

Synthesis and Characterization of Polybenzoxazinones by Palladium-Catalyzed Cyclocarbonylation Polycondensation of Bis(2-iodoaniline) with Various diacid chlorides

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ABSTRACT

The synthesis of polybenzoxazinones was performed by palladium-catalyzed cyclocarbonylation polycondensation of methylenebis(2-iodoaniline) with various diacid chlorides and carbon monoxide. 2-Step polymerization which proceed via polyamide intermediates afforded high thermal-stable polybenzoxazinones with high molecular weight, compared with 1-step polymerization and 1-pot-2-step polymerization.

INTRODUCTION

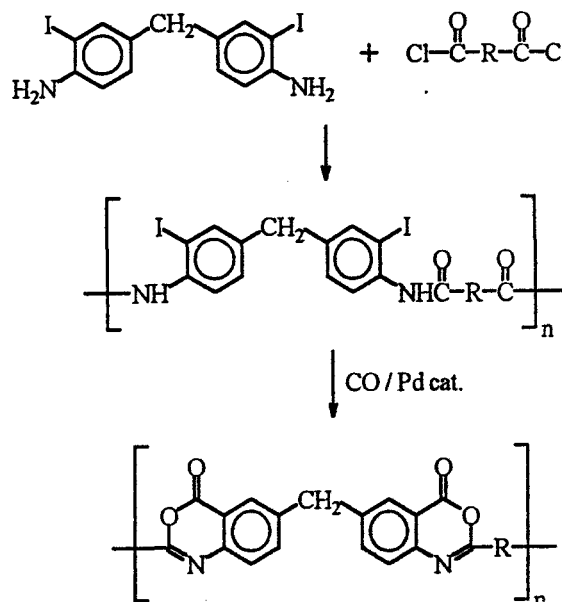
Polybenzoxazinones have excellent heat-resistance ($T_{10} > 430^{\circ}\text{C}$) and are used as the electrical insulation films and fibers. The classic methods of their synthesis are the melt polycondensation and the two-step low-temperature solution polymerization of bis(anthranilic acids) [bis(o-amino acid)s] with diacid chlorides.¹⁾ The method most widely employed in the synthesis of polybenzoxazinones is often represented by the two-step condensation of bis(o-amino acid)s with diacid chlorides in poly(phosphoric acid) (PPA). The first step is the production of poly(amic acid)s as the intermediates. The second step is a cyclization reaction by heating poly(amic acid)s in PPA for 1-3 hours at 200-250°C. The one-pot reaction of bis(anthranic acid) with diacids in the mixture of phosphorus pentoxide and methanesulfonic acid provides polybenzoxazinones with high molecular weights.²⁾

All these polymerizations necessitate bis(anthranilic acid)s or their salts as monomers. The synthesis of bis(anthranilic acid)s required many steps such as reduction, oxidation, and so on.

Recently it has been reported that one-pot reaction of 2-iodoanilines with acid chlorides and carbon monoxide in the presence of a palladium catalyst and diisopropylethylamine affords 2-substituted-4H-3,1-benzoxazin-4-ones in good to excellent yields.³⁾ The reaction is believed to proceed via in situ amide

formation from an 2-iodoaniline and an acid chloride, followed by oxidative addition to Pd(0), CO insertion, and intramolecular cyclization to form the 2-substituted-4H-3,1-benzoxazin-4-one derivatives. This palladium-catalyzed reaction promised the novel polymerization method for the polybenzoxazinones without the use of bis(anthranilic acid)s.

In the present study, the novel synthesis of polybenzoxazinones from bis(2-iodoaniline), diacid chlorides, and carbon monoxide has been performed (scheme1).



Scheme 1

Polymerization procedures have three routes, such as "1-step", "2-step", and "1-pot-2-step". 1-Step polymerization is the synthesis of polybenzoxazinones directly from bis(2-iodoaniline), diacid chlorides, and carbon monoxide in the presence of a palladium catalyst. 2-Step polymerization proceeded via the isolation of polyamides containing iodides. 1-Pot-2-step polymerization proceeded without the isolation of the intermediate polyamides.

The characterizations of polybenzoxazinones obtained has been also examined.

