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Polycondensation of haloarylketones catalyzed by palladium compounds bearing N-heterocyclic carbene (NHC) ligands

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Abstract

Palladium-catalyzed α-arylation of ketones, which can efficiently give coupling products by using appropriate ligands and bases, could be applied to a polycondensation reaction. Stable N-heterocyclic carbenes (NHC) were used as favorable ligands coordinating the Pd catalysts, which were generated in situ from commercially available palladium compounds such as $Pd(OAc)_2$ and $Pd_2(dba)_3$ as suitable catalyst precursors in this polymerization. Using small amounts of binary catalysts, poly(aryl alkyl ketone)s were afforded in high yields from haloarylketones in the presence of a base. A primarily prepared palladium catalyst having an NHC ligand, $[Pd(OAc)_2(NHC)]$, also efficiently catalyzed the polycondensation, whereas a palladium compound bearing two carbene ligands, $[PdX_2(NHC)_2]$, did not.
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1. Introduction

Among the powerful C–C bond-forming reactions, catalytic α-arylation of carbonyl compounds mediated by palladium(0) complexes, which catalyzes the substitution reaction of halogen on the arene by enolate, is one of the highly efficient methods for combining aromatic molecules with various carbonyl compounds [1]. When Buchwald [2], Hartwig [3], and several other researchers [4,5] widely developed this catalytic reaction, several effective ligands on the palladium catalysts were found, such as tri(*tert*-butyl)phosphine, BINAP, DPPF, N-heterocyclic carbenes, and so on. These are important in that having electron-donating and bulky properties has resulted in high-yield formation of desired cross-coupling products, since strong donation from the ligand to the metal may induce the facile

oxidative addition of arylhalides, and steric demands of the ligand may make reductive elimination of arene and enolate groups on the metal efficient. Also, the bulkiness of the ligand may prevent a side reaction (β-elimination of the palladium enolate of which the palladium directly bound to the carbon) when the carbonyl compounds have hydrogen at the β-position [1]. Thus, α-arylation of carbonyl compounds, especially of ketones, could be applied to step-growth polycondensation by employing the appropriate ligands on the palladium. Wu et al. showed that the polycondensation reactions of haloarylketones or dihaloarenes and aromatic diketones form several poly(aryl-ketone)s as starting materials of π-conjugated polymers [6]. They found that using the bulky phosphines, such as P^tBu_3, $P(o\text{-Tol})_3$, and BINAP, in the presence of palladium acetate or $Pd_2(dba)_3$ (dba: dibenzylideneacetone) resulted in good yield formation of polymers with high molecular weight, but adding triphenylphosphine caused the production of oligomers [6]. The obtained polymers had carbonyl, aromatic, and alkyl groups in the polymer main chain, and also some attractive factors in them, such as

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thermal stability and facile solubility in the usual organic solvents, were also pointed out.

However, the details, including the polymer structures, were not clear and, furthermore, the employment of 10 mol% of palladium compounds and toxic/air-unstable phosphines is a drawback. Alternatively, N-heterocyclic carbenes (NHC) are well-known as stable compounds binding to metals as typical σ-donor ligands that can replace classical 2 e-donor ligands such as amines, ethers, and phosphines in metal coordination chemistry [7]. Nolan et al. demonstrated catalytic α-arylation of ketones efficiently, mediated by palladium complexes binding to bulky N-heterocyclic carbenes and concluded from structural and thermochemical studies that these ligands behave as better donors than the best phosphine donor ligands [8].

These factors prompted us to construct a polycondensation system in which N-heterocyclic carbenes were employed as ligands on the palladium catalysts. As a result, 4′-haloarylketones were efficiently polymerized in a THF solution mediated by (1) in situ-generated palladium catalysts or (2) a palladium NHC complex, [Pd(OAc)₂(NHC)] [9,10], as shown in Scheme 1.

