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Articles

Successful Synthesis of Wholly Aromatic Polyketones via Nickel-Mediated Aromatic Coupling Polymerization

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ABSTRACT: Novel aromatic polyketones (**8a**, **8b**) without ether linkage in the main chain were successfully synthesized via nickel-mediated aromatic coupling polymerization of bis(chlorobenzoyl)-dimethoxybiphenyls (**3a**, **3b**). The polymers affording flexible films were obtained in the reaction where an excess amount of bipyridyl and a stoichiometric amount of the nickel(II) bromide were present. The resulting polyketones (**8a**, **8b**) have sufficiently high molecular weight (inherent viscosity: 0.59 dL/g for polyketone **8a**; 0.35 dL/g for polyketone **8b**) and a highly amorphous nature with a rather high glass transition temperature: 218 °C for polyketone **8a**; 192 °C for polyketone **8b**.

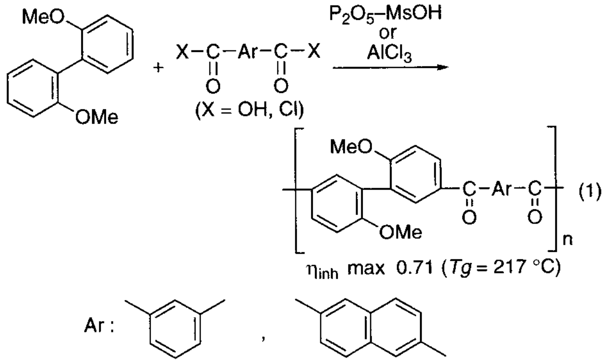
Introduction

A major advantage of aromatic polyketones over other condensation polymers is that high-performance chemical and physical properties are achieved for the polymer skeleton consisting of only hydrogen, carbon, and oxygen atoms.[1] However, most aromatic polyketones are aromatic poly(ether ketone)s which contain an ether bond in their main chain.[2] Accordingly, a large part of the properties of aromatic poly(ether ketone)s is considered to depend on the nature of poly(arylene ether)s. On the basis of these considerations, wholly aromatic polyketones, which have no ether bond in their main chain, have been reasonably distinguished from aromatic poly(ether ketone)s.[3]

While some syntheses of wholly aromatic polyketones by a palladium-catalyzed coupling reaction have been reported,[4] high-molecular-weight polymers have not been obtained yet.

Except for the above syntheses, few examples of wholly aromatic polyketones have been reported. The paucity of reports on wholly aromatic polyketones has been presumably due to the difficulty in their synthesis. One reason is suspected to be its rigid skeleton caused by an aromatic ring moiety and a carbonyl moiety aligned on the same plane, which accelerates aggregation of oligomers and lowers their solubility, resulting in suppression of the molecular weight.

In our previous paper we reported the synthesis of wholly aromatic polyketones by electrophilic aromatic substitution (eq 1).[3] These polymers have a highly amorphous nature and high glass transition temperatures compared to PEEK. The reason is that a 2,2′-dimethoxybiphenylene unit is superior in respect to its acyl-accepting and -distorting abilities, which suppress the aggregation of the resulting polymer and maintain its solubility during polymerization.



On the other hand, transition-metal-catalyzed homocoupling polymerization has been utilized for the synthesis of polyphenylenes and polyacetylenes.[5] However, this reaction has not been utilized for the synthesis of wholly aromatic polyketones. In this paper, we wish to report the first successful synthesis of wholly aromatic polyketones employing nickel-promoted aromatic coupling. In addition, we also describe the results of a model reaction on nickel-promoted aromatic coupling of *p*-chlorobenzophenone.

Results and Discussion

Monomer Synthesis. As described above, we have already reported 2,2′-dimethoxybiphenyl (**2**) is an effective acyl-acceptant monomer for the electrophilic aromatic substitution synthesis of wholly aromatic polyketones. To utilize the structural preference of this biphenyl

