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[Ph₃C][B(C₆F₅)₄]: Highly Efficient Metal-Free Single-Component Initiator for Helical-Sense-Selective Cationic Copolymerization of Chiral Aryl Isocyanide and Achiral Aryl Isocyanide

Xinwen Yan,^[a] Shaowen Zhang,^[a] Pengfei Zhang,^[a] Xiaolu Wu,^[a] An Liu,^[a] Ge Guo,^[a] Yuping Dong^{*[b]} and Xiaofang Li^{*[a]}

Abstract: Commercially available $[Ph_3C][B(C_6F_5)_4]$ serves as a highly efficient, metal-free, and single-component initiator not only for carbocationic polymerization of polar and bulky aryl isocyanides with extremely high activity up to 1.2×10^7 g of polymer/(mol_{cat.} h) but also for helical-sense-selective polymerization of chiral aryl isocyanides and copolymerization with achiral aryl isocyanide, affording high molecular weight functional poly(aryl isocyanide)s with good solubility, AIE nature, and/or one-handed helical conformation.

Optically active poly(isocyanide) (PI) with single-handed helical conformation^[1] has attracted extensive attention for its excellent properties, important functions of realizing biological activities, and significant applications in many fields, such as molecular recognition, photoconductivity, liquid crystal, asymmetric synthesis and so on.^[2] In general, the PIs are mainly synthesized from the coordination-insertion polymerization of isocyanides catalyzed by late transition metal catalysts based on Rh, Pd, Ni and Co (Chart 1).^[3] However, most of these catalysts exhibit low to moderate activities for the (co)polymerization of isocyanides (< 10⁵ g of polymer/(mol_{cat}.·h)).^[4] More importantly, the issue of metal residue in the PIs significantly affects their properties and restricts their applications as biomimetic materials. For example, traces of transition metal residue can serve as degradation catalysts and reduce the thermal stability of PIs.^[5] The high metal residue exceeding the standard greatly limits the medical applications of PIs as well-defined micelles for drug carrier and cell imaging materials in living cell.^[6] Therefore. developing metal-free catalysts with advantages of availability. high efficiency, and no toxicity for the polymerization of isocvanide is very essential. Some early efforts for the cationic polymerization of isocyanides by using metal-free initiators such as strong protonic acid-coated ground glass or Lewis acid BF₃ were independently reported by Millich, Stackman, and Yamamoto in 1960s (Chart 1).^[7] In 2005, Cronelissen et al. also polymerization reported trifluoroacetic acid-initiated of isocyanopeptides.^[8] However, the activities of these metal-free catalysts are very low (< 10³ g of polymer/(mol_{cat.}·h)) and only

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the document.

one example of protonic acid-coated ground glass can promote the helical-sense-selective (co)polymerization of isocyanides.^[7] Up to now, no more metal-free catalyst is reported for the polymerization of isocyanides as far as we know. Developing highly efficient metal-free catalysts for the helical-senseselective (co)polymerization of isocyanides is still a critical challenge.



Chart 1. Catalysts for the Polymerization of Isocyanides.

The metal-free fluorosubstituted borate compound (such as $[Ph_{3}C][B(C_{6}F_{5})_{4}]$ and $[PhNHMe_{2}][B(C_{6}F_{5})_{4}])$ and borane compound $B(C_6F_5)_3$ usually serve as activators or cocatalysts in the coordination-insertion polymerization.^[9] For example, we have reported a series of cationic rare-earth metal alkyl species in-situ generated from the rare-earth metal dialkyl complexes and such activators as highly efficient catalysts for both the highly regio-/stereoselective polymerization of conjugated dienes and the helical-sense-selective polymerization of arvl isocyanides.^[10] Moreover, such compounds alone can also serve as metal-free catalysts for the organic synthesis reaction.[11] Despite these efforts, these compounds never serve as singlecomponent initiators for the carbocationic polymerization as far as we known.

Herein, we present the commercially available borate complex $[Ph_3C][B(C_6F_5)_4]$ serves as highly efficient metal-free single-component initiator for the carbocationic polymerization and copolymerization of five functional aryl isocyanides containing polar, bulky, and chiral groups with extremely high activities, affording high molecular weight poly(aryl isocyanide)s with good solubility, aggregation-induced emission (AIE) nature, or one-handed helical conformation. Moreover, the optically

active chiral isocyanide sequences in the copolymer chain can induce the helical-sense-selective polymerization of achiral isocyanide monomer to final produce the random copolymers adopting a helical conformation with an excess screw sense in different degrees and AIE nature (Chart 1).

