

Polyelectrolyte-catalyzed Diels–Alder reactions

Nellepalli Pothanagandhi, Akella Sivaramakrishna, Kari Vijayakrishna *

Department of Chemistry, School of Advanced Sciences, VIT University, Vellore 632014, Tamil Nadu, India



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ABSTRACT

Imidazolium-based poly(ionic liquids) bearing bromide and bis(trifluoromethane)sulfonimide as counteranions [**poly(ViEIm)Br** and **poly(ViEIm)NTf₂**] derived from reversible addition fragmentation chain transfer (RAFT) polymerization techniques are used in polymer-assisted solution phase Diels–Alder reactions between isoprene and a variety of dienophiles. With 5 mol% loading, these polyelectrolytes exhibit very good catalytic activity toward Diels–Alder reaction with quantitative yields within 30 min at room temperature. These polyelectrolyte-catalyzed reactions resulted in good *para/meta*-like product ratios. Here, the coordination nature of the positively charged imidazolium groups in polyelectrolyte with dienophiles plays a key role in catalyst activity and selectivity. These polyelectrolytes were reused for 4 cycles without a significant loss in their catalytic activity and selectivity.

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1. Introduction

Poly(ionic liquids) (PILs), also known as polyelectrolytes, have attracted much attention because of their unique properties [1–3]. Their potential applications involve use as catalysts, electrolytes, coating materials, stabilizers for metal nanoparticles, CO₂ absorbing materials, use in vermicial activity, water purification, DNA binding, etc. [1–13]. Polymerization of any type of monomers in a controlled manner is a great challenge [14,15]. Reversible addition fragmentation chain transfer (RAFT) polymerization technique has facilitated the polymerization of a number of functionalized ionic liquid monomers in a much controlled manner [16,17]. RAFT polymerization can be carried out in aqueous medium, and this technique has less impact on the environment. Moreover, this technique facilitates the preparation of polymers with different architecture because this technique belongs to the group of reversible deactivation radical polymerization techniques [14–17].

The Diels–Alder (DA) reaction is a [4 + 2] cycloaddition-type pericyclic reaction, and is one of the important synthetic tools for C–C bond forming reactions in the construction of new adduct molecules having a significant impact on the organic synthesis [18–22]. The DA reactions proceed extremely slowly unless a catalyst is present; to accelerate the reactions, different Lewis acid catalysts such as AlCl₃, Sc(CF₃SO₃)₃ and BF₃ have been frequently used [23,24]. The use of Lewis acid catalysts has some drawbacks such as the requirement of laborious work-up procedures, formation of environmentally hazardous wastes, and difficulty in catalyst recovery and reuse [23]. To overcome these problems, in recent years, ionic liquids and solid supported ionic liquids are widely

used in Diels–Alder (DA) reaction [25,26]. The first study of IL mediated DA reaction of cyclopentadiene with methyl acrylate and methyl vinyl ketone in [EtNH₃][NO₃] was reported by Jaeger [27]. There are several reports on DA reaction catalyzed by chloroaluminate- [28], imidazolium- [29], pyridinium- [30], phosphonium- [31], and metal-based [32] ILs. The combination of Lewis acids with imidazolium salts catalyzing DA reactions is also reported [33]. In recent years, there have been an increasing number of studies conducted on ionic liquid (IL)-supported polymers for DA reactions. In 2007, Bae et al. used pyridinium-based polymers supported by chloroaluminates for DA reactions of cyclopentadiene with methyl methacrylate that yielded DA products in good yields with low *endo/exo* (60.6/39.4) selectivities [23]. In 2010, Haraguchi et al. reported the polymer-supported IL-catalyzed DA reactions between cyclopentadiene and trans-cinnamaldehyde with good conversions and less *endo/exo* (55/45) selectivities [24]. Six-membered cyclohexyl derivatives as synthons in organic synthesis can be prepared through DA reactions between isoprene and different dienophiles. Very few reports are available on polymer-supported/catalyzed DA reactions of isoprene cyclized with different dienophiles [34–36]. Organocatalyzed reactions are attracting much attention over conventional metal-catalyzed reactions, as the final products are free from metals [37–39]. However, these organocatalysis reactions require high catalyst loading and are associated with difficulties in product separation and catalyst reusability when compared with conventional metal-mediated catalysis. Immobilization of organocatalysis on inorganic or polymer materials is of significant interest, as it can address most of the raised issues [40–43]. However, multi-step synthesis and decay in the catalyst activity during recycling are the two major concerns of these immobilized catalysts. In the present work, for the first time, we have used simple Poly(ionic liquids) (PILs) as

* Corresponding author.