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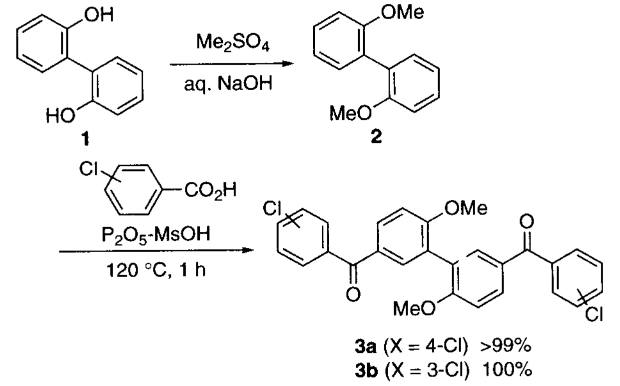
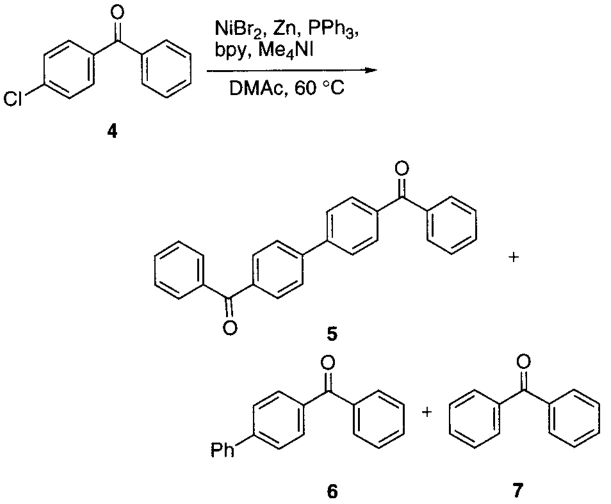
Scheme 1. Synthesis of Monomers 3a and 3b



monomer, we designed the following two monomers which have a 2,2′-dimethoxybiphenylene part and two chlorobenzoyl groups. Each monomer was prepared by introducing two chlorobenzoyl groups onto the nucleus of 2,2′-dimethoxybiphenyl (**2**). Acylation onto 2,2′-dimethoxybiphenyl (**2**) was carried out with P_2O_5–MsOH[6] as a direct condensing reagent to give the corresponding monomer (**3a**) quantitatively. This reaction proceeded at the para position to the methoxy group selectively. According to this method, *m*-chloro-substituted monomer **3b** was prepared quantitatively from 2,2′-dimethoxybiphenyl (**2**).



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Model Reaction: Nickel-Promoted Aromatic Coupling of *p*-Chlorobenzophenone. We first examined polymerization of monomer **3a** using a nickel-catalyzed homocoupling reaction. We referred to Ueda's method,[5a,b] which was proved to be useful for the synthesis of poly(phenylene)s containing a carbonyl part in the side chain and poly(ether ketone)s. When monomer **3a** was treated with 5 mol % of $NiBr_2$, 3 equiv of zinc powder, 10 mol % of PPh_3, 5 mol % of 2,2′-bipyridyl (bpy), and 1.4 equiv of Me_4NI in DMAc at 90 °C for 3 h, polymerization proceeded to some extent. However, the inherent viscosity of the obtained polymer was only 0.12 dL/g (in concentrated H_2SO_4, 30 °C). The failure to obtain a high-molecular-weight polymer was presumed to be attributed to the slow reaction rate, which allowed a side reaction to proceed over the polymerization.

Then we reexamined nickel-mediated aromatic coupling of the model compound. In this aromatic coupling reaction, besides the desired homocoupling reaction, side reactions are suspected to proceed to give another coupling product between aryl halide and a phenyl group transferred from PPh_3[5b,7] and a protonated product by water contaminated in the solvent. In our model study, we specified the factors to accelerate the reaction rate of the self-coupling and restrain the production of phenyl-migrated or protonated products. We examined the reaction of *p*-chlorobenzophenone (**4**). The results are shown in Table 1.

Table 1. Coupling Reaction of *p*-Chlorobenzophenone (4)[a]

run	bpy[b]	Me_4NI[b]	$NiBr_2$/**4** (mol %)	method[c]	product ratio (%)[d] **4**	**5**	**6**	**7**
1	○	×	50	A	0	95	2	3
2	×	×	50	A	48	50	2	0
3	○	○	50	A	1	96	1	2
4[e]	○	×	5	B	74	4	0	22
5	○	×	50	B	59	41	0	0
6	○	○	50	C	30	55	2	13

