**Novel Terpolymers from Borane Initiated Copolymerization of Triphenyl Arsonium and Sulfoxonium Ylides: An Unexpected Light Emission**

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Authors: Nikos Hadjichristidis and De Wang

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COMMUNICATION

Novel Terpolymers from Borane Initiated Copolymerization of Triphenyl Arsonium and Sulfoxonium Ylides: An Unexpected Light Emission

De Wang*[a] and Nikos Hadjichristidis*[b]

Abstract: We report the first synthesis of well-defined poly[(phenylenemethylene-co-methylpropylene)-b-methylene, [(C1-co-C3)-b-C1]], terpolymers via one-pot borane initiated random copolymerization of ω-methylallyl (C3 units, chain is growing by three carbon atoms at a time) and benzyltriphenylarsonium (C1 units, chain is growing by one carbon atom at a time) ylides, followed by polymerization of sulfoxonium methyldie (C1 units). Other substituted arsion ylides, such as prenyltarylanyl, propyltriphenyl and (4-substituted-2-methylallyl)triphenyl can also be used instead of benzyltriphenylarsonium. The obtained terpolymers are well-defined, possess a predictable molecular weight and low polydispersity (Mw/Mn = 1.83–9.68×10^2 g/mol, D = 1.09–1.22). An unexpected light emission phenomenon was discovered in these non-conjugated terpolymers as proved by fluorescence and NMR spectroscopy. This phenomenon can be explained by the isomerization of the double bonds of allylic monomeric units along the chain of the terpolymers (isomerization-induced light emission).

Boron compounds have been used as initiators in the polymerization of dimethylsulfoxonium methyldie, a living C1 polymerization (chain is growing by one carbon atom at a time) discovered by Shea et al and coined the name polyhomologation.1 This polymerization, leading to well-defined ω-hydroxyl polymethylene (PM, equivalent to polyethylene), was used to synthesize PM-based homo- and block copolymers with different topology (linear, star, cyclic, etc).2 Our group was also used polyhomologation of dimethylsulfoxonium methyldie to obtain well-defined PM-based linear, miktoarm star and brush copolymers by designing/synthesizing novel borane initiators or by combining polyhomologation with other living/controlled living polymerization methods such as anionic, cationic, atom transfer radical, ring-opening, and ring-opening metathesis polymerization.3 Later, efforts were focused in the synthesis of substituted ylides, such as dimethylaminophenylsulfoxonium methyldie, diethylsulfoxonium methyldie, (dimethylamino)tolylsulfoxonium cyclopropylidy, with the hope of obtaining poly(substituted methylene).4 Although the homopolymerization of substituted sulfoxonium ylides were unsuccessful (due to the steric hindrance around boron centers), however, the copolymerization of these substituted ylide monomers with sulfoxonium methyldie was successful. Limited by the synthetic difficulty and diversity of sulfoxonium ylides, the development of new ylide monomers in boron-catalyzed polymerization was highly demanded.

In 2003, Mioskowski et al reported that 2-methylallyltiphenyl arsion ylide is compatible with borane initiated polymerization,5a However, this monomer did not lead to polymer substituted on every one carbon atom (C1), but rather on every three carbon atoms (C3 polymerization), meaning that the chain is growing by three carbon atoms at a time. In 2005, the same authors realized that a few others 2-allylstibutriphenylarsonium ylides show the same behavior.5b Later, Mioskowski et al discovered that by using a non-substituted allylarsion ylide as monomer a C1/C3 random copolymer was obtained, whereas by using terminal dimethyl substituted allylic arsion ylde a C1 homopolymer was obtained.6 They explained the differences by using sigmatropic rearrangement arguments.

Encouraged by this work, our group discovered that 3-methylallyltiphenylarsonium ylide, a ω-monomosubstituted allylarsion ylide, leads also to C3 polymerization. Moreover, by combining ω-monomosubstituted allylic arsion ylde (C3) with sulfoxonium methyldie (C1) we were able to synthesize well-defined methylene/3-methylpropylene block and random copolymers (Scheme 1, A).7 Encouraging by these discoveries we started exploring the borane initiating polymerization of other arsion ylides hoping to obtain novel polymeric materials with unprecedented properties (Scheme 1, B).