EXPERIMENTAL

Materials

4,4'-Methylenedianiline was purified by recrystallization from benzene. Terephthaloyl dichloride, isophthaloyl dichloride, and adipoyl dichloride were purified by vacuum distillation. 4,4'-Biphenyldicarbonyl chloride was synthesized from 4,4'-biphenyldicarboxylic acid and thionyl

chloride. $\text{PdCl}_2(\text{PPh}_3)_2$ was prepared according to literature⁴⁾. CaCO_3 , NaHCO_3 , I_2 , and $\text{C}_2\text{H}_5\text{OH}$ were used as received. *N,N*-Dimethylacetamide (DMAc), 1-methyl-2-pyrrolidone (NMP), and diisopropylethylamine (*i*- Pr_2NEt) were purified by vacuum distillation.

Synthesis of methylenebis(2-iodoaniline)

Into a flask were placed 2.436g (12mmol) of 4,4'-methylenedianiline, 4.032g (48mmol) of NaHCO_3 , 9.137g (36mmol) of I_2 , and 50ml of $\text{C}_2\text{H}_5\text{OH}$. The mixture was stirred for 96 hours at room temperature. Excess NaHCO_3 and NaI were filtered off. The filtrate was concentrated. 200ml of 5% aq. NaHSO_3 solution was added to the residue obtained. The mixture was extracted with dichloromethane (100ml \times 5). The dichloromethane layer was dried over MgSO_4 and evaporated *in vacuo* to give the product. Methylenebis(2-iodoaniline) was purified by column chromatography on silica gel using dichloromethane as an eluent. Yield was 4.5832g (10.19mmol, 85%).

IR 609 cm^{-1} (C-I). ^1H NMR (DMSO-d_6) δ : 3.54(s, 4H, $-\text{NH}_2$), 5.00(s, 2H, $-\text{CH}_2-$), 6.67(d, 2H, Ar), 6.98(d, 2H, Ar), 7.35(s, 2H, Ar) ppm. ^{13}C NMR (DMSO-d_6) δ : 37.96, 83.35, 114.39, 129.40, 131.60, 137.96, 146.43 ppm.

Synthesis of polymer

"1-step" polymerization

In a three-neck flask equipped with stirrer, a carbon monoxide inlet, and a reflux condenser were placed 0.4521g (1mmol) of methylenebis(2-iodoaniline), 0.2030g (1mmol) of terephthaloyl dichloride, 0.0351g (0.05mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$, and 5ml of DMAc. The flask was purged with carbon monoxide and warmed at 115 $^\circ\text{C}$. To the mixture, 0.52ml (0.3mmol) of *i*- Pr_2NEt was added with syringe. The reaction mixture was stirred at 115 $^\circ\text{C}$, until the consumption of carbon monoxide stopped. The reaction solution was poured into 400ml of methanol. The precipitated polymer was filtered, refluxed in methanol, and dried at room temperature *in vacuo*. Yield was 0.3938g (120%). Inherent viscosity was 0.55 g/dL, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 $^\circ\text{C}$. IR 1765 (C=O), 1510 (N=C), 1255 (C-O-C), 540 cm^{-1} (C-I).

Other polybenzoxazinones were prepared by the same procedure from isophthaloyl dichloride, 4,4'-biphenyldicarbonyl dichloride, and adipoyl dichloride.

"2-step" polymerization

Synthesis of polyamide containing iodides (first

step)

Into a flask were placed 1.1248g (2.5mmol) of methylenebis(2-iodoaniline) and 10ml of DMAc. The solution was frozen by liquid nitrogen. To the flask 1.1710g (2.5mmol) of terephthaloyl dichloride was added. The polymerization mixture was stirred at 0 $^\circ\text{C}$ for 3 hours under nitrogen. The solution was poured into 400ml of methanol. The precipitated polymer was filtered, refluxed in methanol, and dried at room temperature *in vacuo*. Yield was 1.5059g (100%). Inherent viscosity was 0.72 g/dL, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 $^\circ\text{C}$. IR 3350 (N-H), 1671 (C=O), 542 cm^{-1} (C-I).

Other polyamides containing iodides were prepared by the same procedure from isophthaloyl dichloride, 4,4'-biphenyldicarbonyl dichloride, and adipoyl dichloride with methylenebis(2-iodoaniline).

Synthesis of polybenzoxazinone (second step)

Into a three-neck flask were placed 0.5802g (1mmol) of polyamide obtained above, 0.0351g (0.05mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$, and 20ml of NMP. The flask was purged with carbon monoxide and warmed at 115 $^\circ\text{C}$. To the mixture 0.52ml (0.3mmol) of *i*- Pr_2NEt was added with syringe. The reaction mixture was stirred at 115 $^\circ\text{C}$, until the consumption of carbon monoxide stopped. The reaction solution was poured into 400ml of methanol. The precipitated polymer was filtered, refluxed in methanol, and dried at room temperature *in vacuo*. Yield was 0.3966g (100%). Inherent viscosity was 1.94 g/dL, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 $^\circ\text{C}$. IR 3380 (N-H), 1760 (C=O, benzoxazinone), 1680 (C=O, amide), 1510 (N=C), 1260 cm^{-1} (C-O-C).