E-mail addresses: kari@vit.ac.in, vijayakrishnakari@gmail.com (K. Vijayakrishna).

reusable catalyst for DA reactions between isoprene and different dienophiles at room temperature with low catalyst loading (5 mol%) that resulted in quantitative yields with good *para/meta* selectivity.

2. Experimental section

2.1. Materials

1-Vinylimidazole, *n*-bromoethane, acrylic acid, acrylonitrile, isoprene, methyl acrylate, ethyl acrylate, potassium ethyl xanthogenate, bis(trifluoromethane)sulfonimide lithium salt, and ethyl-2-bromopropionate were purchased from Sigma-Aldrich Chemicals, India, and used as received. 2,2'-Azo-bis isobutyronitrile (AIBN) was purchased from AVRA Chemicals, India, and recrystallized from methanol before further use. All solvents used in the reactions were purchased from Rankem Chemicals, India, and distilled before use.

2.2. Measurements

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-400 spectrometer in appropriate deuterated solvents. Gas chromatography–mass spectrometry (GC–MS) images were recorded on PerkinElmer Clarus 680 (GC) and Clarus 600 (EI Mass). Molecular weights of poly-1-vinyl-3-ethylimidazolium bis(trifluoromethane)sulfonimide [**poly(ViElm)NTf₂**] were determined by a Waters gel permeation chromatography instrument with Styragel columns equipped with refractive index (RI) detector using tetrahydrofuran (THF) as solvent at an elution rate of 1 mL/min. Differential scanning calorimetry (DSC) of **poly(ViElm)Br** was performed using a DSC Q2000 V24.10 Build 122 instrument, between –70 and 150 °C at a heating rate of 10 °C min^{–1}. DSC analysis of **poly(ViElm)NTf₂** was performed using a DSC Q2000 V24.11 Build 124 instrument, between –80 and 150 °C at a heating rate of 10 °C min^{–1}. Thermogravimetric analysis (TGA) of **poly(ViElm)Br** was conducted using a TA Thermogravimetric analyzer model TGA Q500 V20.13 Build 39, from 10 to 800 °C at a heating rate of 10 °C min^{–1}. TGA analysis of **poly(ViElm)NTf₂** was conducted using a TA Thermogravimetric analyzer model TGA Q50 V6.7 Build 203, from 10 to 600 °C at a heating rate of 10 °C min^{–1}.

Single-crystal X-ray diffraction measurements for 4-methylcyclohex-3-enecarboxylic acid were acquired at room temperature (293 K) on a Bruker axs SMART APEXII single-crystal X-ray diffractometer equipped with graphite monochromatic Mo K α ($\lambda = 0.71073$ Å) radiation and CCD detector. The structure was solved by direct methods and refined by full-matrix least-squares method with the program SHELXL-97 refining on F² [44,45]. Packing diagrams were produced using the program PovRay and graphic interface X-seed [46]. The crystals of C₈H₁₀O₂ are triclinic, space group P1; (a) 6.870(5) Å, (b) 7.695(5) Å, (c) 8.948(5) Å. α 66.949(5)°, β 68.280(5)°, γ 82.533(5)°. $V = 404.3(5)$, Goodness-of-fit on $F^2 = 1.793$. A total of 5877 reflections were collected, and 1681 reflections were used for further refinement. The structure of 4-methylcyclohex-3-enecarboxylic acid was solved by direct methods and refined by a full-matrix technique against F^2 in the anisotropic approximation. Crystallographic data for 4-methylcyclohex-3-enecarboxylic acid have been deposited with the Cambridge Crystallographic Data Centre and assigned the number CCDC 1018086. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/structures.