Five aryl isocyanide monomers a-e containing polar ester (4-ethoxycarbonyl phenyl isocyanide (EPI, a)), bulky naphthyl (2naphthyl isocyanide (NI, b)) or tetraphenylethylene (4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (ITPB, c)), or chiral ester substituents ((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4isocyanobenzoate (D-IMCI, d) and (1R,2S,5R)-2-isopropyl-5methylcyclohexyl 4-isocyanobenzoate (L-IMCI, **e**) were synthesized and polymerized by use of single-component, metal-free borate compounds $[Ph_3C][B(C_6F_5)_4]$ (A) and $[PhNHMe_2][B(C_6F_5)_4]$ (B) or borane compound $B(C_6F_5)_3$ (C). The representative results were summarized in Table 1.

The experiment results showed that the structure and type of catalyst had a profound impact on the EPI polymerization (Table 1. runs 2. 5–6). The isolated ion pair borate A $[Ph_3C][B(C_6F_5)_4]$ exhibited a very high activity up to 1.0×10^6 g of polymer/(mol_{cat}.h) for the polymerization of EPI at room temperature in chlorobenzene within 1 min, suggesting that the cation Ph₃C⁺ is an excellent cationic initiator for the EPI polymerization under mild conditions (Table 1, run 2). While the similar isolated ion pair borate **B** [PhNHMe₂][B(C₆F₅)₄] showed lower activity ca. 2.7 × 10^3 g of polymer/(mol_{cat.}·h) under similar conditions within 3 h, implying that the more charge dispersion on the proton of cationic initiator [PhNHMe₂]⁺ due to strong electron-donating ability of the nitrogen atom of the coordinated PhNMe₂ slowed down the polymerization rate to some extent (Table 1, run 5). If neutral borane C $B(C_6F_5)_3$ was used as catalyst, the lowest activity ca. 7.3×10^2 g of polymer/(mol_{cat.}·h) was obtained under similar conditions within 12 h, which might attribute to the weakly electropositive Lewis acid and the large steric hindrance around the boron atom of $B(C_6F_5)_3$ which significantly limited the coordination of isocyanide monomer with $B(C_6F_5)_3$ in PhCI (Table 1, run 6). Other important factors such as solvents, molar ratio of monomer to catalyst and reaction temperature also played important roles in the EPI polymerization (Table 1, runs 1-4, 7-12). The highest activity up to 1.15×10^7 g of polymer/(mol_{cat}.·h) was achieved at 70 °C under molar ratio of [EPI]/[[Ph_3C][B(C_6F_5)_4]] ca. 2000 : 1 within 1 min in PhCl (Table 1, run 11). In contrast, [Ph₃C][B(C₆F₅)₄] exhibited a very low activity ca. 64 g of polymer/(molcat. h) for NI polymerization at 70 $^{\circ}\text{C}$ (Table 1, run 13). This might be attributed to both of the big steric hindrance of naphthalene and the weak electronegativity of the carbon atom of the C \equiv N triple bond due to the strong conjugated effect of naphthalene, resulting in the weak attraction for the strong electropositive carbon cation catalyst. In the polymerization of ITPB and D/L-IMCI, the high activities ca. $5.1-8.8 \times 10^5$ g of polymer/(mol_{cat}·h) were achieved by using [Ph₃C][B(C₆F₅)₄] at 25 °C for 3 min (Table 1, runs 14-16).

All of the resulting polyisocyanides showed good solubility in commonly used organic solvents such as THF, toluene and CHCl₃. Among them, the poly(EPI), poly(ITPB) and poly(D/L-IMCI) were characterized by using FT-IR, ¹H NMR spectroscopy and GPC analysis. Poly(D/L-IMCI)s were also characterized by using CD and SEM (Figure 1 and ESI). Poly(ITPB) was also

Table 1. Homopolymerization of Aryl Isocyanides Catalyzed by Metal-Free Borate and Borane Compounds $^{\left[n\right] }$



