purified polymers (ca. 0.1 g in 0.6 mL of solvent) were acquired respectively on a Bruker Avance DRX spectrometer (400 MHz) and JEOL ECA multinuclear NMR spectrometer (470 MHz). Differential Scanning Calorimetry (DSC) studies were performed on a Netzsch DSC 214 Polyma instrument at a heating rate of 10 °C min⁻¹ under nitrogen flow (50 mL min⁻¹) with samples weighed in Al pans. The glass transition temperatures (Tₛ) of the polymers were determined during the second heating cycle. The contact angles of droplets of various liquids on glass surfaces coated with polymers were measured by using a DataPhysics dynamic goniometer (Model ES) equipped with an automated micrometer.
droplet regulator. Poly($n$-$C_{9}F_{19}CO_2$, I) (see below for explanation of the nomenclature used) was dissolved in PhCF$_3$ (1 wt%), while polyIP and all other modified polymers were dissolved in CH$_2$Cl$_2$ (1 wt%). Then, polymer films were prepared by the spin-coating method (2000 rpm, 30 s) on clean glass slides, which were dried in vacuum for 24 h. The glass slide with the sample was mounted on the stage of the goniometer, and droplets were deposited with a 500-$\mu$L Hamilton syringe. Since the measured contact angles are droplet size-dependent, the volumes of the sessile droplets for each measurement were kept constant (50 $\mu$L) by using an automated dispense unit. The contact angles were measured 5 s after the liquid droplet was plunged onto the surface. The SCA20 software was employed to analyze the data.

3.3.3. Synthetic Methodologies

3.3.1. Synthesis of Fluorine-Containing HV Iodine(III) Compounds

Synthesis of PhI(O$_2$CR)$_2$

The formation of PhI(O$_2$C$_6$F$_5$)$_2$ was investigated by $^1$H NMR spectroscopy. First, PhIO (0.022 g, 0.1 mmol, 1 eq.) and C$_6$F$_5$CO$_2$H (0.0466 g, 0.22 mmol, 2.2 eq.) were combined in a test tube. Then, CDCl$_3$ (1.0 mL) was added, the test tube was sealed and the mixture was stirred at 30 °C. After 5 min, the reaction mixture became clear and homogeneous, and a sample was withdrawn and analyzed by $^1$H NMR spectroscopy. The appearance of peaks centered at 8.2 ppm, 7.7 ppm, and 7.6 ppm indicated the formation of PhI(O$_2$C$_6$F$_5$). A similar experiment was conducted to study the formation of PhI(O$_2$C($n$-)C$_9$F$_{19}$)$_2$. PhIO (0.022 g, 0.1 mmol, 1 eq.) and $n$-C$_9$F$_{19}$CO$_2$H (0.1131 g, 0.22 mmol, 2.2 eq.) were mixed in CD$_3$CN (1 mL), and the reaction was monitored by $^1$H NMR spectroscopy.
Synthesis of Iodo-Fluorinated PolyIP (Poly(F, I)).

I$_2$ (0.63 g, 2.5 mmol, 0.5 eq.) was dissolved in anhydrous CHCl$_3$ (10 mL) in a 50-mL Teflon vial. The reaction mixture was then cooled in an ice bath and 4-TolIF$_2$ (1.33 g, 5.0 mmol, 1.0 eq.) was added upon stirring to the above solution. After 10 min, solution of polyIP (0.34 g, 5.0 mmol C=C groups, 1.0 eq.) in CHCl$_3$ (10 mL) was added slowly. The formed dark brown homogeneous solution was stirred at 0 °C for 30 min. The solvent was then evaporated under vacuum. The residue was purified by re-dissolving in CH$_2$Cl$_2$ and precipitating in methanol. This procedure was repeated two more times. Then the precipitate was filtered and dried under vacuum at room temperature to a constant weight.

Synthesis of 2-Iodobenzyloxy-Trifluoromethylated PolyIP (poly(CF$_3$, 2-IC$_6$H$_4$CO$_2$)).