2.3. Synthesis of chain transfer agent

Potassium ethyl xanthogenate (5 g, 31.7 mmol) was dissolved in ethanol. To this mixture, ethyl-2-bromopropionate (5 g, 27.6 mmol) was added and stirred at room temperature overnight to produce 2-ethoxythiocarbonylsulfanyl-propionic acid ethyl ester (**Scheme 1**) in good yield [36].

2.4. Synthesis of poly-1-vinyl-3-ethylimidazolium bromide [**poly(ViElm)Br**]

1-Vinylimidazole (5 g, 53.1 mmol) was taken in a 100-mL round-bottomed flask. To this, *n*-bromoethane (6.947 g, 63.7 mmol) was added and heated at 60 °C for 3 h to produce 1-vinyl 3-ethylimidazolium bromide [ViElm]Br in quantitative yields.

[ViElm]Br was polymerized through the RAFT technique using AIBN as an initiator (**Scheme 2**). A general procedure for RAFT polymerization of [ViElm]Br is as follows. A flame-dried Schlenk flask was charged with 2 g (9.90 mmol) of [ViElm]Br and 5 mL of dry dimethylformamide (DMF). To this mixture, 44 mg of chain transfer agent (CTA, 0.19 mmol) and 6.5 mg of AIBN (0.039 mmol) were added and stirred to obtain a homogeneous mixture. Three freeze–thaw cycles were conducted in this reaction mixture to eliminate any dissolved gas. Subsequently, the reaction mixture under nitrogen protection was heated to 70 °C for 24 h. The aliquots were precipitated in cold chloroform (3 \times 100 mL) and dried under vacuum to produce **poly(ViElm)Br** in 82% yield [6].

2.5. Synthesis of poly-1-vinyl-3-ethylimidazolium bis(trifluoromethane)sulfonimide [**poly(ViElm)NTf₂**]

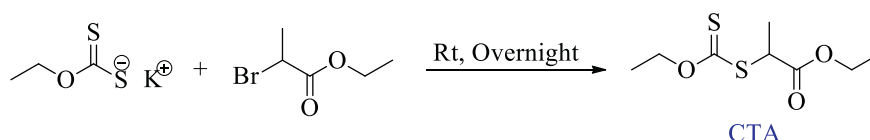
Poly-1-vinyl-3-ethyl-imidazolium bis(trifluoromethane)sulfonimide was synthesized by simple anionic metathesis reaction (**Scheme 3**) between poly-1-vinyl-3-alkyl-imidazolium bromide and lithium bis(trifluoromethane)sulfonimide according to our previous reports [6]. Briefly, 1 g (4.95 mmol) of **poly(ViElm)Br** was dissolved in 10 mL of distilled water; to this mixture, 1.84 g (6.43 mmol) of lithium bis(trifluoromethane)sulfonimide dissolved in distilled water (10 mL) was added dropwise and stirred at room temperature until the reaction completes. Then, the product was washed with water several times and dried in vacuum.

2.6. General procedure for DA reaction

The PILs-catalyzed DA reaction of isoprene with different dienophiles was carried out as follows. In a typical reaction, **poly(ViElm)Br** (0.012 g, 0.059 mmol) was dissolved in an appropriate solvent. To this mixture, isoprene (0.24 g, 3.60 mmol) and acrylic acid (0.086 g, 1.20 mmol) were added and stirred at room temperature (30 °C) for 30 min. After completion of the reaction, all the volatiles were removed under reduced pressure. As the catalyst was insoluble in ethyl acetate, the products were extracted into it, and crude products were analyzed by NMR and GC–MS.

3. Results and discussion

In this study, imidazolium-based PILs, namely poly-1-vinyl-3-ethylimidazolium bromide **poly(ViElm)Br**, was synthesized through RAFT polymerization of 1-vinyl-3-ethylimidazolium bromide using xanthate-



Scheme 1. Synthesis of CTA.

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