Title	Recyclable and efficient polyurethane-Ir catalysts for direct borylation of aromatic compounds
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Citation	Polymer chemistry, 8(47), 7406-7415 https://doi.org/10.1039/c7py01509g
Issue Date	2017-12-21
Doc URL	http://hdl.handle.net/2115/72196
Type	article (author version)
File Information	Polyurethane ligand Polym Chem_r2.1.pdf

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ARTICLE

Recyclable and Efficient Polyurethane-Ir Catalysts for Direct Borylation of Aromatic Compounds†

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Four polyurethanes having 2,2'-bipyridyl moieties incorporated in the main chain were synthesized as novel polymer ligand for Ir(I)-catalyzed direct borylation of aromatic compounds. The polyurethanes were insoluble in common organic solvents and soluble in dimethylsulfoxide. The borylation reaction of benzene catalyzed by Ir(I) in the presence of the polymer prepared from 4,4'-bis(hydroxylmethyl)-2,2'-bipyridyl and 1,6-diisocyanatohexane led to catalytic activities comparable to that in the presence of 2,2'-bipyridyl while the polymers prepared by the reactions of 4,4'-bis(hydroxylmethyl)-2,2'-bipyridyl with 1,4-diisocyanatobenzene, 1,4-diisocyanato-3-methylbenzene, and bis(4-isocyanatophenyl)methane resulted in lower catalytic activities. The high activity observed using the 1,6-diisocyanatohexane-based polyurethane catalyst may have a connection to the fact that this polymer has the highest tendency to form inter-chain hydrogen bond. The borylation reaction systems with the polymers were biphasic where the top and bottom layers contained the product and the polymer-based catalysts, respectively. Due to the phase separation, the product isolation and catalyst recycle were readily performed through simple decantation. The catalyst prepared from the 1,6-diisocyanatohexane-based polyurethane was able to be recycled at least five times without a serious decrease in activity. Further, regio-selectivity in borylation of toluene, anisole, and trifluoromethybenzene was studied using the polyurethane ligands as well as correnponding small-molecular ligands.

Polymer-based catalysts have an advantage of facile isolation of the product and recovery of the catalyst through simple repreciptation/filtration using a proper solvent rather than more laborious procedures such as chromatographic separation that is often used for reactions using small-molecular catalysts.[1-3] From a view of polymer backbone architecture, polymer-based catalysts can be prepared on the basis of either a linear polymer or from a cross-linked polymer gel.[2] Also, from a view of catalyst structure, a polymer catalyst may be either a combination of a polymer having coordinating sites and metallic species or a single-component polymer having organic catalytic sites covalently attached to the backbone. It is generally expected that polymer-bound catalysts may exhibit lower catalytic activities compared with corresponding small molecular systems due to steric hindrance

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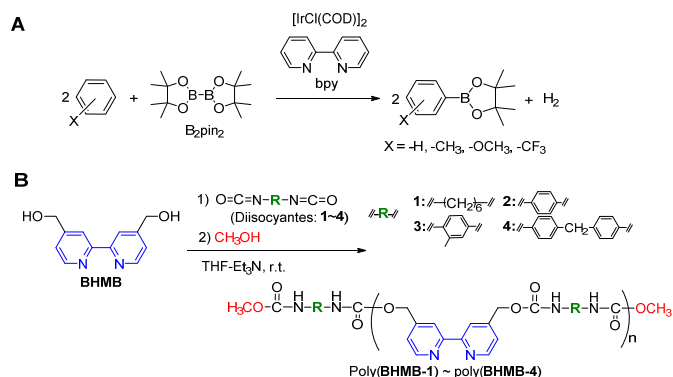
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† Electronic supplementary information (ESI) available: Experimental details, spectroscopic data and tabulated results of catalytic reactions. See DOI:xxxx.

and low molecular mobilities except for those having active centers only at chain terminus; however, recent examples include polymeric catalysts showing activities comparable to their small-molecular equivalents on the basis of molecular designes.[2b,3a]

Herein we introduce linear, soluble polyurethanes having coordinating 2,2'-bipyridyl (bpy) group incorporated in the main chain as novel polymer ligands for immobilization of catalytic metal species. Although polymers having bpy moieties in the main-chain have been prepared and their metal complexes have been studied,[4] they have barely been used as macromolecular ligands for metal-catalysed, practical synthesis of useful organic compounds in spite of the fact that bpy is a widely used small-molecular ligand for catalytic syntheses of a variety of chemicals.

In addition, application of polyurethanes for catalysis is unprecedented to the best of our knowledge while various linear macromolecular architectures have been applied for polymer ligands[2,3] in catalysis including polystyrenes,[5] polyacrylamides,[6] poly(meth)acrylates,[7] polyacrylonitrile,[8] polyquinoxalines,[9] polyacetylenes,[10] polyarenes including those having 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) or 1,1'-bi(2-naphthol) (BINOL) moiety in the main-chain,[11] polymers having Schiff base moieties in the main chain,[12] polyethers,[13] polysiloxanes,[14] polyvinylalcohol,[15] and polymers having quaternary salt bonds in the main chain.[16] In comparison with the existing macromolecular ligands, polyurethanes can be more readily prepared from a diol and a diisocyanate.[17,18] In addition, they tend to form intermolecular hydrogen bonding (H-bonding)[19] and are hence expected to exhibit characteristic features through inter-chain interactions. In this work, we found that the polyurethane-based catalysts

form a biphasic reaction mixture probably due to chain aggregation where simple decantation leads to facile product isolation and catalyst recycle.

Scheme 1. Direct borylation of aromatic compounds using Ir-bpy catalyst (A) and synthesis and expected structures of polyurethane ligands (B).

