

# Synthesis of Poly(aryl ether) by Pd-Catalyzed Polycondensation

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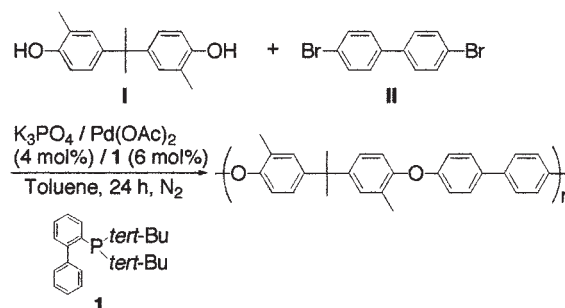
High molecular weight poly(aryl ether)s were successfully prepared by the Pd-catalyzed polycondensation of 2,2-bis(4-hydroxy-3-methylphenyl)propane (**I**) with 4,4'-dibromobiphenyl (**II**). The polycondensation proceeded in toluene in the presence of 4 mol% Pd(OAc)<sub>2</sub>, 6 mol% 2-(di-*tert*-butylphosphino)biphenyl, and 6 equiv K<sub>3</sub>PO<sub>4</sub> at 90 °C for 24 h, giving the polymer with a number-average molecular weight (*M<sub>n</sub>*) of 18000. The resulting polymers were fully characterized by IR and NMR spectroscopies.

Poly(aryl ether)s are a class of macromolecules known as engineering thermoplastics.<sup>1</sup> They are of commercial importance and have been studied extensively in both academic and industrial laboratories.<sup>2–15</sup> Nucleophilic aromatic substitution reactions are one of the way for the preparation of poly(aryl ether)s.<sup>4</sup> With wide array of bisphenols, activated bisaryl halides containing a variety of functional groups such as sulfone, sulfoxide, ketone, azo, oxadiazole,<sup>4</sup> imine,<sup>13</sup> azine,<sup>14</sup> fused heterocycles,<sup>15</sup> and perfluoroalkyls are required to synthesize high molecular weight poly(aryl ether)s. However, this was limited for the use of electron deficient aryl halides. Of the methods used for the preparation of diaryl ethers, the classical Ullmann ether synthesis is the most important, but it is often limited by the need to employ harsh reaction conditions and stoichiometric amounts of copper.<sup>16</sup> In fact, this was applied to the synthesis of poly(phenylene ether)s and poly(phenylene sulfide)s, the inherent viscosities of resulting polymers, were quite low (about 0.1).<sup>17</sup> The Pd-catalyzed polycondensations are utilized for the preparation of conducting polymers like poly(thiophene)s,<sup>18</sup> poly(aryl ethynylene)s,<sup>19</sup> and poly(phenylene)s.<sup>20</sup> Buchwald et al. recently reported the successful synthesis of diaryl ethers from phenols and electron rich aryl halides as well as electron deficient ones by use of Pd with sterically bulky aryl dialkylphosphines as ligands.<sup>21</sup> This might be expected to constitute an another promising synthetic route for poly(aryl ether)s. The Pd-catalyzed coupling was extended to the polymerization with bifunctional monomers.

In this paper, we describe the successful synthesis of poly(aryl ether) by the Pd-catalyzed polycondensation of a bisphenol with a non-activated bisaryl halide in toluene.

In the diaryl ether synthesis reported by Buchwald et al., the use of ortho alkyl substituted phenols improved the yield of the reaction. Thus, 2,2-bis(4-hydroxy-3-methylphenyl)propane (**I**) was selected as a bisphenol. The polymerization of **I** with 4,4'-dibromobiphenyl (**II**) was carried out in toluene in the presence of 4 mol% Pd(OAc)<sub>2</sub> and 6 mol% 2-(di-*tert*-butylphosphino)biphenyl (**1**) under nitrogen (Scheme 1 and Table 1). All resulting polymers were isolated by pouring the heterogeneous solution into excess amounts of methanol, followed by dissolving in hot toluene, and reprecipitating with hexane. First, the polymerization was performed at 90 °C in the presence of K<sub>3</sub>PO<sub>4</sub> (4 equiv of

**I**) for 24 h. The hexane-insoluble polymer having the number average molecular weight (*M<sub>n</sub>*) of 5600 was obtained in 33% yield (run 1). By increasing the amounts of K<sub>3</sub>PO<sub>4</sub> up to 6 equiv of **I**, the polymer yield and *M<sub>n</sub>* increased to 75% and 14000, respectively (runs 2 and 3). No significant improve was observed in the yield and *M<sub>n</sub>* of polymer over 6 equiv of K<sub>3</sub>PO<sub>4</sub> (runs 3–5). The polymer with the higher *M<sub>n</sub>* was obtained when the initial monomer concentration [M]<sub>0</sub> was set in 0.5 mol/L (run 6), whereas decreasing the [M]<sub>0</sub> value made the *M<sub>n</sub>* of polymer low (run 7). Furthermore, a higher polymerization temperature resulted in decreasing the *M<sub>n</sub>* of resulting polymer (run 8).



