Synthesis of Novel Polyimides Containing Phenyl-substituted Diphenylether Moieties

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Introduction

4,4'-Oxydianiline (4,4'-ODA) has been widely used as the diamine component for the synthesis of polyimides such as Kapton. However, reports regarding the substituted 4,4-ODAs are relatively rare. These published substituted 4.4'-ODAs were synthesized by either nucleophilic substitution or homo-coupling of the corresponding aromatic half. In this presentation, we propose a new method to prepare the substituted 4,4'-ODAs. The substitution can be controlled to occur multiply at 2, 2', 6, and 6' positions of 4,4'-ODAs. The new diamines can be symmetrical or asymmetrical. This method can be further applied to synthesize diacid, tetraamine containing substituted diphenylether moieties for other high performance polymers. Here, we reported the synthesis and properties of polyimides derived from four phenyl-substituted 4,4'-ODAs.

Results and Discussion

The phenyl-substituted diamines were prepared by using 4,4'-ODA as the starting material, followed by oxidation, bromination, Suziki coupling then reduction. The oxidation allows the following bromination to occur at 2, 2', 6, and 6' positions. The number of substituents is controlled by the amount of the brominating agent, N-bromosuccinimide. The ^{1}H NMR spectra of 1Ph-ODA and 4Ph-ODA are shown in Figure 1. The two amino groups in 1Ph-ODA and 3Ph-ODA are in different chemical environments due to structural asymmetry. This can be confirmed by the presence of two amino peaks in the ^{1}H-NMR spectrum shown in Figure 1. However, the difference in the reactivity of these two amino groups is relatively small. From the ^{1}H NMR spectrum of polyimide PMDA/3Ph-ODA, the ratio of head-to-head, head-to-tail, and tail-to-tail in polyimide backbone is 1:2:1, indicating that the two amino groups react with dianhydride in a random manner. Polyimides were synthesized by one-step method in *m*-cresol. All the polyimides remained in the solution throughout the polymerization without premature precipitation. These polyimides with moderate to high molecular weights exhibited good solubility in the test organic solvents as shown in Table 1 and Table 2. For example, polyimide PMDA/3Ph-ODA can be dissolved in all test solvents except acetone. The enhancement in solubility might be attributed to the bulky substituent and the structural asymmetry in some cases. Thermal stability of these polyimides will be discussed also.

Conclusions

Four new phenyl-substitued 4,4'-ODAs were prepared by using 4,4'-ODA as the starting material, followed by oxidation, bromination, Suziki coupling reaction, and reduction. The number of substituents can be controlled by the amount of brominating agent. Polyimides derived from these four diamines exhibited excellent solubility without sacrificing their thermal stability.

Reference

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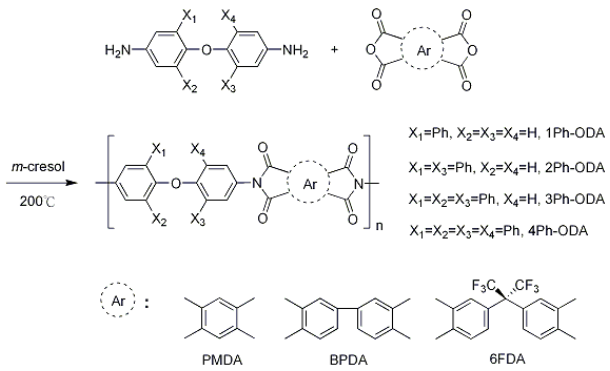

Scheme 1. Synthesis and structures of polyimides containing phenyl-substituted diphenylether moieties.