The target reaction in this work is the direct borylation of aromatic compounds using bis(pinacolato)diboron (4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane)) (B_2pin_2) as the source of B atom (Scheme 1 A).[20] This reaction can produce borylated aromatic compounds that are substrates for the Suzuki-Miyaura cross coupling reaction for the synthesis of various, valuable chemicals[21] and has been reported to be catalysed by Ir(I) species coordinated by bpy as a small-molecular ligand.[20] In this work, in order to incorporate bpy moieties into a polyurethane chain, polyaddition reactions were conducted between 4,4'-bis(hydroxylmethyl)-2,2'-bipyridyl (BHMB) and four isocyanates (**1~4**) (Scheme 1 B).

The conditions and results of polyaddition are summarized in Table 1. The reactions were conducted in a mixture of tetrahydrofuran (THF) and Et_3N in an excess of the isocyanates relative to BHMB and were terminated using MeOH so the both ends of the chain will have $CH_3OC(O)$-NH-R-NH-C(O)- groups arising from the reaction of terminal isocyanate group and MeOH. The signals of CH_3O- groups in ^{1}H NMR spectra were used as reference in terminal group analysis to estimate the degree or polymerization (DP) and averaged molar mass (M_n) (ESI, Fig. S3). The products were soluble only in dimethylsulfoxide (DMSO), and the reaction systems were heterogeneous. The facts that BHMB was not completely consumed and that the products had rather low DP's may be ascribed to precipitation of the products during the reactions. The polymers were purified by reprecipitation in MeOH; however, BHMB was not able to be removed from the reaction mixture except in run 6 in Table 1. For run 2 in Table 1, the amount of BHMH was virtually unchanged through three, repeated reprecipitations. In addition, for the combination of BHMB and **1**, a higher [BHMB] in feed and a [**1**]/[BHMB] ratio closer to unity tended to result in a higher DP (runs 1-4 in Table 1).

Fig. 1 shows the DSC profiles and IR spectra of the polymers. In the DCS analysis (Fig. 1A), poly(BHMB-**1**) indicated a clear glass transition temperature with an onset point of 48.5^{o}C while the other polymers did not exhibit any clear thermal transitions. This suggests that poly(BHMB-**1**) has more flexible nature due to the –

$(CH_2)_6$- spacer group in the main chain than the other polymers having rather rigid, aromatic spacer groups.

Table 1. Polyaddition between BHMB and diisocyanates ($R(NCO)_2$) (**1**-**4**) in THF-Et_3N mixture at 23°C[a]

Run	$R(NCO)_2$	[BHMB] (M)	$[R(NCO)_2]$ /[BHMB]	BHMB Conv.[b] (%)	MeOH-insoluble polymer[c]		
					Yield (%)	DP[d]	M_n[e]
1	**1**	0.36	1.1	74	28[f]	14	5,700
2	**1**	0.23	1.1	75	89[g]	11	4,600
3	**1**	0.24	1.2	75	66[h]	7.5	3,400
4	**1**	0.12	2.5	77	34[i]	2.8	1,400
5	**2**	0.23	1.1	82	69[j]	29	11,000
6	**3**	0.23	1.1	>99	97	8.0	3,400
7	**4**	0.23	1.1	86	65[h]	2.5	1,400

[a]Time = 24 h; THF = 2 mL; Et_3N = 0.11 mL (runs 1-3, 5-7), 0.07 mL (run 4). See Scheme 1 for the structures of **1**-**4**. [b]Determined by ^{1}H NMR analysis of crude product in DMSO-d_6. [c]Reprecipitated in methanol and collected with a centrifuge. [d]Determined by ^{1}H NMR terminal analysis where DP = 1 correspondes to an adduct consiting of one BHMB and one diisocyanate residues. [e]Calculated from the DP values. [f]Contained 9% of unreacted BHMB. [g]Contained 6% of unreacted BHMB. [h]Contained 5% of unreacted BHMB. [i]Contained 3% of unreacted BHMB. [j]Contained 12% of unreacted BHMB. [k]Contained 8% of unreacted BHMB.
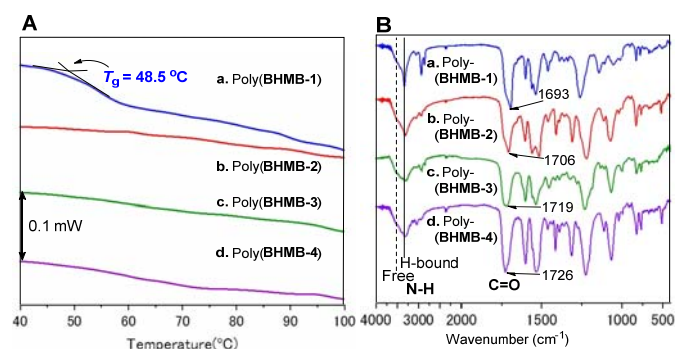

Fig. 1. DSC profiles on the 2nd heating scan (A) and FTIR spectra (KBr pellet) (B) of poly(BHMB-**1**) (run 2 in Table 1) (a), poly(BHMB-**2**) (run 5 in Table 1) (b), poly(BHMB-**3**) (run 6 in Table 1) (c), and poly(BHMB-**4**) (d) (run 7 in Table 1). [Sample amounts in A: 4.0 mg (a), 4.5 mg (b), 5.7 mg (c) and 5.1 mg (d)].