To a 100-mL round bottom flask equipped with a magnetic stir bar, polyIP (0.50 g, 7.35 mmol C=C groups, 1.0 eq.), CuI (0.28 g, 1.47 mmol, 0.2 eq.), and Togni reagent II (3.48 g, 11.0 mmol, 1.5 eq.) were added, followed by the addition of DCE (50 mL). The mixture was stirred at 60 °C for 16 h, and then the solvent was removed under reduced pressure. The resulting residue was re-dissolved in CH$_2$Cl$_2$ and precipitated in methanol. This procedure was repeated two more times. The precipitate was collected and dried under vacuum to obtain modified polyIP containing 2-iodobenzyloxy and trifluoromethyl groups (poly(CF$_3$, 2-IC$_6$H$_4$CO$_2$)).
Synthesis of Unsaturated Polymers with Pendant Trifluoromethyl Groups (Poly(CF₃, =)).

To a solution of poly(CF₃, 2-IC₆H₄CO₂) (0.21 g, 0.5 mmol of 2-iodobenzoxyloxy groups, assuming complete functionalization of the double bonds in polyIP in the previous step, 1.0 eq.) in CH₂Cl₂ (50 mL), TfOH (0.45 mL, 5.0 mmol, 10.0 eq.) was added. The reaction mixture was stirred for 24 h at room temperature and then the solvent and remaining TfOH were removed under reduced pressure. The product, poly(CF₃, =), was purified by re-dissolving it in CH₂Cl₂, followed by precipitation in methanol. This purification process was performed two more times and the polymer was dried under vacuum at room temperature to constant weight.

Synthesis of Chloro-Trifluoromethylated PolyIP (poly(CF₃, Cl)) and Bromo-Trifluoromethylated PolyIP (poly(CF₃, Br)).

In a dry round bottom flask, polyIP (0.25 g, 3.68 mmol C=C groups, 1.0 eq.), Togni reagent II (1.39 g, 4.42 mmol, 1.2 eq.), and CuBr₂ (0.041 g, 0.184 mmol, 0.05 eq.) were added to anhydrous CHCl₃ (30 mL) under N₂. Then, the thionyl halide, SOCl₂ or SOBr₂, (3.67 mmol, 1.0 eq.) was added dropwise and the mixture was stirred at room temperature for 16 h. The solvent was evaporated using a rotary evaporator, the functionalized polymer was isolated and purified by re-dissolving it in CH₂Cl₂ and subsequent precipitation in methanol. The product was then dried in vacuum at room temperature for 24 h.

Synthesis of Azido-Trifluoromethylated PolyIP (poly(CF₃, N₃)).

A dry 50 mL round-bottom flask was charged with poly(CF₃, Cl) described above (0.174 g, 1.0 mmol of alkyl chloride groups, 1.0 eq., assuming complete chloro-trifluoromethylation in
the previous step), NaN₃ (0.13 g, 2 mmol, 2.0 eq.), and DMF (20 mL). The mixture was stirred at 60 °C for 24 h, and then poured into methanol. The white precipitate was dissolved in CH₂Cl₂ and precipitated in methanol. This purification procedure was repeated two additional times. The obtained white powder was washed with water (200 mL) and methanol (200 mL) and then dried in vacuum for 24 h.

**Synthesis of Pyrene-Labeled Polymers by Click-type Functionalization of Poly(CF₃, N₃).**

Poly(CF₃, N₃) (0.181 g, 1.0 mmol of azide groups, 1.0 eq, assuming complete of azidation in the previous step), CuBr (0.143 g, 1.0 mmol, 1.0 eq.), and propargyl 4-(1-pyrenyl)butyrate (0.312 g, 1.0 mmol, 1.0 eq.) were mixed in a glass tube and a magnetic stir bar was added. The tube was then sealed with a rubber septum, which was secured with electric tape, and the air was removed by applying vacuum and back-filling the tube with N₂ (five times). DMF (5 mL), which had been sparged with N₂, was injected in the reaction vial using a nitrogen-purged syringe. The mixture was stirred at 60 °C for 24 h. At the end of the reaction, the resulting polymer was precipitated into methanol, filtered off and dried under vacuum at room temperature for 24 h.

**Synthesis of Iodo-Pentafluorobenzoxyloxylated PolyIP (poly(C₆F₅CO₂, I)).**

To a solution of polyIP (0.25 g, 3.68 mmol repeat units, 1.0 eq.) in CHCl₃ (30 mL), PhI(O₂CC₆F₅)₂, (2.30 g, 3.68 mmol, 1.0 eq.), and I₂ (0.47 g, 1.94 mmol, 0.5 eq.) were added, and the mixture was stirred at room temperature for 10 min. The solvent was then removed using a rotary evaporator. The product was re-dissolved in CH₂Cl₂ and precipitated with methanol (three times in total) and it was then collected and dried under vacuum for 24 h at room temperature.
Synthesis of Iodo-Perfluorodecanoyloxylated PolyIP (poly(n-C₉F₁₉CO₂, I)).