As a known procedure, N-heterocyclic carbene can be produced in situ from a reduction of the inert imidazolium salts, **1** and **2**, with a strong base [7a]. Palladium compounds, such as Pd(OAc)₂, PdCl₂, and Pd₂(dba)₃, successfully became more active in situ in the presence of 1 equiv. of an imidazolium chloride than those in the absence of a ligand precursor, when a base, NaOᵗBu, was in existence (Scheme 1). The molar ratio of the carbene ligand to the metal was quite sensitive toward the activity of the catalyst. This result prompted us to use two palladium complexes having one and two carbene ligands on the metal, which was prepared in advance. The palladium monocarbene complex, [Pd(OAc)₂(NHC)] (**3**), made the catalytic reaction more efficient than that using the binary catalyst in combination of Pd(OAc)₂ and the imidazolium chloride, whereas the biscarbene complexes [PdX₂(NHC)₂] (X = Cl, I) deactivated the reaction (Scheme 1). Characterization of the polymers and oligomers was carried out on the basis of

NMR and IR spectroscopy and preliminary analyzed MALDI-TOF MS measurement.

2. Experimental

2.1. General procedures

All manipulations were carried out using standard Schlenk technique or using globe box, MBraun UNI-Lab, under an inert gas atmosphere. Solvents were distilled in the presence of standard drying reagents (THF, 1,4-dioxane, and toluene; benzophenone ketyl: DMF, CDCl₃; CaH₂) and stored under an argon atmosphere. All reagents commercially available were used without further purification. NMR spectra were taken with a VARIAN Mercury Y plus 400 MHz spectrometer. Chemical shifts were recorded in ppm from the internal standard (¹H, ¹³C: solvent). Assignments of the NMR signals were performed with the aid of DEPT and 2D [¹H–¹H, ¹H–¹³C COSY] techniques. IR spectra were recorded in cm⁻¹ on a Perkin–Elmer Spectrum One spectrometer equipped with a universal diamond ATR. MALDI-TOF MS measurement was carried out on a Applied Biosystems Voyager-DE STR Biospectrometry calibrated with Angiotensin I (M_w = 1296.68, av. mass = 1297.51). And α-CHCA (Alpha-cyano-4-hydroxy cinnamic acid) was used for matrix of the polymer sample. The elemental analysis was carried out with YANACO CHN Corder MT-5, AUTO-SAMPLER. GPC analyses of the polymers were performed with a JASCO DG-2080-53 degasser, PU-2080 Plus HPLC pump, UV-2075 Plus UV/vis detector, RI-2031 Plus RI detector, and CO-2065-plus column oven (at 40 °C) connecting two Shodex GPC KF-804 L columns in series. Samples were eluted with THF. Calibration was carried out on the basis of retention time of a standard sample of polystyrene (8 samples (M_w/M_n ⩽ 1.07), of which M_n range is 1.31×10^3–3.85×10^6). The 1,3-biaryl-imidazolium chlorides [11] and the palladium compounds, Pd₂(dba)₃ [12], **3b** [9], **4a** and **4b** [13] were prepared according to the literature. Pd(OAc)₂ and PdCl₂ were purchased from commercial sources and used with purification.