In the IR spectra (Fig. 1B), the signals due to N-H stretching in the range of 3000-4000 cm^{-1} are indicative of H-bonding; the peak at around 3320 cm^{-1} may be assigned to H-bound NH and the shoulder signals at around 3440 and 3550 cm^{-1} to free NH. This assignment was supported by DFT calculations on a H-bound polymer chain model and a free, single chain model (ESI, Fig. S11). The intensity ratios of these two signals obtained by wave-form separation were as follows (ESI, Fig. S4): H-bound/free = 63/37 (poly(BHMB-**1**)), 56/44 (poly(BHMB-**2**)), 52/48 (poly(BHMB-**3**)), and 54/46 (poly(BHMB-**4**)), indicating that poly(BHMB-**1**) has the highest tendency to form inter-chain H-bonding among the four polymers. H-bonding is also evaluated by the positon of the C=O stretching signals at around 1700 cm^{-1} where H-bonding interactions decrease the wavenumber of the stretching; poly(BHMB-**1**) indeed indicated

the lowest wavenumber of C=O stretching, which supports that this polymer had the highest propensity of H-bonding formation among the four polymers.

Prior to the studies on catalysis, complex formation of poly(BHMB-**1**) was assessed. While the polymer was colorless and IrCl(COD), the source compound of Ir, was reddish purple, the color of their heterogeneous mixture in THF was orange which looked very similar to that of a mixture bpy and IrCl(COD), supporting the complex formation between the polymer and Ir species (ESI, Figs. S5 and S6). This was further confirmed by UV-vis spectra where [IrCl(COD)]$_2$ and the bpy-Ir mixture had the longest-wavelength peaks at 450 nm and 575 nm, respectively, and the polym(BHMB-**1**)-Ir mixture had broad signals in the range from 700 nm through 300 nm which overlap the band of the bpy-Ir mixture (700-500 nm) (ESI, Fig. S7).

In addition, the complex formation between the bpy moiety in polymer and Ir species was confirmed by FTIR spectra (Fig. 2). Fig. 2 shows the FTIR spectra in the C=N and C=C vibration range of bpy, poly(BHMB-1), and their complexes with Ir. The signal assignments for bpy were made according to the literature (Fig. 2A a).[22] Comparing the bpy and bpy-Ir complex spectra (Fig. 2A a and b), one can conclude that the signal at 1602 cm^{-1} in Fig. 2A b which is absent in the pure bpy spectrum in Fig. 2A a is based on complexation; this signal may arise from blue shifted C-N vibration. In the spectrum of poly(BHMB-**1**)-Ir complex (Fig. 2B b), the signal at 1620 cm^{-1} which is not observed in the pure poly(BHMB-1) spectrum (Fig. 2B a) is proposed to reflect complexation; this signal may result from blue shifted C=N vibration similarly to the one at 1602 cm^{-1} in the bpy-Ir complex. It has been reported that bpy-metal interactions cause blue shifts of C=N ring vibration,[23] which supports our observations and conclusions. The polymer-Ir complexation has thus been supported not only by UV spectra but also by IR spectra.
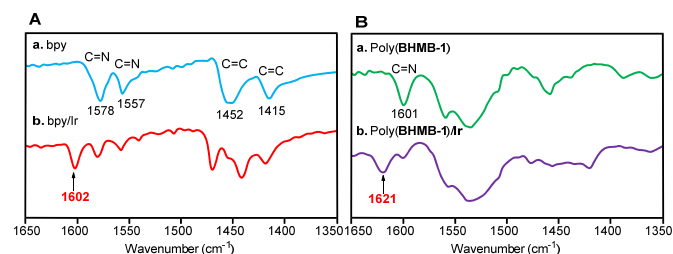
Fig. 2. FTIR spectra (KBr pellet) of bpy (a) and bpy-Ir complex (b) (A) and those of poly(BHMB-**1**) (run 2 in Table 1) (a) and poly(BHMB-1)-Ir complex (b) (B). The complex samples were prepared by mixing the ligands with IrCl(COD) in benzene and removing volatile species under reduced pressure.

Table 2 summarizes the direct borylation reactions of benzene, toluene, anisole, and trifluoromethylbenzene catalyzed by bpy-Ir and polymer-Ir complexes conducted under N$_2$ atmosphere using B$_2$pin$_2$ as borane source and nonane as internal standard for quantification of the product by calibrated GC-Mass (ESI, Figs. S1 and S2). The loading of catalyst per Ir was 3mol% of B$_2$pin$_2$, the aromatic compounds were used as the substrates and the solvents at the same time, and the ratio of bpy (bpy moiety in polymer) to Ir was unity. As a small-molecular ligand, BHMB, the monomer in the polymer synthesis, was also used for catalysis; it led to activities in the borylation of bezene, toluene, and anisole similar to those with bpy while the BHMB-Ir catalyst resulted in a much lower TON in the borylation of trifluoromethylbenzene than the bpy-Ir catalyst (runs

3, 13, 19, and 25 in Table 2). These observations seem to be in line with the fact that the direct borylation is rather sensitive to steric hindrance as reported in refs. 20a,b.

Table 2. Ir-catalyzed direct borylation of aromatic compounds (Ar-H) using bpy, BHMB and polyurethane as ligand at 80°C[a-c]

Run	Ar-H	Ligand	Time (h)	Yield[d] (%)	TON[e]
1		bpy	4	98	66
2			24	95	64
3		BHMB	24	88	58
4		Poly(BHMB-1)	4	81	54
5			24	78	52
6	Benzene	Poly(BHMB-2)	4	1	1
7			24	47	31
8		Poly(BHMB-3)	4	1	1
9			24	70	46
10		Poly(BHMB-4)	4	~0	0
11			24	61	40
12		bpy	24	86	57
13		BHMB	24	78	52
14	Toluene	Poly(BHMB-1)	24	72	48
15		Poly(BHMB-2)	24	15	10
16		Poly(BHMB-3)	24	9	6
17		Poly(BHMB-4)	24	1	1
18		bpy	24	83	55
19		BHMB	24	78	52
20	Anisole	Poly(BHMB-1)	24	1	1
21		Poly(BHMB-2)	24	8	5
22		Poly(BHMB-3)	24	6	4
23		Poly(BHMB-4)	24	15	10
24		bpy	24	96	64
25		BHMB	24	1	1
26	Trifluoromethyl-benzene	Poly(BHMB-1)	24	27	18
27		Poly(BHMB-2)	24	~0	~0
28		Poly(BHMB-3)	24	1	1
29		Poly(BHMB-4)	24	3	2

