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Microwave-assisted synthesis of tetrasubstituted aryl imidazole based polymers via cascade polycondensation process

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ABSTRACT

Poly(Tetrasubstituted Aryl Imidazole)s (PTAIs), a new class of poly(heteroaromatic) polymers was prepared via a cascade polycondensation process, under microwave irradiation. These polymers were obtained by the tetrasubstituted aryl imidazole ring formation involving bis(aryl α-diketone)s, bis(arylaldehyde)s, mono(arylamine)s and ammonium acetate. The polymerization performed under microwave irradiation allowed to get high molecular weight PTAIs in very short reaction times. The chemical structure of these PTAIs was confirmed by NMR spectroscopy. Thermogravimetric analyses (TGA) showed a very good grade of thermal stability of these polymers. Glass transition temperatures (T_g) of PTAIs ranging from 155 °C to 265 °C were determined by Differential Scanning Calorimetry (DSC).

1. Introduction

Multicomponent reactions (MCRs) are very useful to design heterocyclic compounds. Through simple synthetic pathways based on one-pot procedures, complex scaffolds can be easily synthesized from three or more reactants [1,2]. As a consequence, MCRs are often alternatives to sequential multi-step syntheses. However, they are most often restricted to the synthesis of small organic molecules. Whereas the use of MCRs for direct polymer synthesis has attracted the attention of chemists for long time [3], rather few works have been reported yet [4–8]. A comprehensive literature survey results in less than 30 publications. Despite their attractive potential in terms of macromolecular innovative design, MCRs have probably been overlooked for a long time in aromatic and heterocyclic polymer synthesis because they usually produce undesirable side-reactions. Such side-reactions are known to prevent the formation of high molecular weight macromolecules in polycondensation reactions. In continuation of our work related to the development of new heteroaromatic macromolecular structures, we have intended to synthesize Poly(Tetrasubstituted Aryl Imidazole)s (PTAIs) by a four-component reaction. In the frame of ongoing studies related to the beneficial effects of microwave irradiation on the synthesis of heteroaromatic polymers by polycondensation [9,10] these polymerizations were performed under microwave irradiation.

2. Experimental section

2.1. Materials

Bis(aryldialdehyde)s (1–2) and bis(aryl α-diketone)s (A–C) were prepared as described elsewhere [11] or commercially available. Butylaniline (α), aniline (β), ammonium acetate (NH_4OAc), trifluoroacetic acid (TFA) and all solvents were used as received. Microwave-assisted experiments were performed with a Milestone ETHOS microwave oven. The reactions were performed in a high pressure Teflon reactor equipped with a pressure sensor and an optical fiber as thermal sensor.

2.2. Characterization methods

Thermogravimetric analyses (TGA) were performed under nitrogen on a TA Instruments model TGQ50 thermogravimetric analyzer from 25 to 550 °C at 10 °C/min. NMR spectra were recorded on a Bruker 200 MHz spectrometer. Deuterated dimethyl sulfoxyde (DMSO-d_6) was used as solvent and tetramethylsilane (TMS) as the chemical shift reference. The polymer glass transition temperatures (T_g) were determined from Mettler-Toledo DSC822e measurements. Analyses were performed under nitrogen, at a heating rate of 5 °C/min, on a 50 °C–300 °C temperature range. Reported values were obtained from a second heat scan, using the midpoint method. The polymer molecular weights were determined by size exclusion chromatography (SEC) on a system equipped with an Agilent G1310A pump coupled with a differential refractive index detector (Wyatt optilab -rEX 25 °C and 658 nm).

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DMF containing 0.05 M LiBr was used as eluant. Analyses were performed on two PLgel Mixed D columns. The mean molecular weights values were determined with polystyrene standards.

2.3. Typical polymerization procedure for the synthesis of PTAIs

A high-pressure Teflon® reactor was charged with 1,5 mmol of bis(aryl α-diketone), 1,5 mmol of bis(arylaldehyde), 9,3 mmol of 4-butylaniline and 6,2 mmol of ammonium acetate.

All reactants were dissolved with 3 mL of acetic acid and 7 mL of dichlorobenzene. A catalytic amount (150 μL) of trifluoroacetic acid (TFA) was added. The reactor was tightly closed and submitted to microwave irradiation (500 W) during 35 min with an upper operating temperature and upper operating pressure respectively set at 140 °C and 25 bars. Once the reaction medium was cooled to room temperature, it was poured into methanol. The polymer was isolated by filtration, washed several times with methanol, water and dried under vacuum.