[a] Reaction conditions: *p*-chlorobenzophenone (**4**), 5 mmol; $NiBr_2$, 2.5 mmol; Zn, 3.75 mmol; PPh_3, 2.5 mmol; 2,2′-bipyridyl (bpy), 2.5 mmol; Me_4NI, 2.5 mmol; DMAc, 10 mL. [b] Key: ○, added; ×, not added. [c] Method A: The reaction was carried out at room temperature for 30 min and then the reaction mixture was warmed to 60 °C. Method B: The reagents except *p*-chlorobenzophenone (**4**) were stirred previously for 30 min and *p*-chlorobenzophenone (**4**) was added and stirred at 60 °C. Method C: All reagents were dissolved in the solvent at the same time in a reaction vessel heated at 60 °C. [d] Determined by HPLC (column, Merck Lichro CART 125–4, Supersphere $100NH_2$; eluent = benzene/hexane = 3/1(v/v); 1 mL/min; UV 285 nm). [e] In run 4, the amounts of $NiBr_2$, PPh_3, bpy, and Me_4NI were reduced to 5 mmol %.

At first, we carried out this reaction using a quantitative amount of nickel(II) bromide. When 1 equiv of bpy was added as an extra ligand in addition to PPh_3, the ratio of coupling product **5** jumped up to 95% (runs 1 and 2). At the same time, the production of protonated product **7** was also increased. However, it is obvious that addition of bpy is essential for this coupling reaction.

Next, we examined the effect on the addition of Me_4NI.[8] As shown in run 3, it was found that the addition of Me_4NI was not so effective. When the amount of nickel(II) bromide was reduced to 5 mol %, the major product obtained was protonated product **7**, and coupling product **5** was obtained only in 4% yield (run 4). This means that in the catalytic system protonation occurs preferentially over the desired coupling reaction.

As shown in Table 1, the optimum procedure for this coupling reaction treatment was that all reagents (the substrate, nickel(II) bromide, zinc powder, PPh_3, and bpy) were added to DMAc at the same time and stirred for 30 min at room temperature and warmed to 60 °C (method A).

These results suggested that the amount of nickel(II) bromide significantly affects the product distribution. Then we examined the effect of the amount of nickel(II) bromide in detail. The results are shown in Figures 1 and 2. Figure 1 shows the effect of the amount of nickel catalyst on the ratios of byproducts **6** (☐ in Figure 1) and **7** (● in Figure 1). The divisions are shown at the right or left vertical axis. Figure 2 shows the correlation between the amount of nickel catalyst and the conversion to desired coupling product **5**. These results imply that the optimum amount of the catalyst

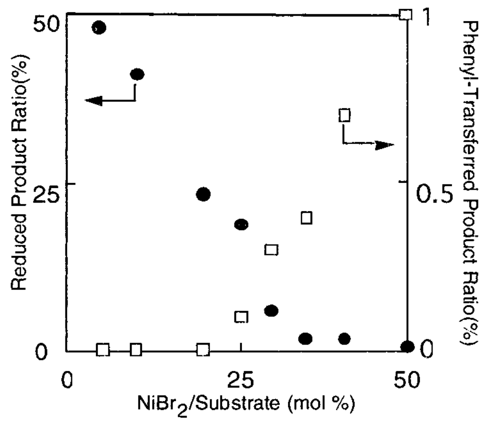


Figure 1. Catalytic amount vs by-product ratio (%) plot. *p*-Chlorobenzophenone (**4**): 1.0 mmol. $NiBr_2$:PPh_3:bpy = 1:1:1. DMAc, 60 °C, 5.5 h.

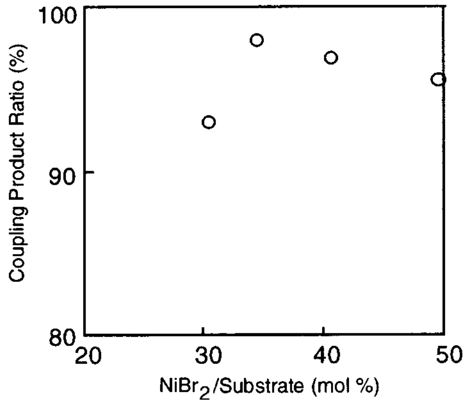


Figure 2. Catalytic amount vs coupling product ratio (%) plot. *p*-Chlorobenzophenone (**4**): 1.0 mmol. $NiBr_2$:PPh_3:bpy = 1:1:1. DMAc, 60 °C, 5.5 h.

is ca. 35 mol % of nickel(II) bromide based on the aryl halide.