Other polybenzoxazinones were prepared by the same procedure from the intermediate polyamides and carbon monoxide.

"1-pot-2-step" polymerization

Into a three-neck flask were placed 0.4521g (1mmol) of methylenebis(2-iodoaniline) and 10ml of NMP. The solution was frozen by liquid nitrogen. To the mixture 0.2030g (1mmol) of terephthaloyl dichloride was added. The reaction mixture was stirred at 0 $^\circ\text{C}$ for 3 hours under nitrogen. Then, 0.0351g (0.05mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$ was added to the polymerization solution. The flask was purged with carbon monoxide and warmed at 115 $^\circ\text{C}$. To the mixture 0.52ml (0.3mmol) of *i*- Pr_2NEt was added with syringe. The reaction mixture was stirred at 115 $^\circ\text{C}$, until the consumption of carbon monoxide stopped. The reaction solution was poured into 400ml of

methanol. The precipitated polymer was filtered, refluxed in methanol, and dried at room temperature *in vacuo*. Yield was 0.4586g (121%). Inherent viscosity was 0.26 g/dL, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C. IR 1760 (C=O), 1510 (N=C), 1255 (C-O-C), 540 cm⁻¹ (C-I).

Other polybenzoxazinones were prepared by the same procedure from isophthaloyl dichloride, 4,4'-biphenyldicarbonyl dichloride with methylenebis(2-iodoaniline).

Measurement

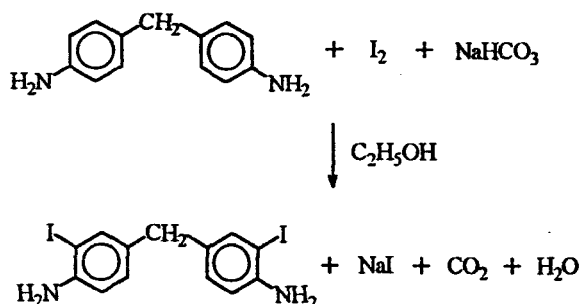
¹H and ¹³C NMR spectra were determined on a JOEL JNM-A500 spectrometer. IR spectra were determined on a JASCO FT/IR-5000 spectrometer. TGA and DSC were performed with Shimadzu TGA-50 and DSC-60, respectively, and all measurements were made at a heating rate of 10°C/min in nitrogen.

RESULTS AND DISCUSSION

Synthesis of methylenebis(2-iodoaniline)

Although halogenation of aromatic compounds with elementally halogens is well-known reaction, bromination and chlorination easily proceed with or sometimes without Lewis acid catalysts, but iodination is a slow reaction and usually requires the presence of oxidizing agents such as CH₃CO₃H, HIO₄, H₂O₂, and so on. Active aniline can be easily iodinated by I₂ and NaHCO₃ in high yield.⁵⁾ Iodination of 4,4'-methylenedianiline using I₂ and NaHCO₃ has been examined in various reaction condition to prepare methylenebis(2-iodoaniline) (scheme 2).

When 12 mmol of 4,4'-methylenedianiline, 36 mmol of I₂, and 48 mmol of NaHCO₃ were used in 50ml of C₂H₅OH, the yield of methylenebis(2-iodoaniline) raise up to 85% and its color was light



Scheme 2

yellow. Therefore, 3.0 equiv. of I₂ and 4.0 equiv. of NaHCO₃ to diamines were necessary for this reaction. When fewer amounts of I₂ and NaHCO₃ were used, 2-iodo-4,4'-diaminediphenylmethane was prepared preferentially.

Synthesis of polybenzoxazinone

"1-Step" polymerization

1-Step polymerization of methylenebis(2-iodoaniline) with various diacid chlorides and carbon monoxide were carried out by using PdCl₂(PPh₃)₂ and *i*-Pr₂NEt in DMAc. During the palladium-catalyzed polycondensation, precipitation of polymers had occurred except for adipoyl dichloride. The inherent viscosities of polybenzoxazinones prepared from aromatic diacid chlorides are 0.30-0.55 dL/g, while no polymer could be obtained from adipoyl dichloride. IR spectra of obtained polymers show an absorption band at about 540 cm⁻¹ due to C-I bond. The results suggest that ring closure reaction did not proceed completely.