2.4. Poly(tetrasubstituted aryl imidazole)s film preparation

Thin dense films of poly(tetrasubstituted aryl imidazole)s were prepared by casting 20 wt% polymer solutions in NMP onto clean glass substrates. The films thus obtained were dried under nitrogen at 50 °C overnight and then successively 1 h at 80 °C, 1 h at 120 °C, 1 h at 150 °C and 1 h at 180 °C. The resulting films were peeled off by immersion in methanol.

3. Results and discussion

In the last decade, the condensation reaction involving benzyl compounds, aldehydes and ammonia has been considered as a powerful synthetic route to form trisubstituted imidazole rings. The resulting 2,3,5-triarylimidazole compounds have generated a growing interest in many fields, such as for the design of bioactive products [12], anti-microbial and anti-bacterial agents [13], chromophore [14] and compounds for molecular photonics and sensing [15]. The additional incorporation of a mono(arylamine) in the course of the chemical reaction was proven to induce the formation of even more highly substituted heteroaryl scaffolds [16] with unique and tunable properties. However, the competitive formation of trisubstituted aryl imidazoles as well as undesirable side-reactions usually decrease the yields of such reactions. Comprehensive work has been published in the last few years in order to improve classical procedures and develop new experimental conditions to produce 1,2,4,5-tetrasubstituted aryl imidazoles with quantitative yields and short reaction times. The influence of various reaction media, such as the nature of solvent, the nature of different catalysts or the effect of microwave irradiation have been investigated [17–23]. Recent advances in this field have led to highly selective reactions. Great improvements have been especially observed in experimental conditions combining both an acidic media and microwave irradiation [24,25]. Such interesting results prompted us to consider this reaction as an efficient and elegant means of synthesizing new macromolecular structures. The synthesis of PTAIs was therefore investigated by reacting bis(aryl α-diketone), bis(arylaldehyde), mono(arylamine) and ammonium acetate in a one-pot process, under microwave irradiation (Fig. 1).

In a typical experiment, all monomers were suspended in a mixture of acetic acid and dichlorobenzene, in a high–pressure Teflon reactor equipped with a magnetic stirrer, a pressure sensor and an optical fiber as temperature sensor. The reaction medium was submitted to microwave irradiation to perform the polycondensation reaction. After cooling to room temperature, polymers were isolated by precipitation in methanol. Several parameters (reaction time, microwave irradiation power, reaction temperature, eventual presence of a catalyst, monomer ratio) have been investigated to obtain high molecular weight polymers. Best experimental conditions involve stoechiometric amounts (1eq) of bis(aryl α-diketone) and bis(arylaldehyde), excess of ammonium

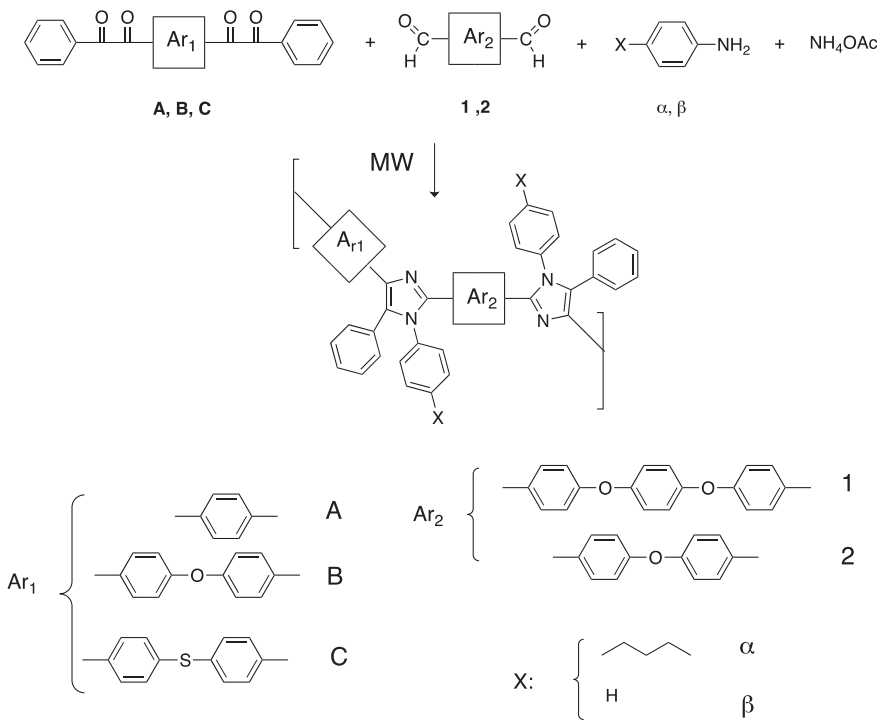

Fig. 1. Microwave-assisted synthesis of PTAIs.