[a]The reactions were conducted in the substrates as solvents where the reaction mixtures were heated at 80°C immediately after they were prepared by mixing a ligand, [IrCl(COD)]$_2$, and B$_2$pin$_2$ in solvent (substrate). Conditions: benzene (volume) = 5.3 mL, [1/2[IrCl(COD)]$_2$] = 5.6 mM (3 mol% of B$_2$pin$_2$), [B$_2$pin$_2$] = 185 mM, [nonane] = 100 mM (runs 1-11); toluene (volume) = 4.8 mL, [1/2[IrCl(COD)]$_2$] = 6.2 mM (3 mol% of B$_2$pin$_2$), [B$_2$pin$_2$] = 208 mM, [nonane] = 110 mM (runs 12-17); anisole (volume) = 6.5 mL, [1/2[IrCl(COD)]$_2$] = 4.6 mM (3 mol% of B$_2$pin$_2$), [B$_2$pin$_2$] = 154 mM, [nonane] = 82 mM (runs 18-23); trifluoromethylbenzene (volume) = 7.4 mL, [1/2[IrCl(COD)]$_2$] = 4.0 mM (3 mol% of B$_2$pin$_2$), [B$_2$pin$_2$] = 133 mM, [nonane] = 72 mM (runs 24-29). [b][bpy]/[Ir] = [bpy moiety in polymer] =1/1. [c]Poly(BHMB-**1**), Mn 4,600 (run 2 in Table 1); poly(BHMB-**2**), Mn 11,000 (run 5 in Table 1); poly(BHMB-**3**), Mn 3,200 (run 6 in Table 1); poly(BHMB-**4**), Mn 1,400 (run 7 in Table 1). [d]Determined by calibrated GC-Mass using nonane as internal standard. [e]Turn over number (TON) = [product]/[Ir].

In the borylation of benzene for 4 h, poly(BHMB-**1**) (run 2 in Table 1) led to activity comparable to that observed with bpy (runs 1, 2, 4, and 5 in Table 2) while only very low TONs were achieved with the other polymers. On the other hand, in 24 h, TONs with the other, three polymers were improved (runs 7, 9, and 11 in Table 2). In the borylation of toluene for 24 h, poly(BHMB-**1**) again led to a TON comparable to that attained with bpy (runs 11, 12 in Table 2)

while the other polymers resulted in much lower TONs compared with those with poly(BHMB-**1**) and bpy. In addition, in the borylation of anisole and trifluoromethylbenzene, all polymer ligands led to much lower TONs compared with bpy.

Thus, poly(BHMB-**1**) was found to be an effective polymer ligand whose performance was much better than those of the other, three polymers and was comparable to that of bpy in benzene and toluene borylation. The observed performance of poly(BHMB-**1**) may have a connection with the proposed flexibility of the –(CH$_2$)$_6$- spacer group and the highest tendency to form inter-chain H-bonding.

The fact that the performance of all polymer ligands was remarkably less than bpy in the borylation of anisole and trifluoromethylbenzene may be ascribed to steric repulsion between the polymer chains and the methoxy group or the trifluoromethyl group of the substrates which can prevent effective coordination of the substrates to Ir.

It is notable that the performances of poly(BHMB-**1**)'s of DPs = 7.5 and 2.8 in the borylation of benzene were similar to that of poly(BHMB-**1**) of DP = 11 (ESI, Table S1). The properties of poly(BHMB-**1**) discussed so far are thus virtually independent of DP and may be considered to be inherent to the chemical structure of poly(BHMB-**1**) though the range of examined DP is rather narrow.

In order to obtain information on the role of H-bonding in the significance of poly(BHMB-**1**), borylation of benzene was conducted using poly(BHMB-**1**) and bpy in the presence of *N,N*-dimethylformamide (DMF) which would inhibit inter-chain H-bonding formation (ESI, Table S4). Although both reactions using poly(BHMB-**1**) and bpy were hampered to an extent possibly through Ir-DMF interactions that may not be favorable for catalysis, it was confirmed that the decrease in TON in the presence of 0.53 mL of DMF dissolved in 5.3 mL of benzene was greater for the poly(BHMB-**1**)-Ir catalyst compared with that for the bpy-Ir catalyst (70% decrease for bpy and 82% decrease for poly(BHMB-**1**)) (ESI, runs 1, 2, 4, and 5 in Table S4). These results may support the importance of inter-chain H-bonding of the polymer ligand in catalysis.

In connection with the studies of poly(BHMB-**1**), a polyester was prepared using BHMB and adipoyl chloride (DP 44) and used for borylation of benzene under the condition same as that for run 4 in Table 2; TON was 37 for reaction for 4 h which was clearly lower than that in the reaction using poly(BHMB-**1**) (ESI, Fig. S10). These results might have a connection to the proposed importance of inter-chain interactions in the polyurethanes through H-bonding although the difference in performance between poly(BHMB-**1**) and the polyester having different chemical structures may reflect properties other than H-bonding formation tendency.

Further, the procedure of the catalytic reactions was found to sensitively affect the reaction results (ESI, Table S2). The reactions in this work were conducted by first pre-mixing an aromatic compound (solvent), [IrCl(COD)]$_2$, B$_2$pin$_2$ and nonane in a flask under N$_2$ by stirring at 23°C and then heating the mixture at 80°C. The highest TONs were achieved at the shortest pre-mixing time where the reaction mixture was heated at 80°C immediately after it was prepared for both systems with bpy and poly(BHMB-**1**) as ligands. When the pre-mixing time was 1.5 h at 23°C for the systems with poly(BHMB-**1**), no reaction was confirmed. Complex structures formed at 23°C might be somewhat different from those formed at 80°C, and the former may not be an active species in the catalysis.