**Scheme 1.** Synthesis of poly(aryl ether) by Pd-catalyzed Polycondensation of **I** and **II**.

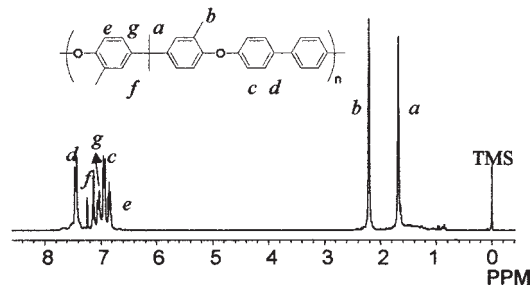
**Table 1.** Synthesis of poly(aryl ether)<sup>a</sup>

Run	[K <sub>3</sub> PO <sub>4</sub> ] <sub>0</sub> /[Bisphenol] <sub>0</sub>	[M] <sub>0</sub> <sup>b</sup> /mol L <sup>-1</sup>	Temp /°C	Yield <sup>c</sup> /%	<i>M<sub>n</sub></i> <sup>d</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>d</sup>
1	4	0.33	90	33	6000	2.8
2	5	0.33	90	52	7000	2.9
3	6	0.33	90	75	14000	3.4
4	7	0.33	90	74	14000	3.3
5	8	0.33	90	76	14000	3.4
6	6	0.50	90	66	18000	4.6
7	6	0.25	90	70	9000	2.5
8	6	0.33	reflux	79	11000	4.1

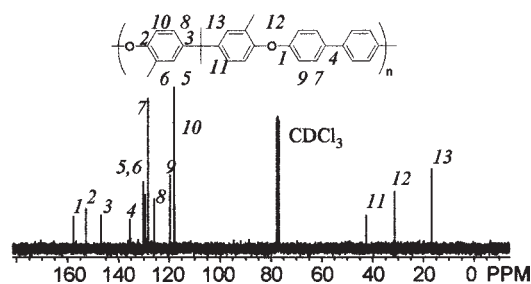
<sup>a</sup>Conditions; 4 mol% of Pd(OAc)<sub>2</sub>, 6 mol% of **1**, in toluene, 24 h. <sup>b</sup>Initial concentrations of monomers. <sup>c</sup>Isolated yield, <sup>d</sup>Determined by GPC(PSt, CHCl<sub>3</sub>).

The structure of polymer was fully characterized by <sup>1</sup>H, <sup>13</sup>C NMR, and IR spectroscopies. The IR spectrum of the polymer showed characteristic absorption attributed to the ether stretching at 1230 cm<sup>-1</sup>. Figure 1 shows the <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the poly(aryl ether) obtained in run 3 of Table 1. In addition to signals assignable to aromatic protons (*c–d*, *e–g*) at 6.8–7.6 ppm, signals corresponding to methyl protons (*a* and *b*) of the isopropylidene group and of the methyl group on benzene ring are observed at 1.68 and 2.22 ppm, respectively. Further spectral evidence for the proposed the structure of the polymer is provided by <sup>13</sup>C NMR spectrum with the assignments of all peaks (Figure

2). No extra signals are observed in this spectrum, suggesting the formation of corresponding poly(aryl ether).



**Figure 1.**  $^1\text{H}$  NMR Spectrum of poly(aryl ether) in  $\text{CDCl}_3$ .



**Figure 2.**  $^{13}\text{C}$  NMR Spectrum of poly(aryl ether) in  $\text{CDCl}_3$ .

In summary, the poly(aryl ether) with the high molecular weight ( $M_n = 18000$ ) was successfully synthesized by the Pd-catalyzed polycondensation of bisphenol **I** with non-activated bisaryl halide **II** in toluene in the presence of a bulky phosphine ligand **1**. This novel synthetic method will open another useful approach for various poly(aryl ether) synthesis.