Scheme 1. (A) New C3/C1 diblock copolymers (previous work); (B) terpolymers (this work) from arsion and sulfoxonium ylides.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.
In this communication, we report the design/synthesis of several novel non-allylic triphenylarsonium ylides and explore their homo- and copolymerization with $\omega$-methylallyltriphenylarsonium ylide using triethylborane as the initiator. Moreover, we report the synthesis of well-defined diblock terpolymers having C1-co-C3 and PM blocks. These terpolymers despite the fact that they don’t possess conjugated double bonds emit light. This unexpected phenomenon, investigated by fluorescence and NMR spectroscopy, revealed that the isomerization of the double bonds of the C3 units, leading to conjugated double bonds, is the cause of the emission. This phenomenon (isomerization-induced light emission) is not present either in polybutadiene-1,4 or polysoprene-1,4 (C4 polymerization, chain growing by four carbon atoms at a time) since the double bonds, unlike in our C3 polymers, are in every four carbons and thus their isomerization does not lead to conjugated double bonds.

We first synthesized benzyltriphenylarsenic tetrafluoroborate salt (Scheme S1 and Figure S1-S4, ESI), which can be transformed to benzyltriphenylarsenic ylide monomer, by treatment with $\text{n}$-butyllithium. The homopolymerization of benzyltriphenylarsenic ylide with triethylborane was failed due to the steric congestion around the boron complex. The copolymerization of benzyltriphenylarsenic ylide and sulfur hexafluoride methylide with triethylborane was also unsuccessful, even after refluxing the mixture of monomers for 3 days (pH=7.0, phenolphthalein indicator) due to the same steric reason. In contrary, the copolymerization of benzyltriphenylarsenic ylide with 3-methylallyltriphenylarsenic ylide was successful because the 1,3-sigmatropic rearrangement releases the steric hindrance around boron. The general reactions for the synthesis of poly[(methylpropylene-co-phenylmethylene)-b-methylene] terpolymers [(PA-co-PBz)-b-PM] are given in Scheme 2. Treatment of benzyltriphenylarsenic and allyltriphenylarsenic tetrafluoroborate salts in tetrahydrofuran (THF) with $\text{n}$-butyllithium at -78 °C under argon, resulted in a clear red solution proving the in situ generation of the corresponding ylide monomers. The red solution was allowed to warm up to room temperature slowly (about 2 hours), and then triethylborane was added, followed by heating at 60 °C for two hours. A clear colorless and neutral solution (pH=7.0, the absence of monomer) was obtained and used to initiate the polyhomologation of sulfur hexafluoride methylide at 80 °C for twenty minutes until the solution became neutral (pH=7.0). The terpolymers (PA-co-PBz)-b-PM were obtained after oxidation/hydrolysis with trimethylamine N-oxide dihydrate (TAO·2H$_2$O) [Scheme S3, ESI]. The $^1$H NMR spectrum of sample corresponding to polymer 3 (Table 1), a representative example, clearly shows the signals of the corresponding monomeric units (Figure S5, ESI). The aromatic protons are appeared at 7.10-7.41 ppm, the peak at $\delta$ = 5.40 ppm assigned to the allylic double bond protons, the aliphatic protons are appeared at 1.11-1.65 ppm and 2.51-2.83 ppm, in agreement with the previous report. The chain-end protons assigned to $-\text{CH}_2-$ connected to the hydroxy group at $\delta$ = 3.66 ppm can be used to calculate the degree of polymerization. The peak at 970 cm$^{-1}$ (FT-IR spectrum) indicates that the double bonds (C3 segment) possess the $E$-configuration (trans), and the two peaks at 699 and 758 cm$^{-1}$ further indicate the aromatic ring (phenyl group) existence (Figure S6, ESI).

The molecular characteristics of three more terpolymers (1, 2 and 4, Table 1) synthesized following the same general procedure described previously, are given in Table 1 and the corresponding GPC traces in Figure 1A. It is clear that the synthesized terpolymers ($M_n$ (NMR) = 1.83·10$^4$ g/mol) posses monomodal and narrow GPC traces ($D$ = 1.09-1.17). In addition, a clear shift of the elution peak from low to high molecular weight was observed, in accordance with the increased degree of polymerization (DP) as determined by NMR. The $DP_{NMR}$ of PM is higher than the calculated values and this could be attributed to the oxidation/decomposition of a part of the 3-arnon macroinitiator during the addition of sulfur hexafluoride methylide. The DSC traces of the diblock terpolymers are shown in Figure 1B. For the low molecular weight (Table 1, entry 1, $M_n$ (NMR) = 1.83·10$^3$ g/mol) terpolymer, the melting temperature ($T_m$) corresponding to PM is 89.4 °C with a crystallinity of about 44%. By increasing the molecular weight (Table 1, entries 2-4, $M_n$ (NMR) = 4.17-9.68·10$^3$ g/mol) of PM, the melting temperature ($T_m$) increases to 114.9 °C, as expected, with a slight decrease of crystallinity (29-35%). It seems that the existence of the “soft” segments (C3 and substituted C1 segments) exercises a small influence on the crystallization.