In a 100 mL round bottom flask, PhIO (0.81 g, 3.68 mmol, 1.0 eq.) was suspended in CH₃CN (30 mL), and n-C₉F₁₉CO₂H (3.78 g, 7.36 mmol, 2.0 eq.) was added. The mixture was cooled to 0 °C in an ice bath and, after a colorless solution formed (ca. 5 min), I₂ (0.93 g, 3.68 mmol, 1.0 eq.) was added. The mixture was stirred at 0 °C until pale pink coloration was observed (ca. 10 min). Then, a solution of polyIP (0.25 g, 3.68 mmol C=C groups, 1.0 eq.) in CHCl₃ (30 mL) was added and the reaction mixture was stirred at 0 °C for 10 min. The solvent was removed under vacuum and the functionalized polymer was purified by re-dissolving in PhCF₃, followed by precipitation in methanol. This purification was repeated two more times. The isolated polymer was dried under vacuum for 24 h.

3.4. Conclusions

Several efficient synthetic approaches to fluorine-containing polymers derived from polyIP are presented, which take advantage of the reactivity of HV iodine(III) compounds with fluorine-containing ligands, including F, CF₃, C₆H₅CO₂, and n-C₉F₁₉CO₂. In some of the modifications of polyIP, in addition to fluorine-containing functionalities, and depending on the structure of the HV iodine(III) reagent, alkyl halide and carboxylate (ester) functionalities were also introduced. Further, additional functionalizations were demonstrated for the polymer with alkyl halide pendant groups, including nucleophilic substitution with azide and subsequent click reactions, e.g., a fluorescent (pyrene-based) alkyne. The incorporation of perfluorinated carboxylate in polyIP markedly increased the hydrophobicity and lowers the surface energy, which makes the modification attractive for applications such as nonstick and self-cleaning coating. All functionalization reactions proceeded at mild conditions and without any notable degradation
and/or crosslinking, which makes them attractive for the modification of high molar mass polyIP as well as natural rubber.

3.5. Acknowledgements

Financial support by the National Science Foundation through a CAREER grant (CHE-1455200) to NVT is gratefully acknowledged. Prof. Tomce Runchevski and Jonathan Lefton are acknowledged for providing access to and helping with DSC and TGA instruments. We also thank Grace Kennedy and Terry Chu from ACD/Labs for helpful discussions related to the simulation of NMR spectra.

3.6. References


CHAPTER 4

4.1. Introduction

4.1.1. Development of Phosphorus-Containing HV Iodine(III) Compounds

Organophosphorus compounds were quickly established as versatile reaction partners for HV iodine(III) reagents. The broad reactivity displayed by HV iodine(III) reagents has easily merged with that inherent to phosphines, phosphites, and other organophosphorus compounds to produce some remarkable transformations. To date, various phosphorus-containing HV iodine(III) reagents have been prepared and studied.\(^1\) In 1988, Koser explored the synthesis of iodanes with phosphate ligands, and detailed that the reaction of PhI(OAc)\(_2\) with diphenyl- or dibenzylphosphate in wet acetonitrile gave [hydroxyl((bis-(alkoxy)phosphoryl)oxy)iodo]benzenes in 90 % and 88 % yield, respectively (Figure IV-1a).\(^2\) Moriarty and Prakash subsequently demonstrated that the analogous derivatives could also be prepared by the reaction of various phosphonic and phosphinic acids with iodosobenzene (Figure IV-1b).\(^3\) In 2010, Zhu and co-workers developed a solvent-free approach to the iodanes, rapidly achieved by grinding PhI(OAc)\(_2\) and the dialkylphosphates (Figure IV-1c).\(^4\) The cyclic phosphorus-containing HV iodine(III) was also reported, being prepared from chlorobenziodoxolone and silver diphenyl phosphate (Figure IV-1d).\(^5\)
Scheme 4-1. Synthesis of phosphorus-containing HV iodine(III) reagents.