## References and Notes

- R. N. Johnson and J. E. Harris, "Encyclopedia of Polymer Science and Engineering," 2nd ed., ed. by H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, John Wiley & Sons, New York (1988), Vol. 13, p 196.
- F. Parodi, "Comprehensive Polymer Science," ed. by G. Annen and J. C. Bevington, Pergamon, Oxford (1989), Vol. 5, p 561.
- S. Maiti and B. K. Mandal, *Prog. Polym. Sci.*, **12**, 111 (1986).
- R. N. Johnson, A. G. Farnham, R. A. Callendinning, W. F. Hale, and C. N. Merian, *J. Polym. Sci., Polym. Chem. Ed.*, **5**, 2375 (1967).
- T. F. Atwood, P. C. Dawson, J. L. Freeman, L. R. J. Holy, J. B. Rose, and P. A. Stanliland, *Polymer*, **22**, 1096 (1981).
- J. L. Hedrick, D. K. Mohanty, B. C. Johnson, R. Viswanathan, J. A. Hinkley, and J. E. MacGrath, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 287 (1986).
- R. Viswanathan, B. C. Johnson, and J. E. McGrath, *Polymer*, **25**, 1827 (1984).
- B. C. Auman, V. Percec, H. Schneider, A. W. Jishan, and H. J. Cantow, *Polymer*, **28**, 119 (1987).
- W. Risse and D. Y. Sogah, *Macromolecules*, **23**, 4029 (1990).
- A. Bhatnagar, B. Weeks, R. S. Mani, and D. K. Mohanty, *J. Mater. Chem.*, **1**, 977 (1991).
- J. M. DeSimone, S. Stoppel, E. T. Samulski, Y. Q. Wang, and A. B. Brennan, *Macromolecules*, **25**, 2546 (1992).
- R. S. Mani, B. Weeks, and D. K. Mohanty, *Makromol. Chem.*, **194**, 1935 (1993).
- C. Yeakel, K. Gower, R. S. Mani, R. D. Allen, and D. K. Mohanty, *Makromol. Chem.*, **194**, 2779 (1993).
- K. K. Carter and J. L. Hedrick, *Macromolecules*, **27**, 3426 (1994).
- J. W. Labadie and J. L. Hedrick, *Makromol. Chem., Macromol. Symp.*, **54**, 313 (1992).
- F. Ullmann, *Chem. Ber.*, **37**, 853 (1904).
- J. H. Kim and S. W. Sang, *Polym. J.*, **32**, 118 (2000).
- Y. Jianfei and S. Holdcroft, *Macromolecules*, **33**, 5073 (2000).
- Y. Nishihara, J. Ando, T. Kato, and A. Mori, *Macromolecules*, **33**, 2779 (2000).
- T. Yamamoto, T. Kimura, and K. Shiraishi, *Macromolecules*, **32**, 8886 (1999).
- A. Aranyos, W. O. David, A. Kiyomori, J. P. Wolfe, J. P. Sadighi, and S. L. Buchwald, *J. Am. Chem. Soc.*, **121**, 4369 (1999).
- Typical procedure; Into a flask equipped with a three-way stop cock, 0.635 g (3 mmol) of  $\text{K}_3\text{PO}_4$  was placed under nitrogen. This was dried at  $200^\circ\text{C}$  for 6 h under reduced pressure. Then, 0.1282 g (0.5 mmol) of 2,2-bis(4-hydroxy-3-methylphenyl)propane (**I**), 0.156 g (0.5 mmol) of 4,4'-dibromobiphenyl (**II**), 4.5 mg (0.02 mmol) of  $\text{Pd}(\text{OAc})_2$ , and 9.0 mg (0.03 mmol) of 2-(di-*tert*-butylphosphino)biphenyl (**1**) were added, and flushed with nitrogen. Toluene was added to the mixture and the mixture was warmed to the set temperature. After the orange colored polymerization solution was kept stirring for 24 h, it was poured into 50 mL of methanol to precipitate the polymer. The precipitate was redissolved with 50 mL of hot toluene, and reprecipitated with hexane. This was dried at  $100^\circ\text{C}$  for 12 h under reduced pressure to give a white solid (75% yield). IR (KBr)  $\nu$  1230 ( $\text{C}-\text{O}$  stretching).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) 1.68 (s, 6H,  $\text{CH}_3$ ), 2.22 (s, 6H,  $\text{CH}_3$ ), 6.84 (d, 2H, aromatic), 6.94 (d, 2H, aromatic), 7.04 (d, 2H, aromatic), 7.13 (s, 2H, aromatic), 7.45 (d, 4H, aromatic);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) 16.78, 31.49, 42.54, 117.92, 119.56, 125.91, 128.34, 129.53, 130.20, 146.80, 152.73, 157.77.