In addition, the ligand-Ir ratio significantly influenced the reaction activity (ESI, Table S3). In the borylation of benzene using poly(BHMB-**1**) as ligand, while the reaction at [bpy moiety]/[Ir] = 1 led to a TON of 52 through the reaction for 24 h, the reaction at [bpy moiety]/[Ir] = 3.3, the reaction did not proceed at all. This observation is in a sharp contrast to the fact that the reactions using bpy and BHMB at [ligand]/[Ir] = 3.3 led to only slightly lower TONs compared with the reactions at [ligand]/[Ir] = 1. The excess bpy units in poly(BHMB-**1**) at [bpy moiety]/[Ir] = 3.3 may exert simple steric effects that prevent the substrates from approaching to Ir.

Table 3. Regio-selectivity in Ir-catalyzed direct borylation of aromatic compounds (Ar-H) using bpy or polyurethane as ligand at 80°C[a,b]

Run	Ar-H	Ligand	Time (h)	TON[c]	o-/m-/p-[d]
1			4	57	1/63/36
2		**bpy**	0.28	3	1/66/33
3			0.25	0.2	7/63/30
4		**BHMB**	24	52	1/61/38
5	Toluene	Poly(**BHMB-1**)	24	48	1/65/34
6		Poly(**BHMB-2**)	24	10	1/64/35
7		Poly(**BHMB-3**)	24	6	1/64/35
8		Poly(**BHMB-4**)	24	1	23/48/28
9			24	55	1/63/36
10		**bpy**	0.27	25	1/66/33
11			0.14	0.05	37/44/18
12		**BHMB**	24	52	2/70/29
13	Anisole	Poly(**BHMB-1**)	24	1	24/41/35
14[e]		Poly(**BHMB-1**)	24	11[e]	3/72/25[e]
15		Poly(**BHMB-2**)	24	5	2/78/20
16		Poly(**BHMB-3**)	24	5	2/76/21
17		Poly(**BHMB-4**)	24	10	2/80/18
18		**bpy**	24	55	~0/71/29
19		**BHMB**	24	1	~0/60/40
20	Trifluoro methyl- benzene	Poly(**BHMB-1**)	24	18	~0/70/30
21		Poly(**BHMB-2**)	24	~0	n.d.
22		Poly(**BHMB-3**)	24	1	~0/58/42
23		Poly(**BHMB-4**)	24	3	~0/58/42

[a]See Table 2 for reaction conditions. [b][bpy]/[Ir] = [bpy moiety in polymer] =1/1. [c]Determined by calibrated GC-Mass using nonane as internal standard. Turn over number (TON) = [product]/[Ir]. [d]Determined by GC-Mass (ESI, Figs. S8 and S9). [e]Reaction at a higher concentration of [1/2[IrCl(COD)]$_2$] (13.86 mM, 9 mol% of B$_2$pin$_2$) to increase TON.

In the borylation of toluene, anisole, and trifluoromethymethylbenzene, regio-selectivity is an aspect of interest as well as catalytic activity[20a,24] (Table 3). Although, in most cases, the polymer ligands resulted in regio selectives similar to those with bpy and BHMB, poly(BHMB-**4**) in the borylation of toluene (run 8 in Table 3) and poly(BHMB-**1**) in the borylation of anisole (run 13 in Table 3) led to much higher *o*-selectivities than bpy and BHMB. As for this point, it is notable that TONs in these two cases are only ca. 1%, suggesting a possibility that the *o*-isomers are the kinetically favored products. This possibility was tested for the borylation of anisole through (A) a reaction with bpy for a shorter time (0.14 h) leading to a TON of 0.05 of the product

(run 11 in Table 3) and (B) a reaction with poly(BHMB-**1**) at the level of catalyst of 9 mol% of B$_2$pin$_2$ leading to a TON of 11 (run 14 in Table 3). In case A, the regio-selectivity was o-/m-/p- = 37/43/18 at a TON of 0.05 in 0.14 h with bpy as ligand while it was = 1/63/36 at a TON of 55 using the same ligand. In case B, using poly(BHMB-**1**) as ligand, the regio-selectivity was o-/m-/p- = 3/72/25 at a TON of 11 using 9mol% of Ir while it was = 24/41/35 at a TON of 1 using 3mol% of Ir. These results support that the rather high *o*-selectivities in runs 11 and 13 are based mainly on kinetic characteristics of the reactions but not on the ligand structure.