Up to today, phosphorus-containing HV iodine(III) reagents have been utilized widely as phosphine-containing groups transfer agents in organic synthesis. For instance, a related iodo-oxyphosphorylation reaction has been reported by Togo and co-workers, wherein alkenes, alkynes and glycals were converted to the vicinal iodo-phosphates and -phosphinates. Cyclohexene reacted with [hydroxyl((bis-(alkoxy)phosphoryl)oxy)iodo]benzene to give the iodo-oxyphosphorylated product in 82 % yield (Scheme 4-2a), as did various glycals, which resulted in mixtures of α- and β-glycosyl phosphinates (Scheme 4-2b) and iodohydrin compound. However, the iodo-oxyphosphorylated product was obtained in 72 % yield, instead of the corresponding glycosyl ester. Probably, the iodophosphoryloxylation of glucal occurred, and the subsequent hydrolysis by the hydroxy group derived from iodane(III) at the reactive anomeric position in the sugar compound occurred to give iodohydrin because of the phosphinate anion as a good leaving group.
Despite various advantages for natural rubber (NR), its inherently high flammability limits its applications in many important fields including conveyor belts for coal mine, power cables, tire treads, etc. The limiting oxygen index (LOI) of pure NR is only about 18.0 %, indicating that NR is flammable. In addition, smoke and toxic gases will emit when NR ignited, which seriously decreases the possibility to escape and thus bring about a great threat to life and property. Much attention has been paid to the flame retardation of NR. To date, the main approach to the flame retardation of NR is incorporating additive-type flame retardants into the matrix. Various additive-type flame retardants, such as halogenated additives, metal hydroxide, phosphorus-containing flame retardants and nano flame retardants, have been successfully introduced to the NR to improve the flame retarding performance. The different flame retardants have their advantages and disadvantages. For instance, inorganic flame retardants such as magnesium hydroxide and aluminum hydroxide are “green” environmentally friendly flame retardants, but they are suffered from low flame-retarding efficiency. The halogenated flame retardants with higher efficiency were
already known to produce toxic substances during burning, which having a great effect on the environment and health.\textsuperscript{12} Nano flame retardants have a unique advantage in maintaining the mechanical properties of NR, but its flame-retarding efficiency is not ideal.

Phosphorus-based flame retardants have developed and utilized as a type of effective and environmentally friendly halogen-free flame retardant. Most of the current phosphorus-based additive flame retardants may act simultaneously in condensed and gaseous phases.\textsuperscript{13} In the condensed phase, phosphorus-based additive flame retardants may enhance the amount of carbonaceous residue or char during burning and then reduce the volatile decomposition products. In the gaseous phase, some phosphorus-based additive flame retardants may produce a lot of free radicals during the thermal decomposition process, and they may react with the free radicals which are generated from polymers, then the free-radicals-supported combustion of polymers might be stopped due to the lack of fuel.\textsuperscript{14, 15} In Menon et al.’s report,\textsuperscript{16} different amounts of 2-ethyl hexyl diphenyl phosphate was added in NR by a two-roll mixing mill, and the Limiting Oxygen Index (LOI) of NR composite increased from 17.0\% to 17.5\% at 15 phr of the additive.

Efficient and reliable methods for the introduction of phosphorus-containing groups in small organic molecules by HV iodine(III) reagents have been reported, but their potential in macromolecular chemistry has not been explored. Encouraged by the above-mentioned work that polyIP can be functionalized efficiently and without apparent degradation or crosslinking with fluorine-containing HV iodine(III) compounds, we attempted simple and efficient synthetic approaches to phosphorus-containing polymers derived from polyIP, based on reactions of the unsaturated polymer with HV iodine(III) reagents with phosphorus-based ligands.
4.2. Results and Discussion