In this way, we found the optimum conditions to achieve nickel-mediated aromatic coupling of *p*-chlorobenzophenone in high yield.

Polymerization of Monomer 3a. According to the results of the model reaction, we examined polymerization of monomer **3a**. The level of polymerization was estimated by the yield, inherent viscosity, ability to form films (cast from CH_2Cl_2 solution), and IR measurement. The extent of consumption of the monomer was estimated with the disappearance of a peak at 1094 cm^{-1} in the IR spectra, which is characteristic of an Ar−Cl structure, such as para-substituted monomer **3a**. First, monomer **3a** was treated with 70 mol % of nickel(II) bromide, 1.5 equiv of zinc powder, 1.0 equiv of PPh_3, 1.0 equiv of bpy, and 1.0 equiv of Me_4NI in DMAc at 60 °C for 1 or 20 h (runs 1 and 2). However, the inherent viscosities of the obtained polymers were 0.19 and 0.21 dL/g.

Then the reactions where the amount of $NiBr_2$ was increased to 100 mol % were undertaken. The product obtained in polymerization for 3 h at 60 °C was insoluble even in concentrated H_2SO_4 (run 3). Though the reactions at other reaction temperatures (room temperature, 40 °C, and 50 °C) were examined, the products were insoluble in concentrated H_2SO_4 (runs 4−6). This problem of production of insoluble materials was solved by reducing reaction time to 1 h (runs 10−13). The highest inherent viscosity of 0.59 dL/g was achieved in the reaction at 50 °C. These polymers afforded transparent and flexible cast films (runs 11−13). When the reaction was undertaken at 70 °C or higher, the viscosity of the obtained polymer was apparently reduced. It was found that the optimum temperature in this polymerization was ca. 50 °C.

Table 2. Nickel-Mediated Aromatic Coupling Polymerization of Monomer 3a[a]

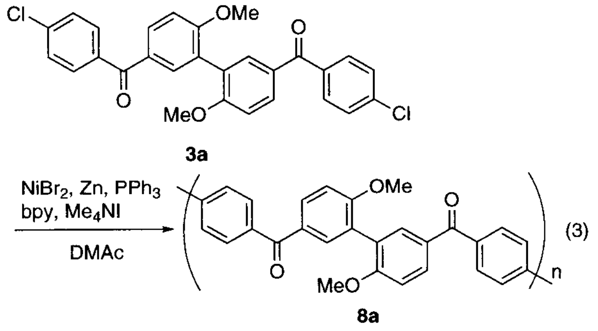
run	temp (°C)	time (h)	yield (%)	inherent viscosity (dL/g)[b]
1[c]	60	1	98	0.21
2[c]	60	20	91	0.19
3	60	3	97	insoluble
4	rt	3	97	insoluble
5	40	3	99	insoluble
6	50	3	96	insoluble
7	70	3	97	0.42
8	80	3	95	0.43
9	90	3	99	0.34
10	rt	1	84	0.19
11	40	1	>99	0.53
12	50	1	97	0.59
13	60	1	96	0.56

[a] Reaction conditions: monomer **3a**, 0.70 mmol; $NiBr_2$, 0.70 mmol; Zn, 1.5 mmol; PPh_3, 1.0 mmol; 2,2′-bipyridyl (bpy), 1.0 mmol; Me_4NI, 1.0 mmol; DMAc, 2 mL. [b] Inherent viscosity measurements were carried out in concentrated H_2SO_4 (0.3 g/dL) at 30 °C. [c] Monomer **3a**, 1.0 mmol; $NiBr_2$, 0.70 mmol; Zn, 1.5 mmol; PPh_3, 1.0 mmol; 2,2′-bipyridyl (bpy), 1.0 mmol; Me_4NI, 1.0 mmol; DMAc, 2 mL.

Table 3. Effect of Solvents at 50 °C

run	solvent	yield (%)	inherent viscosity (dL/g)[b]
1	DMAc	quant.	0.59
2	NMP	quant.	insoluble
3	HMPA	12	
4	THF	0	

[a] Reaction conditions: time, 1 h; monomer **3a**, 0.70 mmol; $NiBr_2$, 0.70 mmol; Zn, 1.5 mmol; PPh_3, 1.0 mmol; 2,2′-bipyridyl (bpy), 1.0 mmol; Me_4NI, 1.0 mmol; solvent, 2 mL. [b] Inherent viscosity measurements were carried out in concentrated H_2SO_4 (0.3 g/dL) at 30 °C.