Table 1. Synthesis of polybenzoxazinones

Diacid chloride	η_{inh} [g/dL] ^{a)}		
	1-step	2-step	1-pot-2-step
	0.55	1.94	0.26
	0.30	0.70	0.39
	0.56	0.71	

a) Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 °C.



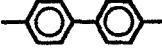
"2-Step" polymerization

Palladium-catalyzed reaction of 2-iodoanilines with acid chlorides and carbon monoxide is presumed to proceeds via 2-iodobenzamide derivatives to afford the desired benzoxazinones. Therefore the classical two-step procedure could be used for this polymerization.

The first step is the conventional low-temperature solution polycondensation of methylenebis(2-iodoaniline) with various aromatic diacid chlorides in DMAc at 0 °C forming precursor polyamides containing iodides. Table 2 shows the results of the synthesis and solubility of polyamides obtained. Polyamide prepared from terephthaloyl dichloride was the highest molecular weight (0.72g/dL), while 4,4'-biphenyldicarbonyl chloride and adipoyl dichloride gave the polyamides with lower molecular

weights (0.19 and 0.11g/dL). Because these polyamides were insoluble in DMAc.

Table 2. Polyamides containing iodides^{a)}

Diacid chloride	$\eta_{inh}^a)$ [g/dL]	Solubility of polyamide ^{b)}			
		DMAc	NMP	DMF	DMSO
	0.72	++	++	±	±
	0.35	++	++	±	±
	0.19	-	++	-	-
-(CH ₂) ₄ -	0.11	-	++	-	±

a) Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C.

b) ++: soluble at room temp., ±: partially soluble, -: insoluble.

In the second step, the palladium-catalyzed cyclocarbonylation reaction of precursor polyamides containing iodides was carried out in NMP, which is good solvent for all polymers, in same condition as 1-step polymerization. As shown in Table 1, inherent viscosities of polybenzoxazinones except for adipoyl dichloride increase after cyclocarbonylation, due to the increase of rigidity of polymer backbone. Adipoyl dichloride gave no polymer. The formation of polybenzoxazinone was confirmed by means of IR spectroscopy. The IR spectra showed three characteristic absorption bands at 1760, 1510, 1260 cm⁻¹ due to C=O, C=N, and C-O-C based on benzoxazinone ring, and also a small absorption band at 1680 cm⁻¹ due to amide bond. The results suggested that second step could not proceed completely to afford benzoxazinone ring.

2-Step polymerization gave the polybenzoxazinone with higher molecular weight, compared to 1-step polymerization.

"1-Pot-2-step" polymerization



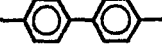
2-Step reaction process consisted of the amide formation and the cyclocarbonylation in each optimum condition is suitable for the palladium-catalyzed synthesis of polybenzoxazinones from bis(2-iodoaniline), diacid chlorides, and carbon monoxide. 1-Pot-2-step polymerizations is more convenient procedure having above benefits and were carried out in NMP, which is good solvent for polyamides as shown in Table 2. The molecular weight of the polymers is still low in this condition compared with other polymerizations (Table 1).

Further study for this polymerization is progressing.

Thermal stability of polybenzoxazinones

Thermal behavior of polybenzoxazinones and polyamides containing iodides was evaluated by means of DSC and TGA, and the results are summarized in Table 3. All polybenzoxazinones showed no distinct glass transition temperatures by DSC. The temperatures of 10 % weight loss (T₁₀) for polyamides were moderate in the range of 290-325 °C in nitrogen. After palladium-catalyzed cyclocarbonylation, T₁₀ of polybenzoxazinones increased to 400-515 °C due to higher heat-resistant nature of benzoxazinone structures.

Table 3. Thermal behavior of polyamides and polybenzoxazinones

Diacid chloride	10% weight loss temperature(°C)		
	polyamid ^e	1-step	2-step
	320	390	505
	325	405	515
	310	400	400
-(CH ₂) ₄ -	290	---	---

a) Determined by TGA at a heating rate of 10 °C/min under nitrogen.

CONCLUSION

Novel Palladium-catalyzed cyclocarbonylation polycondensation of methylenebis(2-iodoaniline) with diacid chlorides and carbon monoxide was performed by three procedure. 2-Step polymerization via intermediate polyamides afforded the polybenzoxazinones with high molecular weight quantitatively.

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