		1.0								
Run	Cat. ^[b]	[Mon.]/	Mon.	Solvent	Temp.	Time	Yield	Act. ^[d]	$M_{n}^{[e]}$	$M_w/M_n^{[e]}$
		[Cat.] ^[c]			(°C)	(min)	(%)		(10 ⁴)	
1	Α	100:1	а	toluene	25	1	87	922	6.4	5.47
2	Α	100:1	a	PhCI	25	1	97	1035	8.1	4.84
3	Α	100:1	а	PhCl ₂	25	1	83	886	7.3	4.92
4	Α	100:1	а	$C_2H_2CI_4$	25	1	97	1035	6.7	7.52
5	в	100:1	а	PhCl	25	180	45	2.7	18.8	2.64
6	С	100:1	а	PhCI	25	720	49	0.73	7.6	3.91
7	Α	500:1	а	PhCI	25	5	79	842	9.0	6.30
8	Α	1000:1	а	PhCI	25	10	68	702	9.6	6.85
9	Α	2000:1	а	PhCI	25	15	54	745	16.8	3.86
10	Α	2000:1	а	PhCI	50	1	55	11419	9.2	3.20
11	Α	2000:1	а	PhCI	70	1	55	11502	6.1	3.30
12	Α	2000:1	а	PhCI	90	1	54	11115	5.1	3.00
13	A	100:1	b	PhCI	70	1440	10	0.064	-	-
14	Α	100:1	С	PhCI	25	3	100	877	4.0 ^f	4.09 ^f
15	Α	100:1	d	PhCI	25	3	94	539	12.7 ^f	3.24 ^f
16	Α	100:1	е	PhCI	25	3	88	506	10.4 ^f	3.18 ^f

[a] Conditions: 8.5 μ mol of catalyst, 5 mL of solvent. [b] Catalysts: **A** = [Ph₃C][B(C₆F₅)₄], **B** = [PhNHMe₂][B(C₆F₅)₄], **C** = B(C₆F₅)₃. [c] Molar ratio of monomer to catalyst. [d] Activity: kg of polymer/(mol_{cat} h). [e] Determined by GPC in CHCl₃ at 25 °C against polystyrene standard. [f] Determined by GPC in THF at 25 °C against polystyrene standard.

characterized by use of UV/Vis transmittance spectroscopy, UV absorption spectroscopy, and fluorescence spectroscopy (Figure 2 and ESI). The FT-IR, ¹H NMR spectra and GPC curves demonstrated the isocyanide monomers had successfully been transformed into PIs with moderate to high molecular weights $(M_{\rm n} = 4.0-18.8 \times 10^4 \text{ g/mol})$ and moderate to broad molecular weight distributions ($M_w/M_n = 2.64-7.52$). CD spectra indicated that both poly(L-IMCI) and poly(D-IMCI) were optically active, and the obvious positive and negative CD signals at 364 nm demonstrated that they had opposite single-handed helical conformations^[12] (Figure 1A). The dropping transmittance in the UV/Vis transmittance spectroscopy and the presence of lightscattering tails above 500 nm in the UV absorption spectroscopy of the poly(ITPB) demonstrated the formation of nanoaggregates when the water fraction in THF/water mixture increased from 0 to 90%. The fluorescence spectrum showed that the fluorescence intensities of poly(ITPB) increased with the increasing water fraction in THF/water mixture from 0 to 30%, suggesting the poly(ITPB) having a AIE feature similar to ITPB monomer (Figure 2A-B).^[13] When the water content was higher than 40%, the aggregation states having a more loose stacking structure were rapidly formed from the polymer chains. For such loose aggregates, the intrinsic rotational confinement of the rotation of the four phenyl rings of TPE units was low. Moreover,

the loss of non radiation energy was still very large. As a result, the luminescence became weak until the luminescence disappeared completely. The blue shift of the maximum emission wavelength was due to the non polarity of the four phenyl rings of TPE units and polymer main chains in the interior of the aggregates. SEM spectra showed that the optically active poly(D/L-IMCI)s had good single-handed helical conformations.



Figure 1. (A) CD spectra of poly(D/L-IMCI), poly(ITPB) and poly(D/L-IMCI-co-ITPB)s in THF (0.2 mg/mL) at 25 °C. (B) Plots of $\Delta\epsilon_{364}$ value of the copolymers as a function of the D/L-IMCI content.



