Photoluminescence

International Edition: DOI: 10.1002/anie.201901094
German Edition: DOI: 10.1002/ange.201901094

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

De Wang and Nikos Hadjichristidis**

Abstract: *The first synthesis of well-defined poly[(phenylmethylene-co-methylpropenylene)-b-methylene, [(C1-co-C3)-b-C1], terpolymers was achieved by 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 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* ($M_{n,NMR} = 1.83$–9.68×10^3 g mol^{-1}, $Đ = 1.09$–1.22)*. An unexpected light emission phenomenon was discovered in these non-conjugated terpolymers, as confirmed 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 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 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)tolylsulfoxonium cyclopropylide, with the hope of obtaining poly(-substituted methylene).[2d,4] Although the homopolymerization of substituted sulfoxonium ylides were unsuccessful (owing to the steric hindrance around boron centers), the copolymerization of these subsituted ylide monomers with sulfoxonium methylide was however 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 other 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, a ω-monosubstituted allylarsonium ylide, leads also to C3 polymerization. Moreover, by combining ω-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] Encouraged 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**).

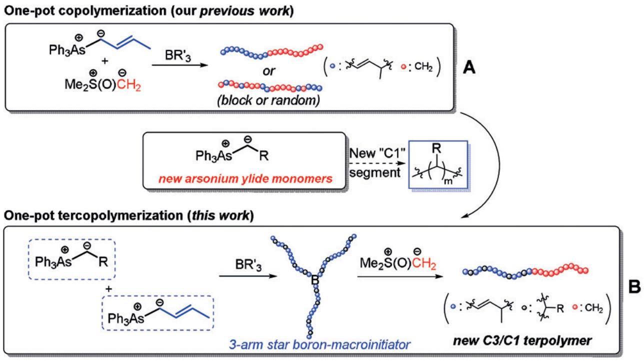
Herein, we report the design and synthesis of several novel non-allylic triphenylarsonium ylides and explore their homo- and copolymerization with ω-methylallyltriphenylarsonium ylide using triethylborane as the initiator. Moreover, we report the synthesis of well-defined diblock terpolymers having C1-*co*-C3 and PM blocks. These terpolymers despite the fact that they do not 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

---

[*] Prof. Dr. D. Wang
Ocean University of China, School of Medicine and Pharmacy
Qingdao, Shandong Province, 266071 (China)
E-mail: wangde@ouc.edu.cn

Prof. Dr. N. Hadjichristidis
King Abdullah University of Science and Technology (KAUST),
Physical Sciences and Engineering Division, KAUST Catalysis Center,
Polymer Synthesis Laboratory
Thuwal 23955 (Kingdom of Saudi Arabia)
E-mail: nikolaos.hadjichristidis@kaust.edu.sa

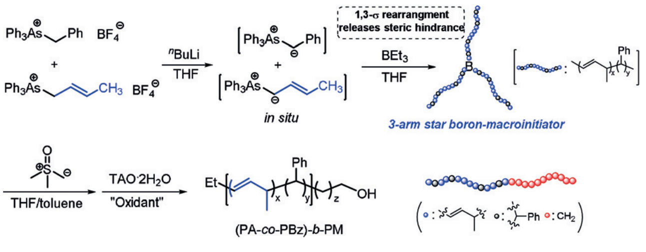
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201901094.



Scheme 1. A) New C3/C1 diblock copolymers (previous work[7]); B) terpolymers (this work) from arsonium and sulfoxonium ylides.

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 (Supporting Information, Scheme S1, Figures S1–S4), which can be transformed to benzyltriphenylarsonium ylide monomer, by treatment with *n*-butyllithium. The homopolymerization of benzyltriphenylarsonium ylide with triethyl borane failed owing 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) owing to the same steric reasons. 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·2H_2O; Supporting Information, Scheme S3). 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 (Supporting Information, Figure S5). 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.[7] The chain-end protons assigned to $-CH_2-$ 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} (FTIR 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 (Supporting Information, Figure S6).