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Next, we examined the reaction in several solvents for 1 h at 50 °C. The results are shown in Table 3. When THF or HMPA was used as the solvent, a large part of the crude product was soluble in acetone, and it was ascertained by IR measurement that most of the monomer was recovered. This is due to the low solubility of $NiBr_2$ in THF. When NMP was used for this reaction, the product was insoluble even in concentrated H_2SO_4. Accordingly, we considered DMAc to be the solvent of choice for this polymerization.

Polymerization of Monomer 3b. We examined the polymerization of *m*-chloro-substituted monomer **3b** under the optimum conditions in the polymerization of monomer **3a**. The representative results are sum-

Table 4. Nickel-Mediated Aromatic Coupling Polymerization of Monomer 3b

run	temp (°C)	time (h)	yield (%)	inherent viscosity (dL/g)[b]
1	rt	24	76	0.13
2	50	1	97	0.26
3[c]	50	3	97	0.35
4	50	24	96	0.31
5	50	1	90	0.19

[a] Reaction conditions: monomer **3b**, 0.70 mmol; $NiBr_2$, 0.70 mmol; Zn, 1.5 mmol; PPh_3, 1.0 mmol; 2,2′-bipyridyl (bpy), 1.0 mmol; Me_4NI, 1.0 mmol; DMAc, 2 mL. [b] Inherent viscosity measurements were carried out in concentrated H_2SO_4 (0.3 g/dL) at 30 °C. [c] T_g by DSC measurement was 192 °C.

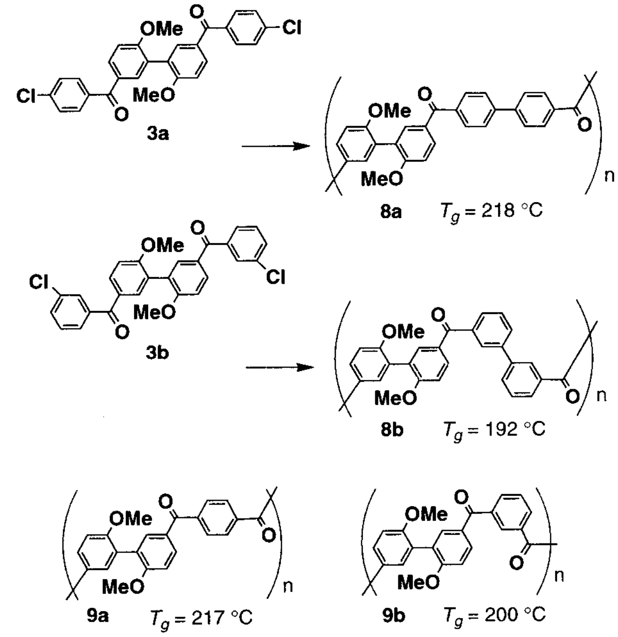
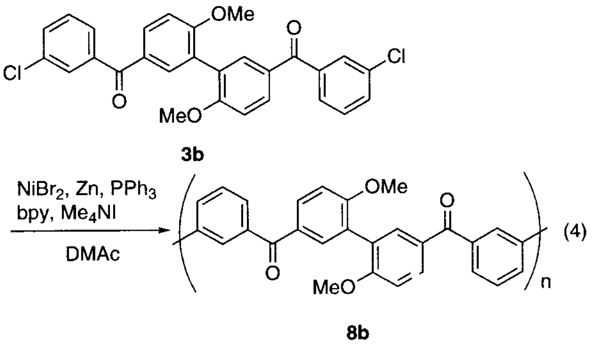


Figure 3. Wholly aromatic polyketones and their T_g’s.

marized in Table 4. As shown in Table 4, the polymerizability of *m*-chloro-substituted monomer **3b** was rather poor compared to that of *p*-chloro-substituted monomer **3a**.