2.2. General procedure for polymerization of 4′-bromopropiophenone using binary palladium catalyst

General procedure for polymerization using the binary catalyst is as follows: sodium *tert*-butoxide (300 mg, 3.12 mmol), palladium acetate (10.1 mg, 0.045 mmol), **1b** (19.1 mg, 0.045 mmol), 4′-bromopropiophenone (320 mg, 1.50 mmol), and finally THF (6.0 mL) were added into a 20 mL Schlenk tube. The solution was heated at 70 °C and stirred for 24 h. After cooling, the resulting suspension was poured into excess amount of methanol, and then the precipitate was filtered, washed with methanol and dried under reduced pressure (188 mg, 95%). The molecular weight determined by SEC (calibration: polystyrene standard) was M_n = 4294, and M_w/M_n = 2.02.
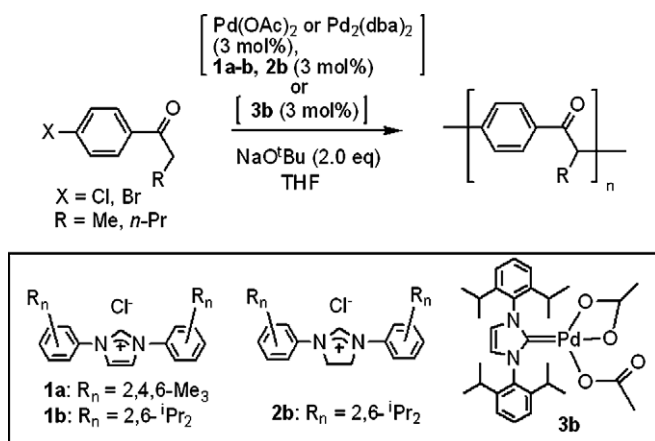
Scheme 1.

2.3. General procedure for polymerization of 4′-bromopropiophenone using 3b

General procedure for polymerization using **3b** as a catalyst is as follows: sodium *tert*-butoxide (300 mg, 3.12 mmol), **3b** (27.6 mg, 0.045 mmol), 4′-bromopropiophenone (320 mg, 1.50 mmol), and finally THF (6.0 mL) were added into a 20 mL Schlenk tube. The solution was heated at 70 °C and stirred for 24 h. After cooling, the resulting suspension was poured into excess amount of methanol, and then the precipitate was filtered, washed with methanol and dried under reduced pressure (176 mg, 89%). The molecular weight determined by SEC (calibration: polystyrene standard) was $M_n = 4591$, and $M_w/M_n = 1.67$.

3. Results and discussion

3.1. Polycondensation of 4′-halopropiophenone catalyzed by in situ generated catalyst

First of all, we demonstrated a reaction in the presence of the bulky 1,3-biaryl-imidazolium chlorides instead of phosphines similar to that carried out by Wu et al. We heated the THF solution of 4′-halopropiophenone with 2 equiv. of NaO^{t}Bu and 10 mol% of palladium acetate and (1,3-R$_2$)imidazolium chloride (**1a**: R = 2,4,6-trimethylphenyl, **1b**: R = 2,6-diisopropylphenyl) at 70 °C for 24 h. The air-stable imidazolium chlorides are enable to be added to the reaction mixture as the carbene ligand precursors, as usual catalytic reactions employing NHC ligands in the presence of base. The dark-red solution of the reaction mixture became turbid in a moment. After quenching with an excess amount of methanol, a brown solid with some amount of palladium black, which prevented further purification, was yielded. Changing the amount of the palladium precatalysts and the ligand precursors to 3 mol% successfully resulted in giving a pale yellow powder after reprecipitation in methanol, which is characterized in detail by means of the spectroscopy written below. This is in contrast to that the palladium–phosphine catalyst system required 10 mol% of palladium species reported by Wu et al. [6]. As shown in Table 1, especially in entries 4 and 7, the polycondensation of 4′-bromopropiophenone medi-

ated by palladium compounds, Pd(OAc)$_2$ and Pd$_2$(dba)$_3$, in the presence of 1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride (**1b**) afforded the polymer in high yields, respectively, whereas employing 1,3-bis(2,4,6-trimethylphenyl)-imidazolium chloride (**1a**) provided the polymer in low yields (entries 1 and 3). And the yields did not increase when the reactions were carried out for more than 24 h. The number-averaged molecular weight of the polymer was 4000–6000 which was rather small than that produced by the palladium–phosphine catalyst system (M_n: ~10 000) [6]. The polydispersity was in the range of the usual polycondensation system, 1.2–2.0 [14]. Another monomer, a chloro-analog which was not used in the early reports [6], also polymerized under the same conditions as those of the bromo-analog to yield a polymer with rather smaller molecular weight. PdCl$_2$ did not catalyze efficient polymerization of 4′-bromopropiophenone (entries 2 and 6). Although Buchwald demonstrated in an early report that Pd(OAc)$_2$ could also catalyze α-arylation of limited number of substrates in the absence of the ligands [2b], the yield and molecular weight of the polycondensation product was low (47% yield, $M_n = 2600$, $M_w/M_n = 1.66$) when polymerization was carried out without the imidazolium chlorides. Nolan et al. reported that a palladium complex bound to a bulky 4,5-*dihydro*imidazolium carbene showed the highest catalytic activity of α-arylation among those bearing the carbenes [8]. However, there was no difference in the yields and molecular weights between polymerizations using **1b** and **2b** as ligand precursors.

