Synthesis of Biphenyl Type Polyimides by Nickal-Catalyzed

Coupling Polymerization of Bis(chloropthalimide)s

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Introduction

Aromatic polyimides (PIs) are known for their mechanical and electrical properties, thermal stability, and chemical resistance [1]. Biphenyl type PIs provide the further advantages of high modulus, high strength, low moisture absorption and processability[2]. Conventional PIs are made from a dianhydride and a diamine (Scheme 1)[3]. However, methods of preparing biphenyltetracarboxylic dianhydride(BPDA) by nickel[4], palladium[5], or copper[6]-catalyzed coupling from monofunctional precursors revealed many disadvantages such as much inorganic salt added[4], or very expensive metal palladium catalyst used[5], or complex reaction conditions, synthesis and purification steps.

Colon and Kelsey[7] demonstrated an efficient synthesis of biaryls from aryl chlorides in the presence of a catalytic mixture of anhydrous nickel salt, triphenylphosphine and reducing metal. Yamamoto et al. reported on the synthesis of poly (p-phenylene) from the Grignard reagent of p-dibromobenzene[8], poly (2,5-thienylene) from 2,5-dihalothiophenes[9] and Ueda et al. also synthesized poly (ether ketone)s from aromatic dichlorides[10] by nickel-catalyzed coupling in presence of zinc.

Herein, we describe an efficient preparation of polyimide via nickel-catalyzed coupling in the presence of zinc powder[4].
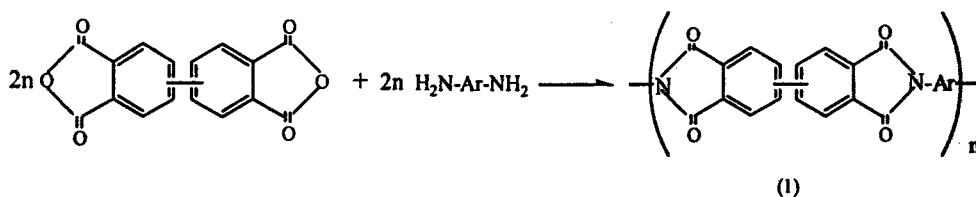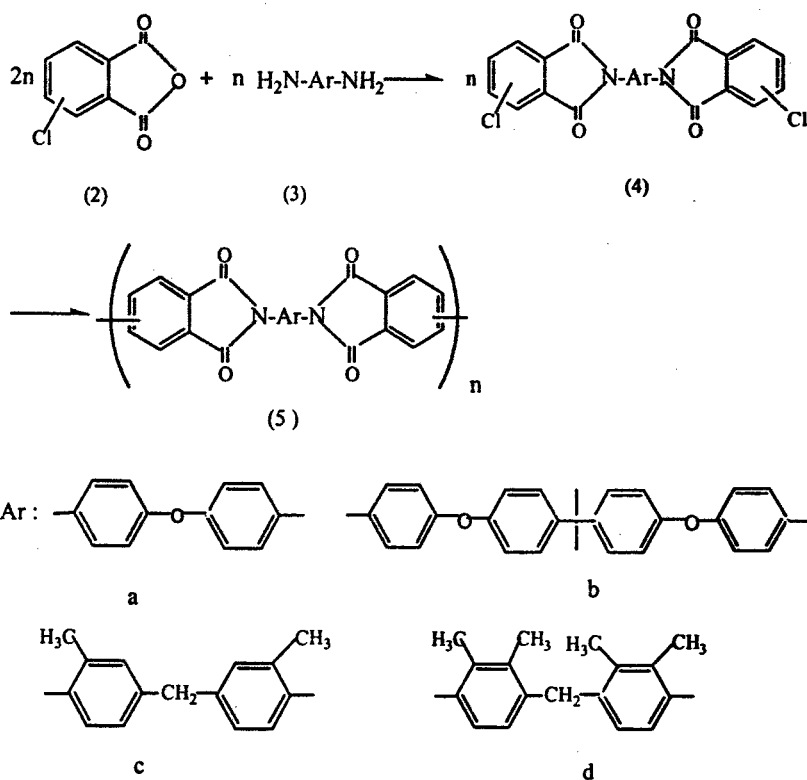

Scheme 1

Experimental Section

Materials. N, N-dimethylacetamide (DMAc) was stirred over phosphorous pentoxide 5hrs and then distilled under reduced pressure, stored over 4-Å molecular sieves. All chemical reagents were used as received. All synthetic mediums were determined by ^{1}H-NMR, FTIR, Element Anal and Melting Point. Inherent viscosities were determined at a concentration of 0.5% in mixed-cresol with an Ubbelohde capillary viscometer at $30 \pm 0.1\,°C$.

Thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elemer TGA-2 thermogravimetric analyzer and experiments were carried out on $10 \pm 2mg$ samples at a heating rate of $10\,°C/min$. The differential scanning calorimetry

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(DSC) experiments were carried out on a Perkin-Elemer DSC-7 system at a heating rate of 20℃/min under nitrogen atmosphere.