**Table 1.** Molecular characteristic and melting temperatures of the synthesized [(PA-co-PBz)-b-PM] diblock terpolymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>$DP_{NMR}$ ($\text{AUM}$)</th>
<th>$M_{NMR}$ (g/mol)</th>
<th>$T_m$ (°C)</th>
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<tr>
<td>1</td>
<td>PA$_x$-co-PBz$_y$-b-PM$_z$</td>
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<td>2</td>
<td>PA$<em>{1.7}$-co-PBz$</em>{1.1}$-b-PM$_{1.1}$</td>
<td>17/17/10</td>
<td>4.35·10$^4$</td>
<td>100.8</td>
</tr>
<tr>
<td>3</td>
<td>PA$<em>{2.7}$-co-PBz$</em>{2.7}$-b-PM$_{1.1}$</td>
<td>271/17/10</td>
<td>4.88·10$^4$</td>
<td>108.3</td>
</tr>
<tr>
<td>4</td>
<td>PA$<em>{2.7}$-co-PBz$</em>{2.7}$-b-PM$_{1.1}$</td>
<td>20/27/250</td>
<td>9.68·10$^4$</td>
<td>114.9</td>
</tr>
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$^{a}$The $DP_{NMR}$ is the degree of polymerization, calculated by [$M_n$ (NMR)]$^{1/2}$.$^b$ $M_{NMR}$ and $DP_{NMR}$ were determined by $^1$H NMR (1.22-2.5 million benzene, 40 °C, 50MHz, $M_{NMR}$ = $M_n$ + $M_{w}$ - $M_c$, $M_{w}$ = $M_{NMR}$ + $M_{NMR}$, $M_{c}$ = $M_{c}$, $F_{D}$) were determined versus polyethylene standards in high-temperature GPC (TCl as solvent at 150 °C). $^c$Isolated yield after precipitation in ethanol/water and drying under vacuum at 50 °C overnight.

Figure 1. (A) HT-GPC traces (TCB at 150 °C, PS standard); (B) DSC traces of terpolymers under nitrogen at a heating rate at 10 °C/min.
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Having shown that the benzyltriphenylarsonium ylide can be used as substituted C1 monomer in the copolymerization with ω-methyallylarsenic ylide initiated with triethyleneborane, we synthesized and investigated other substituted ylides such as propyltriphenylarsonium, (3-methylbut-2-en-1yl)triphenylarsenium and (4-fluorobenzene)triphenylarsenium ylide (Figure S7-8, ESI). For the synthesis of the corresponding terpolymers 5-7 (monomer to initiator mole ratio was \([M_{\text{Bz}}]/(M_{\text{Allyl}}+M_{\text{PBz}}) = 17/17/100/1]\), the same procedure as of terpolymer (PA-co-PBz)–b–PM was followed. The \(^1\)H NMR spectra displayed the expected signals corresponding to the two arsonium ylides and sulfoxonium methylide (Figure S9-10, ESI). The molecular weights of terpolymers 5-7 were determined by \(^1\)H NMR end group analysis (\(M_n = 4.3\times10^3\) g/mol) and polydispersities were detected by HT-GPC with polystyrene as standards (\(D = 1.16-1.22\)). The HT-GPC traces were monomodal with narrow dispersity, proving that our strategy is efficient and powerful for the construction C1/C3 terpolymers (Figure 2A).

Representative \(^1\)H NMR, \(^{19}\)F NMR spectra, corresponding to polymer 7, are shown in Figure 2B. The peak at \(\delta = -116.39\) ppm (\(^{19}\)F NMR) further proving the introduction of substituted C1 segment to polymer chain.