3.2. Polycondensation of 4′-halopropiophenone catalyzed by Pd–NHC catalyst

Of furthermore interest is that the addition of 2 equiv. of **1a** or **1b** to the palladium precursor deactivated the catalytic system, as shown in Table 2. For instance, polycondensation with 1 equiv. of **1a** to Pd(OAc)$_2$ took place giving a polymer, whereas that with 2 equiv. of **1a** did not proceed (Table 2, entries 1–2). Using 2 equiv. of **1b** also made the yield lower (Table 2, entry 4). When 2 equiv. of **1a** were employed, the ^{1}H NMR measurement of the crude mixture revealed that almost all of the monomer remained. This suggested that a deactivated palladium species might be generated in situ in the reactions of the palladium

Table 1
Polycondensation of 4′-halo-propiophenone Using N-heterocyclic ligands[a]

Entry	Pd species	Ligand precursor	X	Yield (%)	M_n[b]	M_w/M_n[b]
1	Pd(OAc)$_2$	**1a**	Br	28	2500	1.25
2	PdCl$_2$	**1a**	Br	0	–	–
3	Pd$_2$(dba)$_3$	**1a**	Br	20	2500	1.22
4	Pd(OAc)$_2$	**1b**	Br	95	4300	2.02
5	Pd(OAc)$_2$	**1b**	Cl	78	3000	1.90
6	PdCl$_2$	**1b**	Br	54	2600	2.07
7	Pd$_2$(dba)$_3$	**1b**	Br	82	4000	1.67

[a] Conditions; Pd catalysts (and ligand precursors): 3.0 mol%, [monomer] = 0.25 mol/L. At 70 °C, for 24 h.
[b] Calibration of SEC was carried out by polystyrene standard.

Table 2
Polycondensation of 4′-bromopropiophenone with Pd-catalysts[a]

Entry	Pd cat.	Ligand precursor	Cat./ligand	Yield (%)	M_n (SEC)[b]	M_w/M_n
1	Pd(OAc)$_2$	**1a**	1/1	28	2500	1.25
2	Pd(OAc)$_2$	**1a**	1/2	0	–	–
3	Pd(OAc)$_2$	**1b**	1/1	95	4300	2.02
4	Pd(OAc)$_2$	**1b**	1/2	71	3800	1.72
5	**3b**	–	–	89	4600	1.67
6	**4a**	–	–	0	–	–
7	**4b**	–	–	0	–	–

[a] Conditions; Pd catalysts (and ligand precursors): 3.0 mol%, [monomer] = 0.25 mol/L. At 70 °C, for 24 h.
[b] Calibration of SEC was carried out by polystyrene standard.