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	$DP_{n,cal}$[a] (A/Bz/M)	$DP_{n,NMR}$[b] (A/Bz/M)	$M_{n,NMR}$[b] $\times 10^3$	PDI[c] [M_w/M_n]	Yield[d] [%]	T_m [°C]
1	PA_5-*co*-PBz_3-*b*-PM_{88}	5/5/60	5/3/88	1.83	1.09	71	89.4
2	PA_{14}-*co*-PBz_{11}-*b*-PM_{171}	17/17/100	14/11/186	4.35	1.15	58	100.8
3	PA_{20}-*co*-PBz_{15}-*b*-PM_{186}	27/17/100	20/15/171	4.88	1.10	67	108.3
4	PA_{29}-*co*-PBz_{32}-*b*-PM_{370}	20/27/250	29/32/370	9.68	1.17	65	114.9

[a] $DP_{n,cal}$ is the degree of polymerization, calculated by [M]/[I]. [b] $M_{n,NMR}$ and $DP_{n,NMR}$ were determined by ^{1}H NMR (1,1,2,2-[D_2]tetrachloroethane, 90 °C, 600 MHz), $M_{n,NMR} = M_{Et} + x M_{CH_2} + y M_{CHPh} + z M_{allyl} + M_{CH_2OH}$. [c] $M_{n,HT\text{-}GPC}$ and PDI were determined versus polystyrene standards in high-temperature GPC (TCB as solvent at 150 °C). [d] Yield of isolated product 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 1 A. It is clear that the synthesized terpolymers ($M_{n,NMR} = 1.83$–9.68×10^3 g mol^{-1}) possess monomodal and narrow GPC traces ($Đ = 1.09$–1.17). Furthermore, 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 $DP_{n,NMR}$ of PM is higher than the calculated values and this could be attributed to the oxidation/decomposition of a part of the three-arm boron macroinitiator during the addition of sulfoxonium methylide.[3,7] The DSC traces of the diblock terpolymers are shown in Figure 1 B. For the low-molecular-weight (Table 1, entry 1, $M_{n,NMR} = 1.83 \times 10^3$ g mol^{-1}) terpolymer, the melting temper-

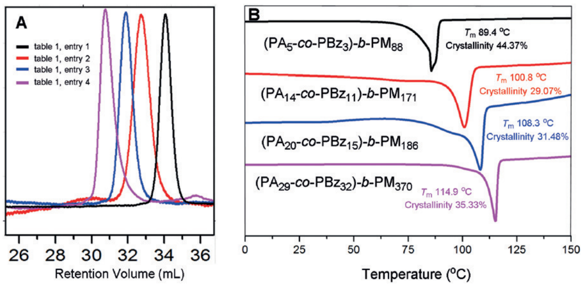


Figure 1. A) HT-GPC traces (TCB at 150 °C, PS standard). B) DSC traces of terpolymers under nitrogen at a heating rate at 10 °C min^{-1}.

ature (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, $M_{n,NMR} = (4.17–9.68) \times 10^3$ g mol^{-1}) 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.[8]

Having shown that the benzyltriphenylarsonium ylide can be used as substituted C1 monomer in the copolymerization with ω-methylallylarsonium ylide initiated with triethylborane, we synthesized and investigated other substituted ylides such as propyltriphenylarsonium, (3-methylbut-2-en-1yl)triphenylarsonium and (4-fluorobenzene)triphenylarsonium ylide (Supporting Information, Figures S7, S8). For the synthesis of the corresponding terpolymers **5**–**7** (monomer to initiator mole ratio was $[M_{As,R}]/[[M_{As,Allyl}]/[\ M_S]/[[I] = 17/17/100/1$), 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 (Supporting Information, Figures S9, S10). The molecular weights of terpolymers **5**–**7** were determined by ^{1}H NMR end group analysis ($M_n = 4.3–9.1 \times 10^3$ g mol^{-1}) and polydispersities were detected by HT-GPC with polystyrene as standards ($Đ = 1.16–1.22$). The HT-GPC traces were monomodal with narrow dispersity, proving that our strategy is efficient and powerful for the construction C1/C3 terpolymers (Figure 2 A). Representative ^{1}H NMR and ^{19}F NMR spectra, corresponding to polymer **7**, are shown in Figure 2B. The peak at $\delta = -116.39$ ppm (^{19}F NMR) further confirms the introduction of substituted C1 segment to polymer chain.

We then investigated the non-conjugated terpolymer fluorescence properties, as we thought that potential π–π stacking (aromatic phenyl rings) in molecular crystals or aggregates may produce emission.[9] To our surprise, the photoluminescence (PL) of terpolymer **3** showed a clear emission peak centered at 473 nm upon photoexcitation (Figure 3 A). The absence of emission from monomers (all arsonium ylides used herein) or the related compounds (triphenylarsine or triphenylarsine oxidizer) excludes the potential contaminant effect and further confirm the emission comes from the terpolymer (Supporting Information, Figure S11). 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 (Supporting Information, Figure S12). Copolymers **5**–**7** also shown a similar light emission phenomenon under UV light irradiation (Supporting Information, Figure S13).