(4)

It is considered that the success in the aromatic coupling synthesis of novel, wholly aromatic polyketones **8a** and **8b** is ascribed to the distorting ability of the 2,2′-dimethoxybiphenylene unit partially at least. This unit and the newly formed 4,4′-biphenylene moiety are presumed to constitute a rather extended but somewhat twisted conformation in the intermediating oligomers. Such configuration is considered to sufficiently retard regular coagulation and precipitation of the molecules maintaining the macromolecular intermediate in solution for the formation of a high-molecular-weight polymer skeleton. This structural advantage is anticipated to be a key factor for achievement of wholly aromatic polyketones, without a flexibilizing effect by an ether linkage such as poly(ether ketone)s.

The T_g of Wholly Aromatic Polyketones. Both polymers **8a** and **8b** have a highly amorphous nature. The glass transition temperatures (T_g’s) of these polymers were compared with those of the related wholly aromatic polyketones **9a** and **9b** obtained by electrophilic aromatic substitution reaction (Figure 3).[3] The amorphism and high T_g's of these four wholly aromatic polyketones are also interpreted in terms of the steric effects of the 2,2′-dimethoxybiphenylene moiety.

The T_g of polyketone **8a** was almost the same as that of the related polyketone **9a**, and the T_g of polyketone **8b** was lower than that of polyketone **9b**. These differences were considered to be in accord with the extent of the rodlike part of the polymer skeleton. The unsubstituted *p,p*-biphenylene moiety is considered to play substantially the same role with the *p*-phenylene moiety as a rigid rod part. Thus, the T_g’s of polymers **8a** and **9a** are essentially the same. The *m*-phenylene moiety is suspected to make the polymer structure less rigid. The T_g’s of para-substituted polymers **8a** and **9a** are higher than those of the corresponding meta-substituted polymers **8b** and **9b**, respectively. Further, the unsubstituted *m,m*-biphenylene moiety is anticipated to distort the polymer alignment such as to result in reduction in the T_g of polymer **8b** more than that of polymer **9b**.[9]

Conclusion

The nickel-mediated aromatic coupling synthesis of wholly aromatic polyketones has been achieved. The resulting polyketones have high T_g’s. In addition, the difference in T_g’s between the obtained wholly aromatic polyketones was determined from the viewpoint of the structural contribution of the repeating unit in the polymers.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-A500 (^1H; 500 MHz, ^{13}C; 125 MHz) spectrometer or a Varian Gemini-200FT spectrometer (^1H; 200 MHz, ^{13}C; 50 MHz) using Me_4Si (^1H, δ 0.00) and $CDCl_3$ (^{13}C, δ 77.0) as internal standards. IR spectra were recorded on a JEOL FTIR-5300 spectrometer. T_g’s were determined by DSC curves of polymers prepared by gradual cooling from 350 °C. DSC curves were recorded on a SEIKO DSC 200 with heating rate of 10 °C/min under nitrogen. Inherent viscosities were determined by measuring the flow time of solutions of polymer samples in concentrated H_2SO_4 (0.3 g/dL) at 30 °C using an Ostwald visometer. HPLC analysis was performed on Merck Lichro CART 125−4, Supersphere 100 NH_2 by UV detection (λ: 285 nm) using a 3/1 mixture (v/v) of benzene/hexane at a flow rate of 1 mL/min.

Materials. $NiBr_2$ was dried at 220 °C in vacuo. Zn (400 mesh) was purified by stirring with acetic acid, filtering, washing thoroughly with ethyl ether, and drying under vacuum. PPh_3 and bipyridyl (bpy) were recrystallized from hexane. Me_4NI was recrystallized from water and dried at 180 °C under vacuum. *N,N*-dimethylacetamide (DMAc) was stirred over powdered calcium hydride for 3 h, distilled under reduced pressure, and stored over Molecular Sieves 4A. P_2O_5-MsOH was prepared according to the reported procedure.[10]

2,2′-Dimethoxybiphenyl (2). 2,2′-Dihydroxybiphenyl (**1**, 25 g, 0.13 mol) was dissolved in 0.8 M aqueous NaOH (330 mL). Into this solution was dropped dimethyl sulfate (53 g, 0.42 mol) over 30 min. The reaction mixture was filtered, and the obtained white solid was dissolved in 430 mL of benzene.

