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

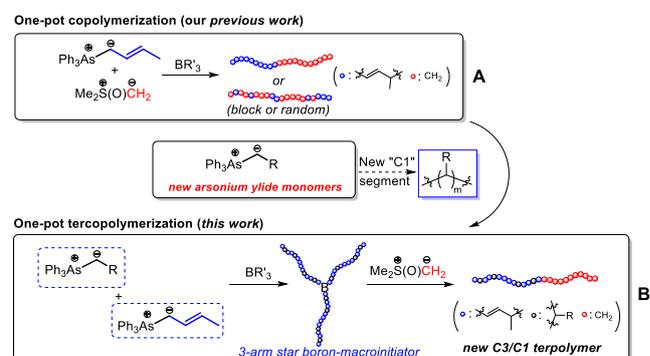
De Wang*^[a] and Nikos Hadjichristidis*^[b]

Abstract: We report the first synthesis of well-defined poly[(phenylmethylene-co-methylpropenylene)-*b*-methylene, [(C1-co-C3)-*b*-C1], terpolymers *via* one-pot borane initiated random copolymerization of 3-methylallyl triphenyl arsonium (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 methylide (C1 units). Other substituted arsonium ylides, such as prenyltriphenyl, propyltriphenyl and (4-fluorobenzyl)triphenyl can also be used instead of benzyltriphenylarsonium. The obtained terpolymers are well-defined, possess a predictable molecular weight and low polydispersity ($M_{n,NMR} = 1.83\text{--}9.68 \times 10^3 \text{ g/mol}$, $M_w/M_n = 1.09\text{--}1.22$). 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 methylide, 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 *n*-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 methylide 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 dimethylaminophenyloxosulfoxonium methylide, diethylsulfoxonium methylide, (dimethylamino)tolylloxosulfoxonium cyclopropylide, 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 methylide 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-methylallyltriphenyl arsonium 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-allylsubstituted triphenylarsonium ylides show the same behavior.^{5b} Later, Mioskowski *et al* discovered that by using a non-substituted allylarsonium ylide as monomer a C1/C3 random copolymer was obtained, whereas by using terminal dimethyl substituted allylic arsonium ylide a C1 homopolymer was obtained.⁶ They explained the differences by using sigmatropic rearrangement arguments. Encouraged by this work, our group discovered that 3-methylallyltriphenylarsonium ylide, $\text{Ph}_3\text{As}^+\text{CH}_2\text{CH}=\text{C}(\text{Me})\text{CH}_2$ -monosubstituted allylarsonium ylide, leads also to C3 polymerization. Moreover, by $\text{Ph}_3\text{As}^+\text{CH}_2\text{CH}=\text{C}(\text{Me})\text{CH}_2$ -monosubstituted allylic arsonium ylide (C3) with sulfoxonium methylide (C1) we were able to synthesize well-defined methylene/3-methylpropenylene block and random copolymers (Scheme 1, A).⁷ Encouraging by these discoveries we started exploring the borane initiating polymerization of other arsonium ylides hoping to obtain novel polymeric materials with unprecedented properties (Scheme 1, B).



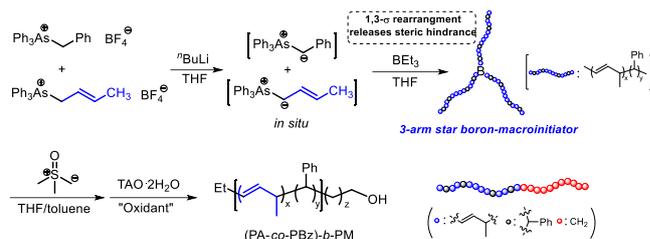
Scheme 1. (A) New C3/C1 diblock copolymers (previous work⁷); (B) terpolymers (this work) from arsonium and sulfoxonium ylides.

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In this communication, we report the design/synthesis of several novel non-allylic triphenylarsonium ylides and explore their homo- and copolymerization with β -methylallyltriphenylarsonium ylide using triethylborane as the initiator. Moreover, we report the synthesis of well-defined diblock terpolymers having C1-co-C3 segments that 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 polyisoprene-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 benzyltriphenylarsonium tetrafluoroborate salt (Scheme S1 and Figure S1-S4, ESI), which can be transformed to benzyltriphenylarsonium ylide monomer, by treatment with *n*-butyllithium. The homopolymerization of benzyltriphenylarsonium ylide with triethyl borane was failed due to the steric congestion around the boron complex. The copolymerization of benzyltriphenylarsonium ylide and sulfoxonium 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 benzyltriphenylarsonium ylide with 3-methylallyltriphenylarsonium ylide was successful because the 1,3-sigmatropic rearrangement releases the steric hindrance around boron. The general reactions for the synthesis of poly[(methylpropenylene-co-phenylmethylene)-*b*-methylene] terpolymers [(PA-co-PBz)-*b*-PM] are given in Scheme 2. Treatment of benzyltriphenylarsonium and allyltriphenylarsonium tetrafluoroborate salts in tetrahydrofuran (THF) with *n*-butyllithium at -78 °C under argon, resulted in a clear red solution proving the *in situ* generations 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 sulfoxonium 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·2H₂O) [Scheme S3, ESI]. The ¹H 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 $\chi = 5.40$ 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.⁷ The chain-end protons assigned to $-\text{CH}_2-$ connected to the hydroxy group at $\chi = 3.66$ 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).