precursor with 2 equiv. of NHC ligands. To confirm this, we prepared palladium NHC complexes, [PdCl$_2$(NHC)$_2$] (**4a**: X = Cl, NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazolium-2-ylidene; **4b**: X = Cl, NHC = 1,3-bis(2,6-diisopropylphenyl)imidazolium-2-ylidene) [12], having two carbene ligands on a palladium. As expected, polymerization of 4′-bromopropiophenone did not proceed at all with **4a** or **4b** (entries **6** and **7**), in sharp contrast to the binary catalysts. These results indicated that an in situ-generated palladium compound having only one NHC ligand catalyzes the polycondensation. Then, we prepared a simple palladium compound bound to one NHC ligand, [Pd(OAc)$_2$(NHC)] (**3b**) as reported by Nolan et al. [9]. This complex **3b** was known to be easily accessed by the reaction of palladium acetate with 1 equiv. of the carbene ligand. Compound **3b** showed high activity for catalytic α-arylation of carbonyl compounds last year [10], and, in our case, **3b** (3 mol%) also acts as an efficient catalyst forming polymers in high yield with molecular weight ($M_n = 4500$) and polydispersity ($M_w/M_n = 1.6$) similar to those yielded by the binary catalysts (entry 5). While it took 24 h by using Pd(OAc)$_2$ and **1b** to complete the polymerization, the new catalyst **3b** reduced the reaction time to 10 h.

As shown above, the palladium complex **3b** successfully catalyzed the polycondensation of 4′-halopropiophenones. While it is not clear that the real active species from the binary catalyst was generated via the formation of **3b** in situ from palladium acetate and the carbene ligand in the THF solution [9], the active catalyst having only one NHC ligand is experimentally indubitable, as was pointed out in the earlier papers [3,4].

When the catalyst concentration loading into the reaction mixture was low, the yield of the polymer went down to 40–60% even after more than 24 h (Table 3, entries 2 and 4), however, a colorless polymer having similar molecular weight (4500–6000) and polydispersity (1.7–2.0) was obtainable [15]. These results suggested that, in the low monomer concentration at the end of the reaction, the catalysts might be deactivated via an unidentified pathway in the reaction medium. In addition, even at 30 °C, the polycondensation also occurred to afford polymers in moderate yield (Table 3, entry 7) [10].

Above result showed that molecular weight of the polymers never increase more than 6000 (M_n). This indicates that some termination process is involved in the polycondensation. To confirm this, we attempted the second polymerization of the isolated polymers from 4′-bromo- and 4′-chloro-propiophenones under the conditions using the binary catalyst in conjunction with Pd(OAc)$_2$ and the bulky imidazolium chloride. However, the molecular weight of the resulting polymers did not changed, suggesting that the terminal units in the polymers does not have halogens.

3.3. Polycondensation of other monomers catalyzed by Pd–NHC catalyst

The molecular weight of the obtained 4′-halopropiophenone polymer was as high as around 6000, which indicates that some termination process occurred in the polymerization system. We noticed dark red precipitation generated in the flask during the polymerization. This solid may be due to the polymer enolate which was formed by the reaction of

Table 3
Polycondensation results for changing catalyst concentration and reaction temperature

Entry	Pd species	Pd conc. (mol%)	Temp. (°C)	Yield (%)	M_n (SEC)[c]	M_w/M_n
1[a]	Pd(OAc)$_2$	3	70	95	4300	2.02
2[a]		0.3	70	41	4500	1.72
3	**3b**	3	70	89	4600	1.67
4		1	70	65	4100	1.56
5		3	60	90	4500	1.65
6		1	60	62	5300	1.63
7[b]		3	30	48	4200	1.42

[a] Conditions; Pd catalysts (and ligand precursors): 3.0 mol%, [monomer] = 0.25 mol/L. At 70 °C, for 24 h.
[b] Polymerization was carried out for 64 h.
[c] Calibration of SEC was carried out by polystyrene standard.

the polymer with a base. In fact, after filtration of the dark red precipitates without quenching, NMR analysis of the solid dissolved in CDCl$_3$ revealed that the polymer had precipitated in the reaction medium. We assumed that the precipitation may stop the polymer growth. So other monomers, such as 3′-bromopropiophenone and 4′-bromo- and 4′-chloro-valerophenone, were employed in order to obtain high-molecular-weight polymers. However, polymerization of 3′-bromopropiophenone was accompanied by precipitation of a yellow solid and afforded a similar molecular weight polymer ($M_n = 5000$, $M_w/M_n = 1.41$, 18% yield) to that of 4′-bromopropiophenone. And also, unfortunately, polymerization of 4′-bromo- and 4′-chloro-valerophenone gave similar results (4′-bromo analog: $M_n = 4500$, $M_w/M_n = 1.51$, 62% yield; 4′-chloro analog: $M_n = 4700$, $M_w/M_n = 1.35$, 30% yield), although no precipitation was observed in these polymerizations. The result suggested that another termination process exists in the **3b**-catalyzed polycondensation system.