To this benzene solution was added 1 M aqueous NaOH, and the crude product was filtered, dissolved in benzene, washed with 1 M aqueous NaOH, and dried over $MgSO_4$. Recrystallization from acetone gave colorless prisms: yield 82%; mp 152−153.5 °C (lit. mp 154−155 °C).[8]

5,5′-Bis(4-chlorobenzoyl)-2,2′-dimethoxybiphenyl (3a). 2,2′-Dimethoxybiphenyl (**2**) (2.1 g, 40 mmol) and *p*-chlorobenzoic acid (80 mL) were stirred in P_2O_5−MsOH (80 mL) at 120 °C for 1 h. The reaction mixture was cooled, poured into water, and neutralized with 1 M aqueous NaOH. The product was filtered, dissolved in chloroform, washed with aqueous NaOH, aqueous NH_4Cl, and brine followed by drying over $MgSO_4$. Recrystallization from acetone gave yellowish prisms: yield 99%; mp 164−166 °C. IR (KBr) 1649, 1094 cm^{-1}. ^1H NMR δ ($CDCl_3$): 3.88 (6H, s), 7.05 (2H, d, $J = 8$ Hz), 7.45 (4H, d, $J = 8$ Hz), 7.75 (4H, d, $J = 8$ Hz), 7.76 (2H, d, $J = 3$ Hz), 7.86 (2H, dd, $J = 3, 8$ Hz). ^{13}C NMR δ ($CDCl_3$): 55.9, 110.5, 126.3, 128.5, 129.4, 131.2, 132.1, 134.0, 136.4, 138.3, 194.1. Anal. Calcd for $C_{28}H_{20}Cl_2O_4$: C, 68.44; H, 4.10. Found: C, 68.40; H, 4.20.

5,5′-Bis(3-chlorobenzoyl)-2,2′-dimethoxybiphenyl (3b). In the same manner as biphenyl **3a** described above, biphenyl **3b** was prepared from 2,2′-dimethoxybiphenyl and *m*-chlorobenzoic acid at 100 °C. Recrystallization from acetone yielded white powders: yield 100%; mp 115.5−117 °C. IR (KBr) 1647, 1078 cm^{-1}. ^1H NMR δ ($CDCl_3$): 3.90 (6H, s), 7.08 (2H, d, $J = 8$ Hz), 7.42 (2H, t, $J = 8$ Hz), 7.54 (2H, dq, $J = 2, 8$ Hz), 7.68 (2H, dt, $J = 2, 8$ Hz), 7.78 (2H, s), 7.79 (2H, s), 7.89 (2H, dd, $J = 2, 8$ Hz). ^{13}C NMR δ ($CDCl_3$): 57.8, 112.6, 128.1, 130.0, 131.1, 131.8, 133.9, 134.2, 136.3, 136.4, 142.0, 163.0, 196.2. Anal. Calcd for $C_{28}H_{20}Cl_2O_4$: C, 68.44; H, 4.10. Found: C, 68.39; H, 4.20.

Polymer 8 from 3. In a 30 mL two-necked flask were placed $NiBr_2$ (0.7 mmol), PPh_3 (1 mmol), bipyridyl (1 mmol), Me_4NI (1 mmol), Zn (1.5 mmol), and monomer **3** (0.7 mmol). The flask was evacuated and filled with N_2 three times. Then, dry DMAc (2.0 mL) was added via a syringe through the serum cap. The mixture became dark brown within 20 min. The mixture was stirred at room temperature for another 10 min, and then the temperature was raised to 50 °C followed by stirring for the prescribed time. The resulting black viscous mixture was diluted with DMAc and poured into HCl/MeOH (v/v = 1/9, 30 mL). The precipitates were collected, washed with acetone by centrifugation, filtered, and dried in vacuo at 80 °C overnight. Polymer **8a**. IR (film): 1651, 1258 cm^{-1}. Anal. Calcd for $(C_{28}H_{20}O_4)_n$: C, 80.00; H, 4.79. Found: C, 79.82; H, 4.92. Polymer **8b**. IR (film): 1651, 1258 cm^{-1}. Anal. Calcd for $(C_{28}H_{20}O_4)_n$: C, 80.00; H, 4.79. Found: C, 79.87; H, 5.05.

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(9) One of the reviewers asked about the relation between T_g and η_{inh}. Our opinion is that there is no relation between T_g and η_{inh}. The difference in T_g's is supposed to be derived from the polymer structures. The η_{inh} of four polymers measured in concentrated H_2SO_4 (0.3 g/dL) at 30 °C are as follows: polymer **8a**, 0.59; polymer **8b**, 0.35; polymer **8c**, 0.71; polymer **8d**, 0.24.

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