Scheme 2. General reaction for the synthesis of diblock terpolymers [(PA-co-PBz)-*b*-PM].

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

Entry	Polymer	DP _{cal} ^a (A/Bz/M)	DP _{NMR} ^b (A/Bz/M)	M _{n,NMR} ^b ×10 ³	PDI ^c (M _w /M _n)	Yield ^d (%)	T _m (°C)
1	PA ₅ -co-PBz ₃ - <i>b</i> -PM ₈₈	5/5/60	5/3/88	1.83	1.09	71	89.4
2	PA ₁₄ -co-PBz ₁₁ - <i>b</i> -PM ₁₇₁	17/17/100	14/11/186	4.35	1.15	58	100.8
3	PA ₂₀ -co-PBz ₁₅ - <i>b</i> -PM ₁₈₆	27/17/100	20/15/171	4.88	1.10	67	108.3
4	PA ₂₉ -co-PBz ₃₂ - <i>b</i> -PM ₃₇₀	20/27/250	29/32/370	9.68	1.17	65	114.9

^a DP_{cal} is the degree of polymerization, calculated by [M]/[I]. ^b M_{n,NMR} and DP_{NMR} were determined by ¹H NMR (1,1,2,2-tetrachloroethane-*d*₂, 90 °C, 600MHz), M_{n,NMR} = M_{Et} + xM_{CH₂} + yM_{CHPh} + zM_{CH₂OH}. ^c M_{n,HT-GPC} and PDI were determined versus polystyrene standards in high temperature GPC (TCB as solvent at 150 °C). ^d Isolated yield after precipitation in ethanol/water and drying under vacuum at 50 °C overnight.

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} = 1.83-9.68×10³ g/mol) possess monomodal and narrow GPC traces (PDI = 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-arm boron macroinitiator during the addition of sulfoxonium methylide.^{3,7} The DSC traces of the diblock terpolymers are shown in Figure 1B. For the low molecular weight (Table 1, entry 1, M_{n,NMR} = 1.83×10³ 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} = 4.17-9.68×10³ 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 is expected that the presence of the phenyl-substituted C1 segments (exercises a small influence on the crystallization.⁸

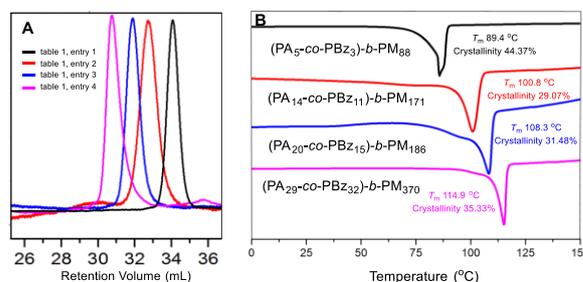


Figure 1. (A) HT-GPC traces (TCB at 150 °C, PS standard); (B) DSC traces of terpolymers under nitrogen at a heating rate of 10 °C/min.

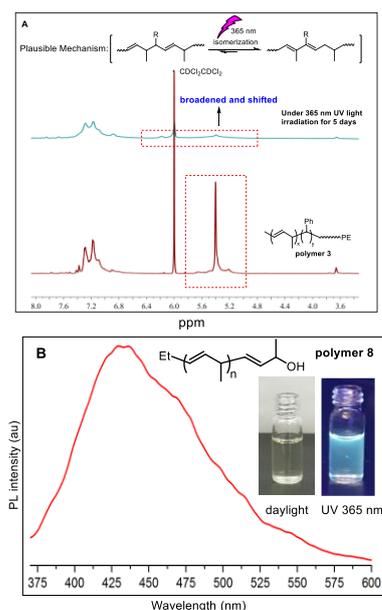


Figure 4. (A) Proposed mechanism of isomerization and ¹H NMR proof under UV irradiation (365 nm) and (B) PL spectrum of homopolymer **8** (C3 polymer), the inset is polymer **8** in THF under daylight or UV light (365 nm). Concentration: 2 mg/mL, Excitation: 342 nm.

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 dimethylsulfoxonium 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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