3.4. Characterization of poly(4′-halopropiophenone)

The obtained poly(4′-bromopropiophenone) was characterized on the basis of SEC, NMR, IR, and MALDI-TOF MAS spectroscopy and melting-point measurement. The polymer was revealed to be thermally stable even when the polymer chain is rather short [6]. Upon slow heating of the polymer ($M_n = 6000$), which was purified after reprecipitation for several times from methanol, with the melting-point apparatus in a N$_2$ atmosphere, the white powder turned black at around 180 °C and melted at 205–218 °C. The color change of the polymer at high temperature was due to the oxidation of the palladium contam-

inants remaining in the polymer matrix. The carbon and hydrogen contents in the polymer ($M_n = 6000$) measured by means of the elemental analysis was 76.34% and 6.01%, respectively, which are not far from the theoretical ratios, 81.79% and 6.10%. The difference of the carbon content indicates existence of a palladium species per 10–20 monomer units.

The ^{1}H NMR spectrum of the polymer ($M_n = 4300$) showed four large signals assigned as hydrogens in the main chain; the signals due to the methyne and methyl groups appeared at δ 4.64 and 1.44, respectively, and due to the phenylene group at δ 7.27 and 7.81. The disappearance of the methylene signal of the monomer at δ 3.00 and appearance of the methyne resonance of the polymer with the lower chemical shift at δ 4.64 clearly revealed that α-arylation of the monomer occurred efficiently. The ^{13}C NMR measurement of the polymer also exhibited that the signals due to both the methyne and methylene moieties appeared at δ 19.6 and 47.4, respectively. And also the resonances due to four phenylene carbons and one carbonyl carbon were observed at δ 128.3, 129.6, 135.0, 146.7, and 198.9, respectively. These NMR results were in good agreement with those reported by Wu et al. [6]. In addition, notably, the resonance due to the chiral methyne carbon, C^3 in Fig. 1 at δ 47.7 was divided into three peaks (maybe three diads, mm + mr + rr), which shows stereosequence distribution in the polymer. Similarly, the resonances assigned as the *ipso*-phenylene carbon, C^1 in Fig. 1, adjacent to the carbonyl carbon and the carbonyl carbon, C^2 in Fig. 1, were observed as three independent peaks.

On the other hand, small peaks due to terminal propiophenone group were assigned in this ^{1}H NMR spectrum. These resonances were confirmed by isolation and ^{1}H
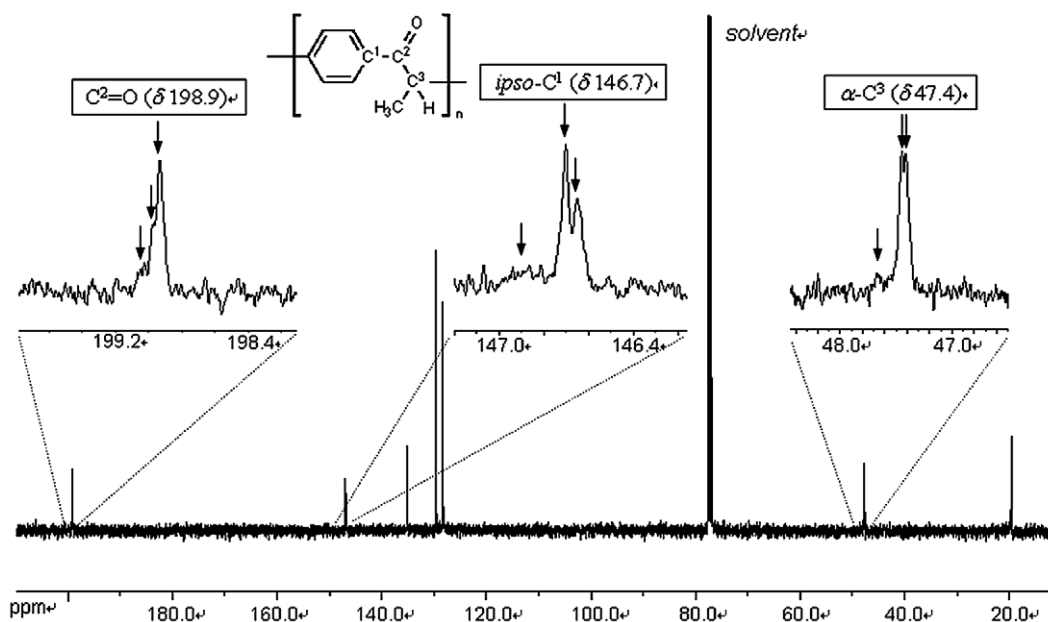