Scheme 2

Polymer 5c. In a 50-mL two-necked round-bottomed flask were placed $(Ph_3P)_2NiBr_2$ (0.125g, 0.169mmol), Ph_3P(0.188g, 0.69mmol), zinc(0.5g, 7.7mmol), and monomer 4c (1.125g, 2.025mmol). DMAc (10mL) was added via syringe. The mixture was stirred at 90℃ for 3 hr. The resulting viscous mixture was diluted with 5ml mixed cresol and filtered then poured into a large amount of methanol. The polymer was collected, washing with methanol, and dried in vacuum at 80℃ for 5 hr. The yield was 0.98g (100%). The inherent viscosity of the polymer in mixed cresol was 0.96 $dL·g^{-1}$.

Results and discussion

Aryl dichlorides containing imide moiety such as 4, 4'-Bis (3-chlorophthalimido) diphenylether (4a), 4, 4'-Bis (4-chlorophthalimido)diphenylether (4a'), 2, 2'-Bis[4-(4'-(3-chlorophthalimido)phenyloxy) phenyl] propane (4b), 2, 2'-Bis[4-(4'-(4-chlorophthalimido)phenyloxy)phenyl]propane (4b'), 4, 4'-Bis(3-chlorophthalimido)-3, 3'-dimethyldiphenylmethane (4c), 4, 4'-Bis(4-chloro phthalimido)-3, 3'-dimethyldiphenylmethane (4c'), 4, 4'-Bis(3-chlorophthalimido) -2, 2', 3, 3'-tetramethyldiphenylmethane (4d), 4, 4'-Bis (4-chlorophthalimido)-2, 2', 3, 3' tetramethyldiphenylmethane (4d'), were prepared following the literature procedure[11]. The nickel-catalyzed polymerization was performed with 1mmol monomer in DMAc in the presence of zinc and triphenylphosphine at 90℃ for several hours. As shown in Table 1, high molecular weight, polyimides have been prepared by nickel-catalyzed polymerization of 4d', 4c' in dipolar aprotic solvents. The polymerization of 4a' and

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4b' proceeded rapidly, the precipitation of polymer was observed after 30min reaction. The molecular weights were low to medium. On the other hand, the polymerization of 4a proceeded homogeneously at beginning and then heterogeneously. The compounds 4b, 4c, 4c', 4d and 4d' proceeded homogeneously .The polymers were isolated in excellent yields. The inherent viscosity of the polymer 5c' reached 0.83 dLg^{-1}. We proposed that the structure of diamines have crucial effect on the effective polymerization. In order to optimize the reaction conditions, the polymer 4c', which gave soluble polymer in DMAc, was studied in detail. The amount of catalyst, the reaction temperature and the concentration of the monomer were optimized as 5%, 100℃ and 0.19-0.20 mole/L, respectively.

Table 1 Preparation of Biphenyl type PIs 5^a

Monomer	Reaction conditions		Polymer		
	Amt of DMAc, mL	Time, h		Yield,%	η_{inh}, dL·g^{-1}
4a	3	8	5a	100	0.25
4a'	3	8	5a'	100	0.20
4b	4	8	5b	100	0.36
4b'	3	8	5b'	100	0.24
4c	3	8	5c	100	0.21
4c'	5	8	5c'	100	0.83
4d	3	8	5d	100	0.23
4d'	5	8	5d'	100	0.77

^{a} Monomer (1mmoL), NiBr$_2$ (0.06mol), PPh3 (0.41mmol), Zn (4mmol), 90℃.

Polymers were characterized by IR and elemental analysis. Thermal properties of the polymers were examined by TGA and DSC as shown in Table 2. The T$_g$s of the polymers were 225-306℃. The thermogravimetry of the biphenyl type PIs showed 5% weight loss in nitrogen at 420-480℃.

Table 2 Thermal properties of Biphenyl Type PIs^a

polymer	η_{inh}, dL·g^{-1}	T$_g$(℃) (DSC)	T$_{5\%}$ (℃) (TG)	T$_{10\%}$ (℃) (TG)
5a'	0.20	306	464	530
5b	0.36	260	450	470
5b'	0.24	225	480	550
5c	0.21	300	430	470
5c'	0.83	299	420	458
5d	0.23	b	427	493
5d'	0.77	297	442	471

a TGA measured at a heating rate of 10℃/min in nitrogen; DSC at a heating rate of 20℃/min in nitrogen.

b undetected.

Conclusions

A facile synthesis of biphenyl type PIs, which involves the nickel-catalyzed coupling of aromatic dichlorides containing imide structures in the presence of zinc and triphenylphosphine has been developed. Polymerizations proceeded smoothly and produced biphenyl type PIs with quantitative yield and inherent viscosities of up to

0.83dL/g under mild conditions. The T_gs of the polymers were 225-306°C. The thermogravimetry of the biphenyl type PIs showed 5% weight loss in nitrogen at 420-480°C.

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