![Figure 2](image_url)  
**Figure 2.** (A) Synthetic route to terpolymers 5, 6, 7 and their HT-GPC traces (TCB, 150 °C); (B) \(^1\)H NMR Spectra of terpolymer 7, inset is the \(^{19}\)F NMR of the terpolymer (\(^1\)H NMR and \(^{19}\)F NMR at 800 MHz in CDCl\(_3\)/CDCl\(_3\) at 90 °C).

Then, we investigated the non-conjugated terpolymer fluorescence properties since we thought that potential π-π stacking (aromatic phenyl rings) in molecular crystals or aggregates may produce emission.\(^6\) To our surprise, the photoluminescence (PL) of terpolymer 3 showed a clear emission peak centered at 473 nm upon photoexcitation (Figure 3A). The no emission of monomers (all arsonium ylides used in this paper) or the related compounds (triphenylarsine or triphenylarsine oxidizer) excludes the potential contaminant effect and further confirm the emission comes from the terpolymer (Figure S11, ESI). The associated UV-Vis spectra reveal an absorption peak at 295 nm, proving the existence of the phenyl rings and conjugated double bonds (Figure 3B). As shown in Figure 3C, the solutions of the four terpolymers in TCB (cloudy at room temperature because of insolubility of PM) emit blue light under UV light (365 nm) irradiation. Similar photoluminescence behavior was also found in bulk sample and film (Figure S12, ESI).

Copolymers 5-7 also showed a similar light emission phenomenon under UV light irradiation (Figure S13, ESI).

After careful study of the structure of the copolymers, we concluded that the unexpected fluorescence phenomenon most probably induced by isomerization (isomerization-induced emission) of aliphatic double bond. The aliphatic double bond isomerization is driven by either light or heat. To prove that we placed the NMR tube, containing the terpolymer (PA-co-PBz)–b–PM (polymer 3 was used in this case) in deuterated 1,1,2,2-tetrachloroethane-\(\delta\) (CDCl\(_3\)/CDCl\(_3\)), under UV light for 5 days. The proton of the allyl (\(\delta = 5.4\) ppm) became broad and shifted to low magnetic field area, indicating the existence of conjugation (Figure 4A). The PL spectra clearly show that the fluorescence intensity increased remarkably after 5 days irradiation under UV light (Figure S14, polymer 7 was used in this case). We also test the temperature effect, by heating the terpolymer 7 in CDCl\(_3\)/CDCl\(_3\) for 24 h at 90 °C, no remarkable changes were detected in both \(^1\)H NMR and PL spectra (Figure S15, ESI). These results indicate that the terpolymer is a light-sensitive but thermodynamics stable polymer. The homo C3 polymer (polymer 8, for synthesis see our previous work,\(^7\) for the \(^1\)H NMR see Figure S16, ESI), gave an emission at 450 nm in THF solution (Figure 4B). Another two homopolymers (polymer 9 and 10) obtained by polymerization of reported allylic arsonium ylide\(^5,6\) have similar emission behavior (Figure S17, ESI). The \(^1\)H NMR of C3 polymer 8 compared with UV irradiated one also showed a clear isomerization phenomenon (Figures S18, ESI). All above evidence proved that the light-induced isomerization plays a key role in the light emission phenomenon.

![Figure 3](image_url)  
**Figure 3.** (A) PL spectra of diblock terpolymer 3 (Table 1) in toluene, concentration: 3 mg/mL. Excitation wavelength: 342 nm; (B) UV-Vis spectrum of diblock terpolymer 3 (Table 1) in toluene; (C) Photographs of polymer in 1, 2, 4-trichlorobenzene (TCB) taken at UV (365 nm) light and daylight.
In summary, a novel method for construction of well-defined C3/C1 containing diblock terpolymers by copolymerization of two arsonium ylides followed by sequential copolymerization of dimethylsulfonium methylide was successfully reported for the first time. The successful application of substituted arsonium ylides as C1 building blocks will widely extend the boron-catalyzed polymerization of ylide chemistry. An unexpected light emission phenomenon of this non-conjugated terpolymer has been observed for the first time. The light emission can be explained by the formation of short conjugated sites along the chain under irradiation. We believe that these C3/C1 copolymers belong to a new family of polymeric materials with interesting properties.

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The first synthesis of well-defined poly{(substituted methylene-co-propylene)-b-methylene} terpolymers via borane-initiated copolymerization of arsonium and sulfoxonium ylides is presented. An unexpected light emission phenomenon, due to the isomerization-induced emission of the double bonds of the propylene units was discovered in these non-conjugated terpolymers.