4.2.1. Synthesis and Characterization of Iodo-Phosphoryloxylated PolyIP

Togo et. al demonstrated the utility of [(diphenylphosphoryloxy)(hydroxy)iodo]benzene (PHIB) and I$_2$ in the iodo-phosphoryloxylation of various alkenes and alkynes. Cyclohexene reacted with PHIB to give the iodo-oxyphosphorylated product in 82% yield (Scheme 4-2a), as did various glycals, which resulted in mixtures of α- and β-glycosyl phosphinates (Scheme 4-2b) in up to 93% yield. However, up to now, there are no reports about the applications of this reaction in polymer chemistry. In this chapter, iodo-phosphoryloxylation of polyIP was achieved by taking advantage of the above-mentioned reaction. As Figure 4-2 shown, two approaches were developed to prepare the iodo-oxyphosphorylated polyIP. In the first approach, (Ph)$_2$PO(OH)(1.0 eq.) was mixed with PhIO (0.5 eq.) to form C$_6$H$_5$I[OPO(Ph)$_2$][OH], PHIB) in situ. Then, I$_2$ (1.0 eq.) was added to generate the reactive intermediate., which then quickly reacted (within 1 h at ambient temperature) with the double bonds of polyIP. As expected, the reactions yielded random copolymers with both secondary and tertiary alkyl iodide and oxyphosphoryl pendant groups, named polymer 1. In the second approach, PHIB was firstly prepared. Then, PHIB(1.0 eq.) was mixed with I$_2$ (1.0 eq.) to form the reactive intermediate, which then quickly reacted with the double bonds of polyIP to yield polymer 2.
Figure 4-1. (a) $^1$H NMR spectra of polyIP, polymer 1, and polymer 2 in CDCl$_3$. (b) $^{31}$P NMR spectra of polymer 1, and polymer 2 in CDCl$_3$. (c) FT-IR spectra of the films of polyIP, polymer 1, and polymer 2.

The structures of polymer 1 and 2 were confirmed by NMR spectroscopy (Figure 4-2a, b). In the $^1$H NMR spectrum of polymer 1, the signals at 8.0-7.0 ppm (H-8-17, H-20-29) in the aromatic proton region confirmed the presence of oxyphosphoryl groups. The new signals appeared at 5.3-4.2 ppm (H-31, H-39) and 4.0-3.0 ppm (H-7, H-35), which corresponded to the methine protons −CHI and −OPO(Ph)$_2$, respectively. In the $^{31}$P NMR spectrum of polymer 1, the characteristic peaks of oxyphosphoryl groups were seen at 32.5 ppm, and 27.3 ppm. These two
isomeric oxyphosphoryl-containing repeat units (a and b), in polymer 1, was calculated as 0.76:0.34, shown in Figure IV-2a. Based on the integration of $^1$H NMR and the IR spectrum (vide infra), the iodohydrin product also formed, which was also observed in the previous literature. The ratios of the repeat units of polymer 1 can be determined as 0.3:0.1:0.3:0.3, based on the integration of the signals in the $^1$H NMR and $^{31}$P NMR spectra. The degree of iodo-oxyphosphorylation of polyIP was 40%. Similar conclusions could be drawn from the $^1$H and $^{31}$P NMR spectra of polymer 2, but the ratio e:f:g:h was determined as 0.3:0.24:0.2:0.26, i.e., 54 mol% of repeat units contained oxyphosphoryl pendant groups.

The IR spectra of polyIP, polymer 1 and 2 are displayed in Figure 4-2c. The presence of O–H stretching (3600–3100 cm$^{-1}$) confirmed the formation of the iodohydrin product. The absorption bands at 1204 cm$^{-1}$ in the spectrum of polymer 1 can be assigned to P=O vibrations, which indicated that the oxyphosphoryl groups were successfully introduced. Similar results were also observed in the IR spectrum of polymer 2.

4.2.2. SEC Analysis

Modifications of unsaturated polymers such as polyIP, often lead to chain-scission or crosslinking reactions that can affect the physical properties of the material. SEC measurements were thus performed to examine polymer 1 and 2 if any changes in the overall molecular weight distributions occurred upon the modifications. The data revealed that the modifications were accompanied with minor increase of Mn and decrease of $M_w/M_n$, without any significant changes in the shapes of the molecular weight distributions, proving that no significant chain degradation or crosslinking occurred. The molecular weight distributions of the modified polymers were
typically narrower than the starting polyIP, likely due to the loss of the low molecular weight “tail” in the distribution during the purification by repeated reprecipitations. The SEC traces are presented in Figure 4-3.

**Figure 4-2.** SEC traces and molar mass distribution characteristics of polyIP, polymer 1, and 2. The numbers at each curve, from left to right, are $M_n$ and $M_w/M_n$.

**4.3. Experimental Section**

**4.3.1. Materials.**

PolyIP (97 %, $M_n = 10,000$ g mol$^{-1}$, $M_w/M_n = 2.8$, Aldrich), I$_2$ (98 %, Aldrich), diphenylphosphinic acid (98 %, Oakwood), and the solvents, namely CH$_2$Cl$_2$ (99 %, Aldrich), acetonitrile (CH$_3$CN, 99 %, Aldrich), tetrahydrofuran (THF, 99 %, Fisher), were used as received. The deuterated solvents used in the NMR analyses, CDCl$_3$ and CD$_3$CN (99.8 % D, Cambridge Isotope Laboratories), contained a small amount of tetramethysilane as the chemical shift reference.
4.3.2. Analytical techniques.