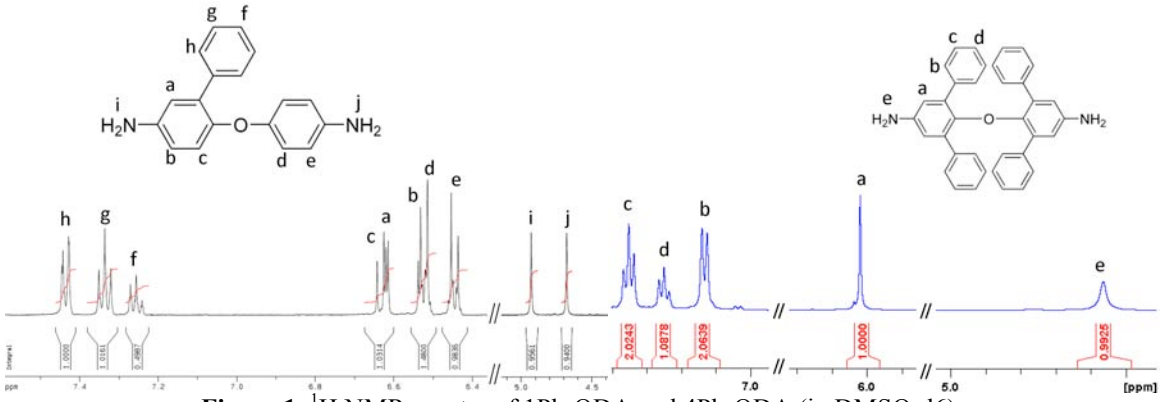

Figure 1. [1]H NMR spectra of 1Ph-ODA and 4Ph-ODA (in DMSO-d6).

Table 1. Inherent viscosities and molecular weights of polyimides

Polyimide	η_{inh}[a] (dL/g)	Mn[b] × 10^{-4}	Mw[b] × 10^{-4}	PDI[b]
PMDA/ 1Ph-ODA	0.78	6.6	9.9	1.50
BPDA/ 1Ph-ODA	0.52	NA[c]	NA[c]	NA[c]
6FDA/ 1Ph-ODA	0.41	3.6	5.5	1.52
PMDA/ 2Ph-ODA	1.50	10	18	1.80
BPDA/ 2Ph-ODA	1.89	NA[c]	NA[c]	NA[c]
6FDA/ 2Ph-ODA	0.51	5.9	9.3	1.58
PMDA/ 3Ph-ODA	0.67	6.6	9.9	1.50
BPDA/ 3Ph-ODA	0.56	5.3	7.6	1.44
6FDA/ 3Ph-ODA	0.44	3.1	6.7	2.16
PMDA/ 4Ph-ODA	0.30	2.7	3.5	1.32
BPDA/ 4Ph-ODA	0.50	NA[c]	NA[c]	NA[c]
6FDA/ 4Ph-ODA	0.31	2.9	4.4	1.52

a Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.
b By GPC in DMAc (relative to polystyrene standards).
c Insoluble in DMAc.

Table 2. Solubility of polyimides

Polyimide	Acetone	THF	DMF	DMAc	DMSO	NMP	m-cresol
PMDA/ 1Ph-ODA	+-	+-	**S**	++	**S**	++	++
BPDA/ 1Ph-ODA	-	-	-	-	+-	++	++
6FDA/ 1Ph-ODA	++	++	++	++	++	++	++
PMDA/ 2Ph-ODA	-	++	++	++	++	++	++
BPDA/ 2Ph-ODA	-	-	-	+-	-	++	++
6FDA/ 2Ph-ODA	+-	++	++	++	++	++	++
PMDA/ 3Ph-ODA	+-	++	++	++	++	++	++
BPDA/ 3Ph-ODA	-	+	++	++	++	++	++
6FDA/ 3Ph-ODA	++	++	++	++	++	++	++
PMDA/ 4Ph-ODA	+-	+-	+-	+-	+	+	++
BPDA/ 4Ph-ODA	-	+-	+-	+-	+-	+	++
6FDA/ 4Ph-ODA	+-	+-	++	++	+-	++	++

a The solubility was determined by using 20 mg of sample in 1 mL of stirred solvent.
Solubility: ++, soluble at room temperatures; +, soluble on heating at 60 ℃; +-, partial soluble in heating at 60 ℃; -, unsoluble ; S, swelling.