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Polymeric Based Materials via Palladium-Catalyzed Polycondensation

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Abstract

The significant access to the structurally pure, high molar mass, N-containing polymers via palladium-catalyzed polycondensation of various aromatic diamines with various aromatic dibromo compounds is an interesting target. One of the major advantages is to apply inexpensive monomers; aromatic amines and aromatic bromides. Furthermore, many diamines are readily available or easy to synthesize giving fast access to numerous new functionalized polymers either by applying amino-functionalized or bromo-functionalized monomers to optimize and improve the polymer properties. With the increasing demand for different functionalized polymers, the focus of relevant studies has been to generate polymers with improved properties by palladium-catalyzed polycondensation. A series of poly(imino ether)s (PIEs), poly(imino ketone)s (PIKs), poly(imino azobenzene)s (PIAzos), poly(imino acridine)s (PIAcs), poly(imino fluorenone)s (PIFOs), and poly(imino carbazole)s (PICs) have been fabricated via palladium-catalyzed polycondensation of different dibromides with different aromatic diamines.

Keywords: Poly(imino ether)s; polycondensation; poly(imino ketone)s; poly(imino azobenzene)s; poly(imino acridine)s; poly(imino fluorenone) s; poly(imino carbazole)s.

Introduction

In the past few years, various categories of new materials such as copolymer/bentonite [1-5], copolymer/kaolinite [6-8], copolymer/pyrogenic silica [9,10], terpolymer/bentonite [11,12], and terpolymer/kaolinite [13,14] composites have been reported due to their distinctive chemistry and physical properties. Moreover, core-shell nanocomposites (CSNCs) based on TiO_2 [15-17], Fe_2O_3 [18], and Al_2O_3 [19,20] nanoparticles have attracted enormous research interest. The Pd-catalyzed arylation amination reaction is a broadly useful method for the construction of a wide variety of aromatic polymers in a one-pot synthesis [21-24]. Consequently, the corresponding high-performance polymers containing varied functionality were constructed. The careful optimization of reaction conditions and reagents, supplemented by a sound mechanistic understanding of both organic and organometallic chemistry was a key to this approach.

Discussion

In continuation of our work, a series of poly(imino ether) s (PIEs), poly(imino ketone)s (PIKs), poly(imino azobenzene)s (PIAzos), poly(imino acridine)s (PIAcs), poly(imino fluorenone)s (PIFOs), and poly(imino carbazole)s (PICs) have been fabricated via palladium-catalyzed polycondensation of various dibromides with various aromatic diamines [21-24]. The catalytic system generated from tris(dibenzylideneacetone)dipalladium (0) [$Pd_2(dba)_3$] and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) has been applied. The chemical inertness, thermal stability, and low dielectric constant characteristics of the polymer materials make them attractive for advanced technology applications since aromatic polyelectrolytes containing azobenzene have photoresponsive properties [22]. The Pd-catalyzed system may be used to synthesize these polyelectrolytes in a one-pot reaction. It is anticipated that future studies might not only improve the scope and understanding of this process but will lead to new types of interesting polymers followed by their new applications by using Pd-catalyzed cross-coupling reactions. One can use cheaper monomers e.g. chloro- or bromo-functionalized aromatic ketones instead of the corresponding difluoro structures. Also using the nitro group leading to the generation of nitrite ions that become reactive and cause side reactions at elevated temperature as is the case for the preparation of poly(arylene ether)s is avoided. Furthermore, many diamines and dibromo compounds are readily available or easy to synthesize giving fast access to numerous new polymers with optimized properties such as thermal stability, mechanical behavior, or solubility.

Conclusion

An efficient approach aimed at producing a series of promising high-performance polymers were successfully achieved by palladium-catalyzed polycondensation. Soluble PIEs, PIKs, PIAzos, PIAcs, PIFOs, and PICs with high molecular weights have been obtained by Pd-catalyzed polycondensation of aromatic dibromides and aromatic diamines. Numerous PIEs, PIKs, PIAzos, PIAcs, PIFOs, and PICs have been fabricated by using different monomers. Pd/BINAP catalyst system is found to be an effective catalyst for the cross-coupling of aromatic diamines with the aromatic dibromides achieving high yields with high molecular weight polymers. Most of these polymers are characterized by high solubility in aprotic solvents and high thermal stability. The amorphous nature of these polymers was proven by X-ray diffraction and was also reflected in their good solubility. The resulting PIEs, PIKs, PIAzos, PIAcs, PIFOs, and PICs are likely to have interesting electronic and chemical properties.

All PIEs, PIKs, PIAzos, PIAcs, PIFOs, and PICs were fully characterized by Fourier transform infrared spectroscopy, elemental analyses, differential scanning calorimetry, thermogravimetric analyses, gel permeation chromatography, and X-ray diffraction. These polymers exhibit high thermal stability and high decomposition temperatures. A model compound for each case has been fabricated and characterized by standard spectroscopic methods to confirm the proposed structure and to assist in the structure proof of the polymer. Most of the objectives of these researches with good characterizations have been achieved. The Pd-catalyzed polycondensation technique familiarizes a valuable setup to produce new high-performance polymers obsessed with varied functionality.

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