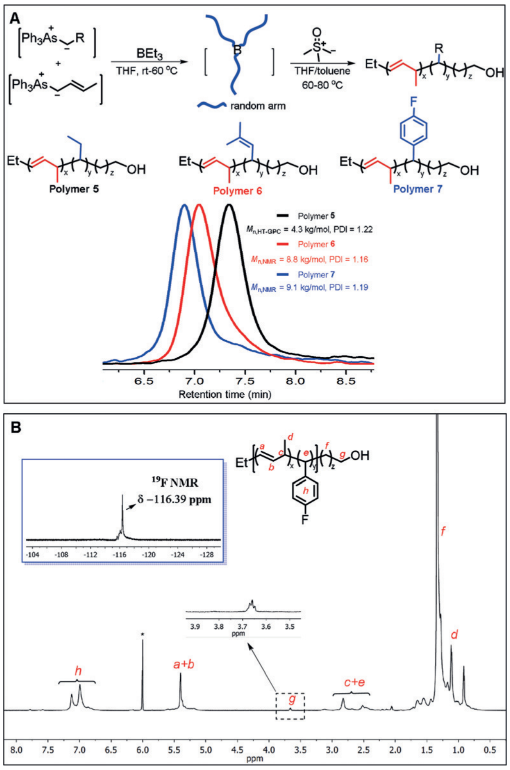


Figure 2. A) Synthetic route to terpolymers **5**, **6**, **7** and their HT-GPC traces (TCB, 150 °C). B) ^{1}H NMR spectra of terpolymer **7**; inset: the ^{19}F NMR of the terpolymer (^{1}H NMR and ^{19}F NMR at 600 MHz in $CDCl_2CDCl_2$ at 90 °C).

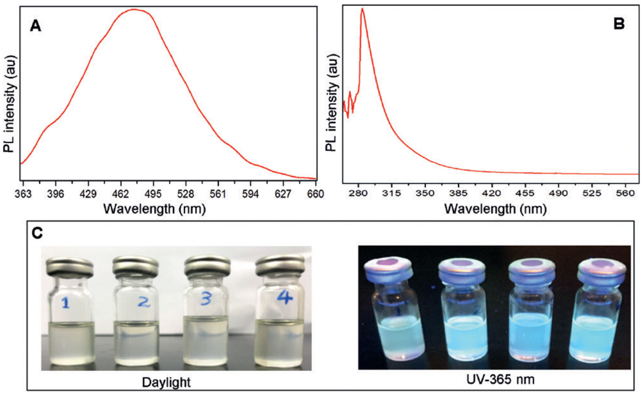


Figure 3. A) PL spectra of diblock terpolymer **3** (Table 1) in toluene. Concentration: 3 mg mL^{-1}. Excitation wavelength: 342 nm. B) UV/Vis spectrum of diblock terpolymer **3** (Table 1) in toluene. C) Photographs of polymer in 1, 2, 4-trichlorobenzene (TCB) taken at UV (365 nm) light and daylight.

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 allylic double bond. The allylic double bond isomerization is driven by either light or heat. To confirm 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-[D_2]tetrachloroethane ($CDCl_2CDCl_2$), 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 4 A). The PL spectra clearly show that the fluorescence intensity increased remarkably after 5 days irradiation under UV light (Supporting Information, Figure S14; polymer **7** was used in this case). We also tested the temperature effect by heating the terpolymer **7** in $CDCl_2CDCl_2$ for 24 h at 90 °C; no remarkable changes were detected in both ^1H NMR and PL spectra (Supporting Information, Figure S15). 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 ^1H NMR spectrum, see the Supporting Information, Figure S16), gave an emission at 450 nm in THF solution (Figure 4 B). Another two homopolymers (polymer **9** and **10**) obtained by polymerization of reported allylic arsonium ylide,[5a,6] have similar emission behavior (Supporting Information, Figure S17). The ^1H NMR of C3 polymer **8** compared with UV irradiated one also showed a clear isomerization phenomenon (Supporting Information, Figure S18). All above evidence proved that the light-induced isomerization plays a key role in the light emission phenomenon.