Figure 2. Plots of fluorescence intensity vs water fraction in THF/water mixture (0.01 mg of ITPB unit/mL). (A) ITPB monomer; (B) poly(ITPB) (Table 1, run 14); (C) poly(D-IMCI-co-ITPB) (Table 2, run 5); (D) poly(L-IMCI-co-ITPB) (Table 2, run 9) (conditions: EX wavelength: 320 nm for A, 290 nm for B-D; EX slit: 2.5 nm for A, 5 nm for B-D; EM slit: 5 nm; 650 V for A, 700 V for B-D).

More importantly, $[Ph_3C][B(C_6F_5)_4]$ could also promote the helical-sense-selective random copolymerization of achiral ITPB (c) with chiral D-IMCI (d) or L-IMCI (e) at 25 °C in PhCI under different molar ratio of D/L-IMCI to ITPB, giving a series of random poly(D/L-IMCI-*co*-ITPB)s with unique properties and excess single-handed helical conformations in different degrees. The experimental results were summarized in Table 2.

As shown in Table 2, when the molar ratios of chiral D/L-IMCI to achiral ITPB increased from 1:10 to 10:1, the activities firstly increased from 9.4×10^5 g of polymer/(mol_{cat}.·h) to 13.4×10^5 g of polymer/(mol_{cat}.·h) then decreased to $6.1-6.6 \times 10^5$ g of polymer/(mol_{cat}.·h) (Table 2, runs 1–10). Correspondingly, the D/L-IMCI contents of these copolymers also gradually increased from 11 to 76 mol% (Table 2, runs 1–10).



				11						
Run	IMCI	ITPB	[IMCI]/	Mon.	Yield	Act. ^[b]	IMCI cont.[$^{[d]}M_{n}^{[d]}$	$M_{\rm w}/M_{\rm n}^{\rm [d]}$	Δ ε ₃₆₄ [e]
	(mmol)	(mmol)	[ITPB]		(%)		(mol%)	(10 ⁴)		(M ⁻¹ cm ⁻¹)
1	0.023	0.23	1:10	c+d	100	938	11	3.3	4.78	-0.59
2	0.046	0.23	1:5	c+d	97	965	19	4.4	4.67	-1.24
3	0.23	0.23	1:1	c+d	91	1324	37	5.6	4.16	-3.88
4	0.23	0.046	5:1	c+d	99	746	69	4.3	3.06	-13.07
5	0.23	0.023	10:1	c+d	99	658	76	6.8	2.70	-16.13
6	0.023	0.23	1:10	с+е	100	938	12	2.2	6.83	0.61
7	0.046	0.23	1:5	с+е	100	1000	17	1.9	7.28	1.14
8	0.23	0.23	1:1	c+e	92	1342	39	4.8	3.88	4.60
9	0.23	0.046	5:1	с+е	92	693	70	4.3	2.70	12.58
10	0.23	0.023	10:1	с+е	92	614	74	5.1	2.94	15.47

[a] Conditions: 2.3 μ mol of [Ph₃C][B(C₆F₅)₄], 5 mL of PhCl as solvent, 25 °C, 3 min. [b] Activity: kg of polymer/(mol_{cat}.-h). [c] Determined by ¹H NMR spectra in CDCl₃ at room temperature. [d] Determined by GPC in THF at 25 °C against polystyrene standard. [e] Determined by CD spectra in THF (c = 0.2 mg/mL, 0.1 cm path length).