Fig. 1. ^{13}C NMR spectrum for poly(4′-bromopropiophenone) and signal-assignments of three carbons (*ipso*-carbon (C^1) adjacent to the carbonyl, carbonyl carbon (C^2), and α-carbon (C^3)) in the main chain divided into three peaks.
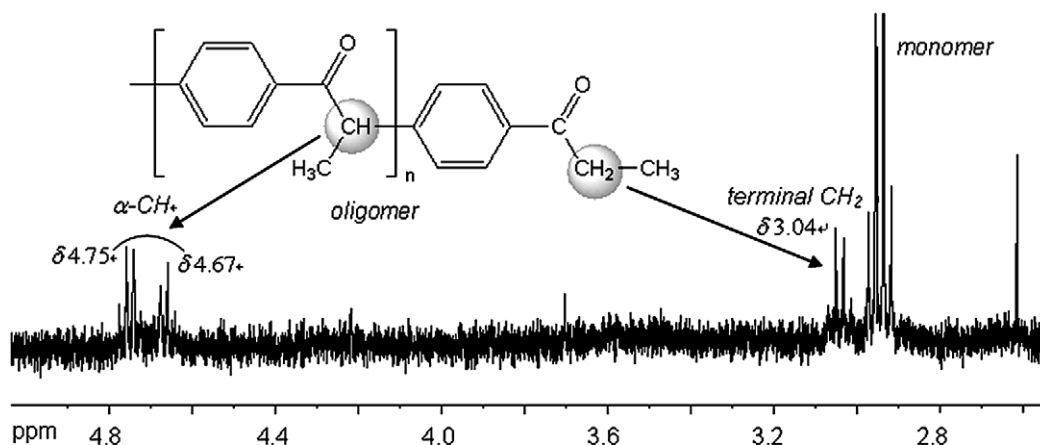
Fig. 2. Partial ^{1}H NMR spectrum chart for the 4'-bromopropiophenone oligomer.
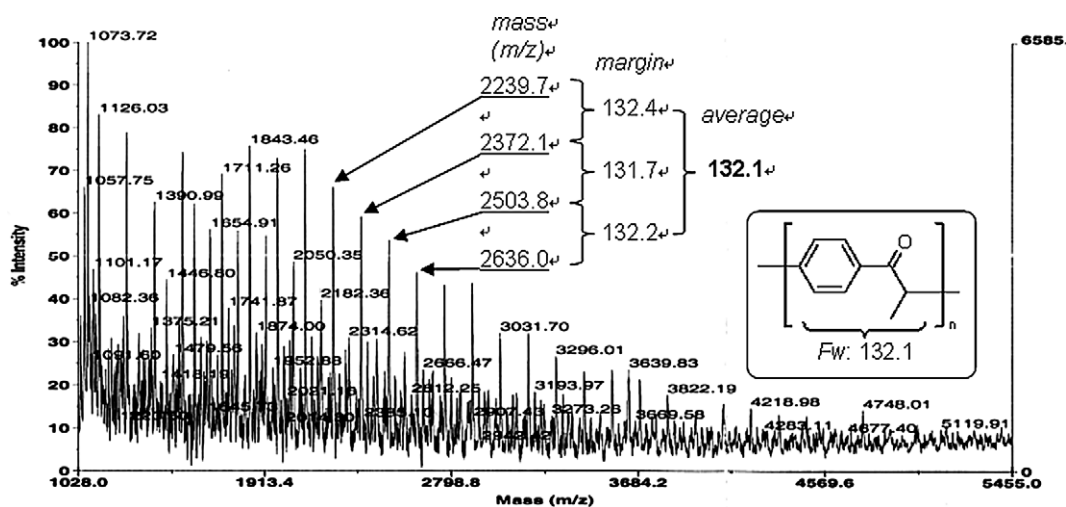

