

Methyl-Substituted Polyarylenes and Their Cross-Linking Properties

Masayuki Takahashi*¹ and Kohei Goto*²

*¹Tsukuba Research Laboratories, *²Research Fellow's Laboratory in Tsukuba, JSR Corporation

25 Miyukigaoka, Tsukuba, 305-0841 Ibaraki, Japan

TEL:+81-29-856-1001, FAX: TEL:+81-29-856-1002, *²E-mail:kouhei_gotou@jsr.co.jp

Methyl-substituted polyarylenes were prepared by Ni-catalyzed coupling of aryl dichlorides and/or bis-mesylates, using 2,4-dichlorotoluene as a key monomer. The novel homopolymer and copolymers with incorporated 2,4-tolylene units were successfully cured at 350°C in air as shortly as for 2 minutes.

1. INTRODUCTION

Polyarylenes are highly thermally stable, but their syntheses and applications are limited because of poor solubility. The improvement of the solubility of polyarylenes can be achieved by several approaches, typically by attaching pendant substituents¹⁾. However, these approaches usually require tedious synthetic efforts, and the resultant polymers tend to become thermally less stable owing to decomposition of substituents at relatively low temperatures. In addition, the chemical resistance of such polymers is poor, since they retain their solubility after processing.

We already reported a series of soluble and thermally stable polyarylenes with bulky fluorenylidene substituents²⁾. However, the chemical resistance of these polyarylenes was not sufficient.

In this article, we report the synthesis and cross-linking properties of a series of methyl-substituted polyarylenes.

2. EXPERIMENTAL

1) Polymer Synthesis

Polyarylenes were synthesized by nickel-catalyzed reductive coupling of aryl dichlorides and/or bis-mesylates, using zinc¹⁾. The literature procedure was slightly modified, and the reactions were carried out in dry NMP at 90°C for 15 hrs. Polyarylenes were coagulated into a large excess of a mixture of methanol and 36% hydrochloric acid. Purification was performed by repeated precipitation from THF solutions in methanol. Recovered polyarylenes were dried under vacuum at 80°C overnight.

2) Measurements

Molecular weights were determined by GPC using THF as eluent and standard polystyrene as reference. Thermal properties were measured by TGA and DSC. Evaluation of the chemical resistance was conducted as follows: the polymer was spin-coated onto Si wafer, baked on a hot plate, and the wafer was immersed into the specified solvent for several minutes. The changes in the film thickness were monitored.

3. RESULTS AND DISCUSSION

Table 1 shows the properties of the prepared polyarylenes. Among these, **3c** was already reported²⁾.

Although the incorporation of methyl group from 2,4-tolylene unit into polyarylenes slightly lowered T_g and T_d , **3a** and **3b** still showed good thermal stability.

It is apparent from Table 1, that the solubility of polyarylenes was improved in the presence of 2,4-tolylene moieties. Polyarylene **3c** without 2,4-tolylene units could be dissolved only in NMP, but **3b**, which contains 67mol% of 2,4-tolylene units, became soluble in less polar cyclohexanone. Moreover, poly(2,4-tolylene) **3a** was soluble even in hydrocarbon solvents, such as toluene. In our previous work, incorporation of *m*-phenylene unit to **3c** did not lead to the improvement of the solubility²⁾. Therefore, it seems the methyl substituent induced the torsion into the polyarylene chain, enhancing solubility.

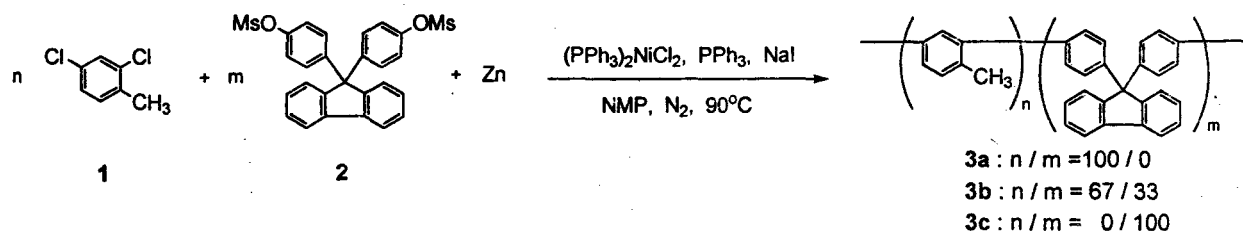


Table 1. Properties of Polyarylenes

Polyarylene	composition n / m	Mw	T_g , °C ^a		T_d , °C ^c	Solubility ^c			
			[I]	[II]		NMP	THF	CHN ^d	Toluene
3a	100 / 0	12,000	220	n.o. ^b	495	+	+	+	+
3b	67 / 33	7,600	270	n.o. ^b	510	+	+	+	-
3c	0 / 100	>13,000	>300	>300	562	+	±	-	-

^a [I] : Before cross-linking, [II] : after cross-linking ^b not observed ^c Temperatures at which a 5% weight loss was recorded by TG under N₂ atmosphere ^d Cyclohexanone

^e + : Soluble at >5 wt% concentration of polymer, ± : Partially soluble, - : Insoluble

Polyarylene **3c** did not cross-link at all even after baking at 350°C for 15 minutes under air or nitrogen atmosphere. The baked film was easily dissolved in NMP. In contrast, **3a** and **3b** became completely insoluble in NMP or cyclohexanone upon baking in air at 350°C for just 2 minutes, and their T_g 's disappeared. However, no cross-linking occurred under nitrogen. According to TGA, cross-linking was not accompanied by increase in weight, while there was a slight (<2%) weight loss. It is likely that the cross-linking proceeds by oxidative coupling of methyl groups with elimination of hydrogen, probably via benzyl radical intermediate. Before cross-linking, TGA of **3a** under nitrogen showed large weight loss above 600°C, with the char yield at 1,000°C being only 5%. But when **3a** was once cross-linked, the char yield increased considerably to 80% under the same TGA condition.

The above results demonstrate the methyl-substituted polyarylenes of this work to be promising for many applications as soluble, thermally stable and chemically resistant polymers.

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