Also, in the borylation of trifluromethylbezene, BHMB, poly(BHBM-**3**) and poly(BHBM-**4**) led to lower *m*-selectivities and higher *p*-selectivities at low TONs of 1-3 (runs 19, 22, and 23 in Table 3) compared with bpy and poly(BHMB-**1**) at higher TONs of 55 and 18 (runs 18 and 20 in Table 3). These observations may also arise from kinetic features of the reaction.
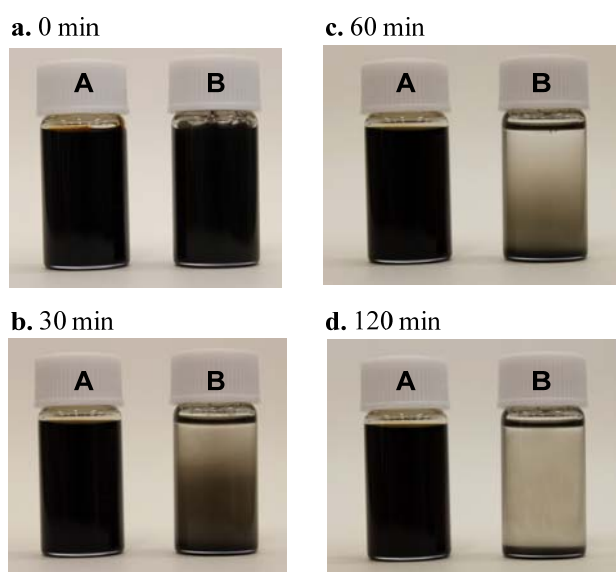
Fig. 3. Photograps of reaction mixtures of benzene borylation systems with bpy-Ir catalyst (A) and poly(BHMB-**1**)-Ir catalyst (B) taken in different durations after stirring was stopped. Conditions were the same as those in runs 2 and 5 in Table 1, respectively.
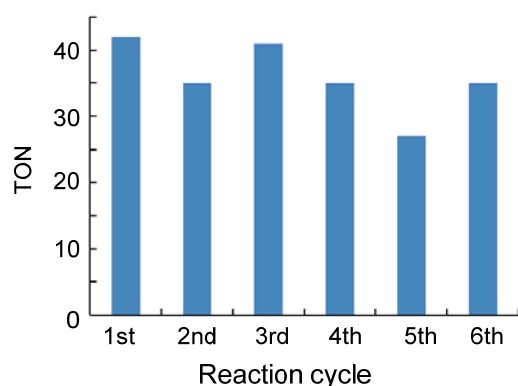
Fig. 4. TONs in the borylation of benzene using the recycled poly(BHMB-**1**)-Ir catalyst. Conditions were the same as those in run 5 in Table 2.

Fig. 5. SEM images of poly(BHMB-**1**) (A), poly(BHMB-**2**) (B), poly(BHMB-**3**) (C), and poly(BHMB-**4**) (D). [magnification x 10,000]

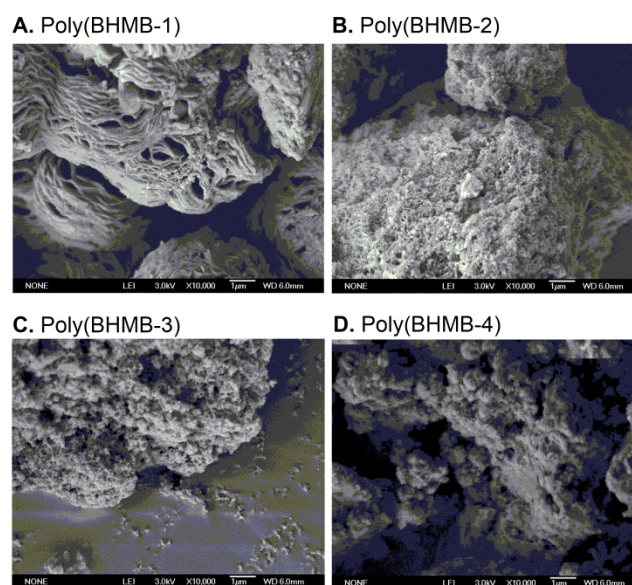A notable characteristic of the polymer catalyst studied in this work is that the reaction mixtures are biphasic, and the clear solution phase (top) and the dark, heterogeneous phase containing the catalyst (bottom) are smoothly separated on standing in 60-120 min, which is in a sharp contrast to the fact that the reaction mixtures of the small-molecular bpy-Ir catalyst appear almost homogeneous even after standing for 120 min (Fig. 3). The phase separation is considered to be caused by insolubility of the polymer-Ir complexes in the aromatic compounds used as substrates and solvents at the same time. An attempt to measure the rate of phase separation failed as the sedimentation was too fast to be followed. This feature allowed facile isolation of the product and recovery of the catalyst for recycled use through simple decantation or with a centrifuge.

The catalyst recycle was confirmed for the benzene borylation using the poly(BHMB-**1**)-Ir catalyst in the following way. After 24 h of reaction, the top layer of the reaction mixture containing the product was separated from the bottom layer containing the catalyst by decantation, a fresh portion of benzene containing B$_2$pin$_2$ and nonane was charged to the recovered catalyst, and the reaction was conducted again for 24 h. As shown in Fig. 4, the catalytic activity was rather well maintained with only a moderate variation which may be due to contamination by oxygen through the separation procedure conducted under air (ESI, Table S5).

Inductively coupled plasma (ICP)-optical emission spectral analysis of the catalyst after the 1st and 4th reactions suggested

that the concentration of Ir decreased by at least ca. 10% which may be ascribed to leaching (ESI, Table S6). The moderate variation in catalytic activity in the catalyst recycle experiments may arise leaching to a certain extent as well as effects of oygen although the exact fate of the polymer catalyst in repeated uses including potential chemical transformations is not yet clear.

Additionally, polymer morphologies were examined by scanning electron microscopy (SEM) (Fig. 5). Among the four polymers, poly(BHMB-**1**)'s morphology is dissimilar to other polymers' morphologies and is characterized by the layer-like structure which may suggest that the polymer has a larger inner space than the other polymers. On the other hand, poly(BHMB-**2**), poly(BHMB-**3**), and poly(BHMB-**4**) indicated rather less-characteristic, similar images where dense polymer particles seem to comprise from many smaller particles. These results may have a connection to the facts that poly(BHMB-**1**) alone showed a Tg in DCS profiles and that it had the highest propensity of H-bonding formation. The combination of strong H-bonding and flexible −(CH$_2$)$_6$- chain may be responsible for the layer-like structure. In addition, the fact that poly(BHMB-**1**) indicated over all the best activities in the borylation reactions excepting for that of anisole may arise in part from the characteristic polymer morphology.