Fig. 3. MALDI TOF-MS spectrum for poly(4'-bromopropiophenone).

NMR measurement of the 4'-bromopropiophenone oligomer (Fig. 2). The resonance due to the terminal methylene proton was observed at δ 3.04 which is independent of that due to the monomer at δ 2.94. Another resonance due to the α-methyne proton of the oligomer was appeared at δ 4.67 and 4.75 similar to that in the polymer main chain (δ 4.64). Two signals observed and assigned as the same proton is maybe due to the differences of substituents at the para-positions of arylketone groups.

From the integral intensity ratio between the signals due to the terminal methylene group at δ 3.04 (2H) and the methyne group at δ 4.64 (1H) in the polymer main chain, the number-averaged polymer weight was around 2300, which was similar to that observed by MALDI-TOF MS spectroscopy [16]. As shown in Fig. 3, average mass values of margins between several sequential independent peaks, for example, 2239.7, 2372.1, 2503.8, and 2636.0, were in good agreement with a molecular weight of each monomer unit in the main chain (mass: 132.1 (m/z)). Thus, the MS measurement of the polymer demonstrated one set of large repeating peaks and some small sets showing every mass as

only 132.1. It is of interest and strongly indicative that the second arylation at the α-position in the polymer main chain did not take place. As results of the chain-end analysis on the basis of NMR and MS spectroscopy, the existence of propiophenone moiety at the chain-ends indicates some termination processes other than β-elimination of palladium enolate may be involved in the polycondensation reaction [8].

4. Conclusion

We successfully carried out polycondensation of haroarylketones catalyzed by palladium compounds using N-heterocyclic carbenes as ligands. And furthermore, the amount of the palladium catalyst could be lower than that using phosphines as ligands [6]. Although the weight of the obtained polymer was not so high, due to the characterization of the terminal structure, it was found that the bulky and donating NHC ligand could successfully prevent chain transfer reactions such as β-elimination, to some extent. As Hartwig and Buchwald suggested [3,4], it was clearly

confirmed, by employing primarily prepared palladium catalysts having NHC ligands, that coordination of only one NHC ligand to the palladium center was essential to catalyze the coupling reaction. We are now carrying out an investigation of the polymerization of other monomers which yield polymers with larger molecular weight and solubility, and applications of the polymer.

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[15] Higher catalyst concentration (5–10 mol%) lowered the molecular weight of the polymer. As a preliminary experimental result, this indicates that termination tends to be induced at high catalyst or polymer concentration, or that chain-growth polycondensation occurs under this condition; for chain-growth polycondensation, see for example, T. Yokozawa, A. Yokoyama, Chem. Record 5 (2005) 57–67, and references cited therein.

[16] This 'number-averaged molecular weight' obtained by means of the MAS and ^{1}H NMR spectra was about 0.6 times lower than that from the SEC analysis. Thus, this information shows that the polymer has about 20–30 averaged monomer units.