Solvent separation experiments of these copolymerization products in toluene indicated negligible quantities of poly(ITPB) impurities. The GPC curves showed that the molecular weight distributions became narrow as the D/L-IMCI contents of the copolymers increased from 11 to 76 mol%. The reactivity ratios $(r_{(\text{ITPB})} = k_{(\text{IPTB})(\text{ITPB})}/k_{(\text{ITPB})(\text{IMCI})}$ and $r_{(\text{IMCI})} = k_{(\text{IMCI})(\text{IMCI})}/k_{(\text{IMCI})(\text{ITPB})}$ for the ITPB/D-IMCI system ($r_{(ITPB)} = 1.335$ and $r_{(D-IMCI)} = 0.310$) and the ITPB/L-IMCI system ($r_{(ITPB)} = 1.623$ and $r_{(L-IMCI)} = 0.247$) were obtained from the Fineman-Ross plots at very low monomer conversion (< 5%).^[14] These results suggested a preference for the reaction of ITPB over those of D/L-IMCI with this carbon cation. The product of the reactivity ratios ($r_{(ITPB)}r_{(IMCI)} = 0.414$ and 0.401, respectively) demonstrated a tendency to form random copolymers, in agreement with the microstructures of the resulting copolymers determined by ¹H NMR analysis. CD spectra displayed that all of the copolymers adopted a helical conformation with an excess screw sense in different degrees, which were significantly affected by the D/L-IMCI contents of the copolymers (Figure 1A). Moreover, a typical nonlinear relationship was found between the strength of CD signals at 364 nm and the D/L-IMCI contents in the corresponding copolymers, which means the helical sense selective random copolymerization of chiral D/L-IMCI and achiral ITPB monomer by using metal free carbon cation (Figure 1B).^[15] The fluorescence spectra revealed that some of poly(D/L-IMCI-co-ITPB)s also had AIE nature similar to poly(ITPB) (Figure 2D, Figure S45, B, C, E, F in ESI). SEM images showed that the optically active poly(D/L-IMCI-co-ITPB)s adopted a helical conformation with an excess screw sense in different degrees.

High resolution ESI-MS spectrum of the NI oligomers obtained by $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene confirmed the end groups by a series of peaks assigned to $Ph_3C(C=N-C_{10}H_7)_{1-1}$

 ${}_{6}C_{10}H_{6}N\equiv C + H^{+}, H(C=N-C_{10}H_{7})_{1-5}C_{10}H_{6}N\equiv C + H^{+}$ respectively (Figure 3, ESI). Based on these results, a possible carbocationic polymerization mechanism was suggested in Scheme 1. The cation Ph₃C⁺ serves as a truly cationic initiator for the polymerization of isocyanides. Moreover, the presence of C₁₀H₆NC end group demonstrates that the termination process undergoes a C-H activation of one carbon-hydrogen bond on the ortho-position of the aryl isocyanide monomer. As a result, the H⁺ proton is produced as new cationic initiator for further polymerization of isocyanide in combination with an polymer chain as $Ph_3C(C=N-C_6H_4R)_{m+1}C_{10}H_6N\equiv C$. Similarly, the polymer chains as $H(C=N-C_6H_4R)_nC_{10}H_6N=C$ will also be synthesized in the following polymerization process. Such C-H activation of aryl isocyanide monomer has never been observed in the polymerization of isocyanide by using late transition metal catalyst, identifying the high catalytic activity of these cationic initiators.



Figure 3. ESI-MS spectrum of NI oligomer obtained by $[Ph_3C][B(C_6F_5)_4]$.



Scheme 1. Possible Carbocationic Polymerization Mechanism.

In summary, commercially available [Ph₃C][B(C₆F₅)₄] serves as a highly efficient metal-free cationic initiator for the helicalsense-selective carbocationic polymerization of chiral aryl isocyanides and copolymerization with achiral aryl isocyanide with extremely high activity (up to 10^7 g of polymer/(mol_{cat}·h)), affording high molecular weight functional PIs with good solubility, AIE nature or single-handed helical conformation. Such highly efficient metal-free catalyst is quite rare for the polymerization of isocyanides, let alone its high helical sense selectivity in both polymerization and copolymerization of isocyanides. Further studies on the (co)polymerization of other functional isocyanide monomers by use of metal-free borate catalyst are in progress.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: isocyanide • (co)polymerization • metal-free • helical-sense-selective • cationic mechanism

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Layout 1:

COMMUNICATION

Commercially available $[Ph_3C][B(C_6F_5)_4]$ serves as a highly efficient, metal-free, and single-component initiator not only for carbocationic polymerization of polar and bulky aryl isocyanides with extremely high activity up to 1.2×10^7 g of polymer/(mol_{cat.} h) but also for helical-sense-selective polymerization of chiral aryl isocyanides and copolymerization with achiral aryl isocyanide, affording high molecular weight functional poly(aryl isocyanide)s with good solubility, AIE nature, and/or one-handed helical conformation.



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[Ph₃C][B(C₆F₅)₄]: Highly Efficient Metal-Free Single-Component Initiator for Helical-Sense-Selective Cationic Copolymerization of Chiral Aryl Isocyanide and Achiral Aryl Isocyanide