Additionally, in order to obtain information on the dark color of the catalysts, transmission electron microscopy (TEM) and SEM-energy dispersive X-ray spectroscopy (EDS) analyses were performed for poly(BHMB-**1**)-Ir catalyst (ESI, Figs. S14 and S15). These experiments were attempted to find out nanoparticles of Ir which could be formed from the catalyst and may be reason of the dark color; however, TEM images did not show any particulate objects, and SEM-EDS mapping only indicated that O, N, and Ir elements have very similar distributions. On the basis of these results, Ir nanoparticles are not likely to form under the current experimental conditions. The origin of the dark color is thus not yet known.

Further, theoretical calculations based on density functional theory (DFT) were performed to obtain information on the mechanism of catalytic reaction involving poly(BHMB-**1**) (Figs. 6 and 7). As a model of polymer chain bearing a bpy moiety, an adduct which can be prepared from one BHMB molecule and two methyl isocyanate was used (A. MoFigdel chain in Fig. 6), and an H-bound stack consisting of *three* model chains was created as a model of H-bound aggregates of polymer chains (B. Trimeric aggregate in Fig. 6). Though there may be a variety of forms of H-bound aggregates of chains, the trimeric stack may reflect the most sterically crowded environment that may lead to catalytic properties characteristic to the polymers studied in this work. In addition, while in experiments, B$_2$pin$_2$ was used as the borane source and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl group coordinates to the Ir center, the four methyl groups at the 4,4,5,5-positions were omitted in the DFT calculations, *i.e.*, 1,3,2-dioxaborolane-2-yl group was used, in order to facilitate computer-resource-efficient examinations.
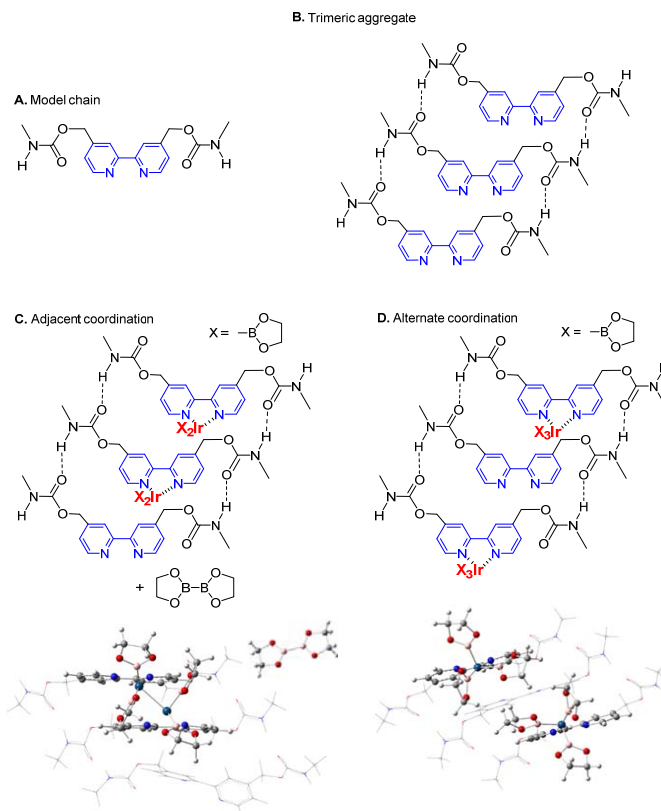
Fig. 6. Chemical structures of model chain (A), trimeric aggregate (B), adjacent coordination model of trimeric aggregate-Ir complex with a 2,2'-bi(1,3,2-dioxaborolane) (C), and alternate coordination model of trimeric aggregate-Ir complex (D) and DFT-optimized coordinates of the coordination models (C and D).

Prior to calculations on the reaction path, how Ir can coordinate to polymer was examined. For this purpose, steric energies of trimeric aggregate models coordinated by two Ir species bearing three 1,3,2-dixoaboralane-2-yl groups (per Ir) in two ways, i.e, coordination of Ir to adjacent bpy moieties (C. Adjacent coordination in Fig. 6) and coordination of Ir to alternate bpy moieties (D. Alternate coordination in Fig. 6), were compared. For the adjacent coordination model, due to steric repulsion between 1,3,2-dioxaborolane-2-yl groups, only two of the groups were able to coordinate to an Ir center and the remaining group was considered as 2,2'-bi(1,3,2-dioxaborolane) molecule while for the alternate coordination model, coordination of three 1,3,2-dioxaborolane-2-yl groups to an Ir centre seemed reasonable. The adjacent coordination model had a 60.1 kcal/mol higher energy compared with the alternate coordination model and may therefore be implausible.

With this result in mind, we chose a trimeric aggregate of chains in which only the central bpy units is coordinated with Ir centre bearing three 1,3,2-dioxaboralane-2-yl groups as a model of catalytic reaction center. Calculations were also conducted for a BHMB-Ir complex as a model of corresponding small-molecular catalyst for comparison.

A. Trimeric aggregate-Ir system

2 (-19.4 kcal/mol)
Ir-C = 3.63 Å

TS2-3 (4.8 kcal/mol, 944i cm^{-1})
Ir-C = 2.23 Å, Ir-H = 1.62 Å
C-H = 1.61 Å

3 (-4.7 kcal/mol)
Ir-C = 2.13 Å, Ir-H = 1.60 Å
C-B = 2.84 Å

TS3-4 (-4.1 kcal/mol, 14i cm^{-1})
C-B = 2.76 Å

4 (-5.3 kcal/mol)
Ir-B = 2.07 Å, C-B = 2.51 Å

TS4-5 (-3.1 kcal/mol, 124i cm^{-1})
Ir-C = 2.26 Å, Ir-B = 2.09 Å
C-B = 1.96 Å

B. BHMB-Ir system

2 (-21.8 kcal/mol)
Ir-C = 2.88 Å

TS2-3 (5.6 kcal/mol, 910i cm^{-1})
Ir-C = 2.21 Å, Ir-H = 1.63 Å
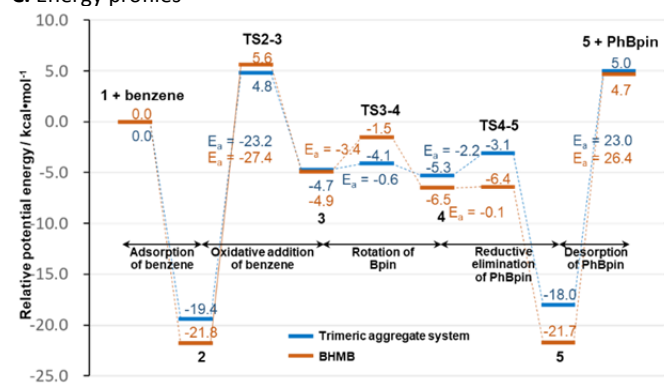C-H = 1.63 Å