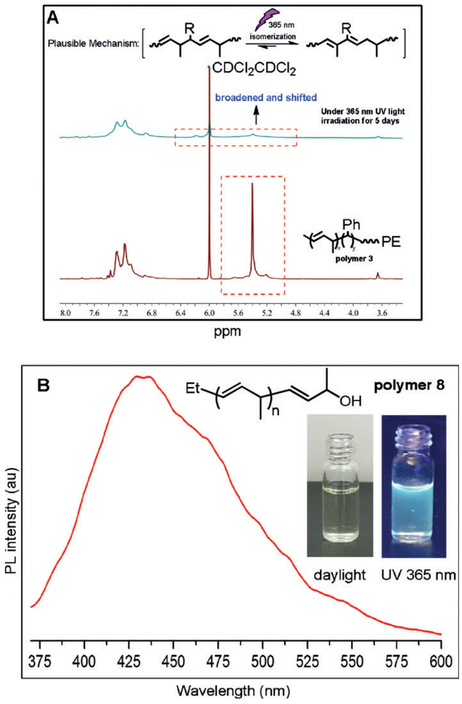


Figure 4. A) Proposed mechanism of isomerization and ^1H NMR proof under UV irradiation (365 nm). B) PL spectrum of homopolymer **8** (C3 polymer); inset: polymer **8** in THF under daylight or UV light (365 nm). Concentration: 2 $mg\,mL^{-1}$, Excitation: 342 nm.

In summary, a 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.

Acknowledgements

The research reported in this publication was supported by the King Abdullah University of Science and Technology (KAUST).

Conflict of interest

The authors declare no conflict of interest.

Keywords: arsonium ylides · boranes · copolymerization · photoluminescence · sulfoxonium ylide

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 6295–6299
Angew. Chem. **2019**, *131*, 6361–6365

[1] K. J. Shea, J. W. Walker, H. Zhu, M. M. Paz, J. Greaves, *J. Am. Chem. Soc.* **1997**, *119*, 9049–9050.

[2] a) J. Luo, K. J. Shea, *Acc. Chem. Res.* **2010**, *43*, 1420–1433; b) B. B. Busch, M. M. Paz, K. J. Shea, C. L. Staiger, J. M. Stoddard, J. R. Walker, X.-Z. Zhou, H. Zhu, *J. Am. Chem. Soc.* **2002**, *124*, 3636–3646; c) X.-Z. Zhou, K. J. Shea, *J. Am. Chem. Soc.* **2000**, *122*, 11515–11516; d) R. Sulc, X.-Z. Zhou, K. J. Shea, *Macromolecules* **2006**, *39*, 4948–4952; e) J. Bai, L. D. Burke, K. J. Shea, *J. Am. Chem. Soc.* **2007**, *129*, 4981–4991; f) J. Bai, K. J. Shea, *Macromol. Rapid Commun.* **2006**, *27*, 1223–1228; g) J. Li, Q.-L. Zhao, J.-Z. Chen, L. Li, J. Huang, Z. Ma, Y.-W. Zhong, *Polym. Chem.* **2010**, *1*, 164–167; h) J.-Z. Chen, K. Cui, S.-Y. Zhang, P. Xie, Q.-L. Zhao, J. Huang, L.-P. Shi, G.-Y. Li, Z. Ma, *Macromol. Rapid Commun.* **2009**, *30*, 532–538; i) J.-Z. Chen, Q.-L. Zhao, L.-P. Shi, J. Huang, G.-Y. Li, S.-Y. Zhang, Z. Ma, *J. Polym. Sci. Part A* **2009**, *47*, 5671–5681; j) C. Yuan, H.-C. Lu, Q.-Z. Li, S. Yang, Q.-L. Zhao, J. Huang, L. H. Wei, Z. Ma, *J. Polym. Sci. Part A* **2012**, *50*, 2398–2405; k) H.-C. Lu, Y. Xue, Q.-L. Zhao, J. Huang, S.-G. Xu, S.-K. Cao, Z. Ma, *J. Polym. Sci. Part A* **2012**, *50*, 3641–3647; l) Y. Xue, H.-C. Lu, Q.-L. Zhao, J. Huang, S.-G. Xu, S.-K. Cao, Z. Ma, *Polym. Chem.* **2013**, *4*, 307–312; m) Y. Xue, S.-S. Zhang, K. Cui, J. Huang, Q.-L. Zhao, P. Lan, S.-K. Cao, Z. Ma, *RSC Adv.* **2015**, *5*, 7090–7097; n) F. Xu, P. Dong, K. Cui, S.-Z. Bu, J. Huang, G.-Y. Li, T. Jiang, Z. Ma, *RSC Adv.* **2016**, *6*, 69828–69835.