Molecular weights (number-average ($M_n$) and weight-average ($M_w$)) and molecular weight distribution dispersities ($D = M_w/M_n$) were determined by size exclusion chromatography (SEC) on a Tosoh EcoSEC system equipped with a series of 4 columns (TSK gel guard Super HZ-L, Super HZM-M, Super HZM-N, and Super HZ2000), and using THF as the eluent (flow rate 0.35 mL min$^{-1}$, 40 °C) and a refractive index detector. The SEC instrument was calibrated using a series of linear polystyrene standards. Infrared (IR) spectra were collected on a Thermo Scientific Nicolet iS10 FT-IR Spectrometer. Each sample was prepared by dissolving ca. 10 mg of polymer in 0.5 mL of CH$_2$Cl$_2$, followed by casting a film on a NaCl plate.

4.3.3. Synthetic Methodologies

**Synthesis of [(diphenylphosphoryloxy)(hydroxy)iodo]benzene (PHIB)**

Diphenylphosphinic acid (10.0 g, 46 mmol) was added to a stirred solution of PhI(OAc)$_2$ (14.8 g, 46 mmol) in MeCN (100 mL) at room temperature. After 1 h, water (1.7 mL, ca. 92 mmol, 2 eq.) was added to this mixture and the whole mixture was stirred for 4 h. The resulting precipitate was filtered and washed with water (ca. 100 mL) and acetonitrile (ca. 100 mL) to give the title compound as a white solid (14.2 g, 70 % yield).

**Synthesis of Iodo-Phosphoryloxylated PolyIP (polymer 1)**

In a 100 mL round bottom flask, PhIO (1.1 g, 5 mmol, 1.0 eq.) was suspended in CH$_2$Cl$_2$ (30 mL), and diphenylphosphinic acid (2.18 g, 10 mmol, 2.0 eq.) was added. The mixture was stirred after a colorless solution formed (ca. 10 min), I$_2$ (1.27 g, 5 mmol, 1.0 eq.) was added. The mixture was stirred until pale pink coloration was observed (ca. 5 min). Then, a solution of polyIP
(0.34 g, 5 mmol C=C groups, 1.0 eq.) in CH₂Cl₂ (20 mL) was added and the reaction mixture was stirred at room temperature for 1 h. The remaining unreacted iodine was removed by washing with saturated sodium thiosulfate solution. The solvent was removed under vacuum and the functionalized polymer was purified by re-dissolving in CH₂Cl₂, followed by precipitation in methanol. This purification was repeated two more times. The isolated polymer 1 was dried under vacuum for 72 h.

Synthesis of Iodo-Phosphoryloxylated PolyIP (polymer 2)

In a 100 mL round bottom flask, PHIB (4.38 g, 10 mmol, 2.0 eq.), I₂ (1.27 g, 5 mmol, 1.0 eq.), and CH₂Cl₂ (30 mL), were added. The mixture was stirred at room temperature for 10 min. Then, a solution of polyIP (0.34 g, 5 mmol C=C groups, 1.0 eq.) in CH₂Cl₂ (20 mL) was added and the reaction mixture was stirred for another 1 h. The remaining unreacted iodine was removed by washing with saturated sodium thiosulfate solution. The solvent was removed under vacuum and the functionalized polymer was purified by re-dissolving in CH₂Cl₂, followed by precipitation in methanol. This purification was repeated two more times. The isolated polymer 2 was dried under vacuum for 72 h.

4.4. Conclusions

Two efficient synthetic approaches to phosphorus-containing polymers derived from polyIP are presented, which take advantage of the reactivity of HV iodine(III) compounds with phosphorus-containing ligands. In addition to phosphorus-containing functionalities, alkyl iodide functionalities were also introduced. The incorporation of phosphinate and alkyl iodide groups in
polyIP markedly makes the modification attractive for developing new flame retardants. The functionalization reactions proceeded at mild conditions and without any notable degradation and/or crosslinking, which makes them attractive for the modification of high-molar-mass polyIP as well as natural rubber.

4.5. References