3 (-4.9 kcal/mol)
Ir-C = 2.13 Å, Ir-H = 1.60 Å
C-B = 2.87 Å

TS3-4 (-1.5 kcal/mol, 19i cm^{-1})
Ir-C = 2.15 Å, Ir-B = 2.05 Å
C-B = 2.81 Å

4 (-6.5 kcal/mol)
Ir-C = 2.17 Å, Ir-B = 2.07 Å
C-B = 2.27 Å

TS4-5 (-6.4 kcal/mol, 36i cm^{-1})
Ir-C = 2.18 Å, Ir-B = 2.08 Å
C-B = 2.18 Å

C. Energy profiles

Fig. 7. Proposed mechanism of direct borylation of benzene by Ir catalysts: molecular coordinates and their energies for the trimeric aggregate system (A) and the BHMB system (B), and energy profiles for the trimeric aggregate-Ir catalyst system (blue) and the BHBM-Ir catalyst system (red) (C). Numbers and E$_a$ values correspond to relative potential energies and activation energies (kcal/mol). Structrue numbers in A and B correspond to those in C.

Fig. 7 shows the structures and corresponding relative potential energy of species which can contribute to direct borylation of benzene (A and B) and energy diagram for the two systems (C). Reactions of trimeric aggregate-Ir and BHMB-Ir with 2,2'-bi(1,3,2-dioxaborolane) as the borane source were found to reasonably lead to the initial complex structures in Fig. 7 A and B through separate calculations (ESI, Fig. S13). In both the polymer (trimeric aggregate)-Ir and the BHMB-Ir systems, benzene approaches and is adsorbed to the Ir center through interactions between π-electrons and empty orbitals of Ir (**2** in Fig. 7 A, B, C), and the reaction then proceeds to the stage of oxidative addition of benzene which involves the first transition state where a hydrogen of benzene is transferred to Ir (**TS2-3**, **3**) and a quasi-octahedral structure is formed (**3**). The rearrangement of the three 1,3,2-dioxaboralane-2-yl groups attached to Ir occures, the group closest to the benzene ring approaches to benzene (**TS3-4**, **4**), and B-C bond is formed (**TS4-5**, **5**). Theoretical reaction paths appear very similar between the trimeric aggregate-Ir and the BHMB-Ir systems. As far as an alternate Ir coordination model is used, steric repulsion seems not to prevent benzene from approaching to the Ir center in the polymer model.

In both the the trimeric aggregate-Ir and the BHMB-Ir systems, activation energy is highest for **TS2-3** and those for **TS3-4** and **TS4-5** are rather low, indicating that the rate-limiting step is oxdative addition of benzene to the Ir center; once a benzene molecule approaches to and is bound to the Ir center, the following reactions proceed smoothly. The theoretical reaction paths disclosed here are similar to that proposed for a bpy-Ir system.[25]

On the basis of the threoretical examinations disclosed here, it can be concluded that active species in the polyurethane-Ir catalysts responsible for the borylation reaction are isolated bpy moiety-Ir coordination sites in a polymer chain rather than densely neighbouring bpy-Ir units. For the former sites, sufficient spaces would be available for substrates to diffuse, adjust molecular orientation to coordinate to Ir, and change molecular shape and size through C-B bond formation.

Conclusions

In summary, we prepared the four polyurethanes bearing 2,2'-bipyridyl moieties in the main chain and examined their efficiencies as ligands for Ir-catalyzed direct borylation reaction of benzene, toluene, anisole, and trifluoromethylbenzene. Poly(BHMB-**1**) was most efficient as ligand among the four polymers for all subtrates. As for region-selectivity in borylation of toluene, anisole, and trifluoromethylbenzene, the polymer ligands did not differ from bpy and BHMB, the small molecular ligands; for both polymer- and small-molecular ligand-based systems, selectivity depended on TON, suggesting that region-selectivity has a connection to kinetic features of reaction. In addition, the reaction systems with the polymer ligand-Ir catalysts in aromatic compounds as solvents and as substrates at the same time were biphasic where the top layer contained the products and the bottom layer the catalysts. Due to this character, isolation of the product was possible by simple decantation or with a centrifuge, and also, the poly(BHMB-**1**)-Ir catalyst was able to be recycled (reused) in the benzene borylation by simply removing the top layer and re-charging fresh benzene containing B$_2$pin$_2$ to the recovered catalyst from the bottom layer. The significance of poly(BHMB-**1**) may be have a connection to the presence of flexbile, hexamethylene spacers connecting bpy moieties in

the main chain and the highest tendency to form inter-chain H-bonding among the four polymers. The combination of a flexible chain and inter-chain interactions is reminiscent of elastomer structures which might be found to be an effective structural motif in designing a macromolecular ligand through our on-going, further studies. This work is believed to be the first example of utilization of polymers bearing bpy moieties in the main chain for practical, catalytic synthesis of useful organic compounds. In addition, polyurethane ligands have been unprecedented.

Acknowledgements

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