[3] a) H. Zhang, N. Alkayal, Y. Gnanou, N. Hadjichristidis, *Macromol. Rapid Commun.* **2014**, *35*, 378–390; b) H. Zhang, N. Alkayal, Y. Gnanou, N. Hadjichristidis, *Chem. Commun.* **2013**, *49*, 8952–8954; c) H. Zhang, Y. Gnanou, N. Hadjichristidis, *Polym. Chem.* **2014**, *5*, 6431–6434; d) H. Zhang, Y. Gnanou, N. Hadjichristidis, *Macromolecules* **2015**, *48*, 3556–3562; e) Z.

Zhang, H. Zhang, Y. Gnanou, N. Hadjichristidis, *Chem. Commun.* **2015**, *51*, 9936–9938; f) H. Zhang, N. Hadjichristidis, *Macromolecules* **2016**, *49*, 1590–1596; g) N. Alkayal, N. Hadjichristidis, *Polym. Chem.* **2015**, *6*, 4921–4926; h) N. Alkayal, H. Durmaz, U. Tunca, N. Hadjichristidis, *Polym. Chem.* **2016**, *7*, 2986–2991; i) D. Wang, N. Hadjichristidis, *Chem. Commun.* **2017**, *53*, 1196–1199; j) Z. Zhang, Y. Gnanou, N. Hadjichristidis, *Polym. Chem.* **2016**, *7*, 5507–5511.

[4] R. Zhao, K. J. Shea, *ACS Macro Lett.* **2015**, *4*, 584–587.

[5] a) J.-P. Goddard, P. Lixon, T. Le Gall, C. Mioskowski, *J. Am. Chem. Soc.* **2003**, *125*, 9242–9243; b) R. Mondière, J.-P. Goddard, G. Carrot, T. Le Gall, C. Mioskowski, *Macromolecules* **2005**, *38*, 663–668.

[6] R. Mondière, J.-P. Goddard, M. Huiban, G. Carrot, T. Le Gall, C. Mioskowski, *Chem. Commun.* **2006**, *42*, 723–725.

[7] D. Wang, Z. Zhang, N. Hadjicristidis, *ACS Macro Lett.* **2016**, *5*, 387–390.

[8] a) Y.-L. Loo, R. A. Register, *Macromolecules* **2002**, *35*, 2365–2374; b) H. Kaneyoshi, Y. Inoue, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 5425–5435.

[9] For non-conjugated polymers photoluminescence, see: a) E. Zhao, J. W. Y. Lam, L. Meng, Y. Hong, H. Deng, G. Bai, X. Huang, J. Hao, B. Z. Tang, *Macromolecules* **2015**, *48*, 64–71; b) R. Ye, Y. Liu, H. Zhang, H. Su, Y. Zhang, L. Xu, R. Hu, R. T. K. Kwok, K. S. Wong, J. W. Y. Lam, W. A. Goddard III, B. Z. Tang, *Polym. Chem.* **2017**, *8*, 1722–1727; c) J. Yan, B. Zheng, D. Pan, R. Yang, Y. Xu, L. Wang, M. Yang, *Polym. Chem.* **2015**, *6*, 4240–4251; d) J. Yan, Z.-K. Wang, X.-S. Lin, C.-Y. Hong, H.-J. Liang, C.-Y. Pan, Y.-Z. You, *Adv. Mater.* **2012**, *24*, 5617–5624; e) B. Saha, K. Bauri, A. Bag, P. K. Ghorai, P. De, *Polym. Chem.* **2016**, *7*, 6895–6900; For select photoluminescence reviews, see: f) S. Zhu, Y. Song, J. Shao, X. Zhao, B. Yang, *Angew. Chem. Int. Ed.* **2015**, *54*, 14626–14637; *Angew. Chem.* **2015**, *127*, 14834–14846; g) J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2015**, *115*, 11718–11940.

Manuscript received: January 26, 2019
Revised manuscript received: February 22, 2019
Accepted manuscript online: February 26, 2019
Version of record online: April 1, 2019