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Polymer Synthesis through Mechanochemistry

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Abstract

Mechanochemical polymerization is a rapidly emerging field and a plethora of polymeric materials can now be synthesized with the help of solvent-free, green and efficient mechanochemical synthesis. In this review, we discuss the recent progress in the area of polymer synthesis through Mechanochemistry. We start by describing the ball milling technique, and cover several examples of the synthesis of polymers using this technique in recent years. A representative procedure for ball milling synthesis of polymers is also described.

Keywords: Mechanochemistry; Ball milling; Synthesis; Polymer; Hyper-crosslinked; Cyclodextrin; Polyamide

Abbreviations: BM: Ball milling; LAG: liquid-assisted grinding; CD-NS: Cyclodextrin nanosponges; 2DAPAs: 2D aromatic polyamides.

Introduction

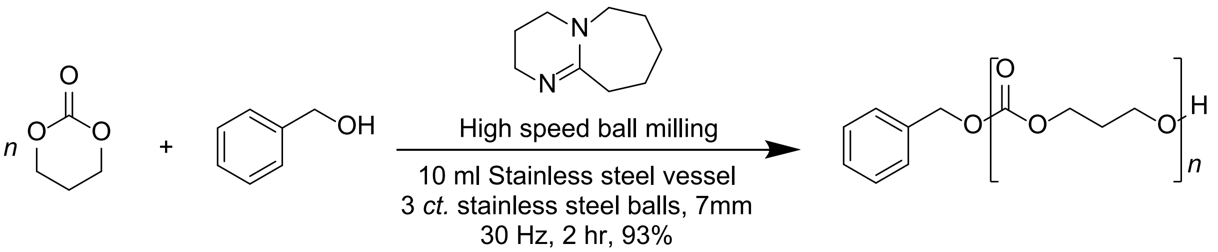
Mechanochemistry or chemical synthesis using mechanical force [1,2], has gained an increasing popularity in recent years [3]. Mechanochemistry facilitates a wide variety of chemical reactions to be carried out in environment friendly solvent-free conditions. Complex molecules and nanostructures can be precisely synthesized by chemical conversions using mechanical energy [4]. In order to transfer energy for the breaking and making of chemical bonds, mechanical forces like shearing, grinding, rapid friction, stretching, compression, milling, scratching, etc. are employed [5]. These reactions are well-established even on large scales in the fields of organic [3,6], inorganic chemistry [7,8], materials chemistry [9,10] and nanoparticle synthesis [11]. In the past decade, this field has seen a growing application in the field of polymer synthesis [12-16] with the help of ball milling (BM) technique. Not only are these processes energy-efficient and robust, they are much less toxic to the environment compared to standard solvent-mediated syntheses.

Ball Milling

Ball milling (BM) is an inexpensive, eco-friendly and efficient technique to obtain a solid homogeneous mixture [17]. Traditional ball mills consist of a conical-shaped or cylindrical-shaped chamber rotating horizontally with steel, ceramic, plastic or rubber balls for grinding. A newer version, known as high-speed ball milling (HSBM), can perform planetary rotation (in an eccentric orbit), with the sun wheel moving in the opposite direction to the grinding jar [17]. This results in a very high degree of fineness, due to the elevated pulverization energy from enormously high centrifugal forces (Coriolis forces). Since the grinding jar and the balls move at different speeds, the high impact and friction results in the decrease in the size of the particles [18]. This technique is also sometimes referred to as high energy ball milling (HEBM) [19]. At present, the following four ball-milling methods are widely used [20]: neat grinding, neat grinding followed by annealing [21], liquid-assisted grinding (LAG) [22]/kneading [23]/solvent-drop grinding [24]/solvent-assisted grinding [25], and ion and liquid-assisted grinding (ILAG) [26]. The addition of small amounts of liquid (LAG, liquid-assisted grinding) during ball milling is one of the most popularly used methods for polymer synthesis. Depending on the liquid's boiling point, this technique reduces the vessel pressure during synthesis and contributes to the texture properties of the polymer.

Synthesis of Poly(Trimethylene Carbonate)S

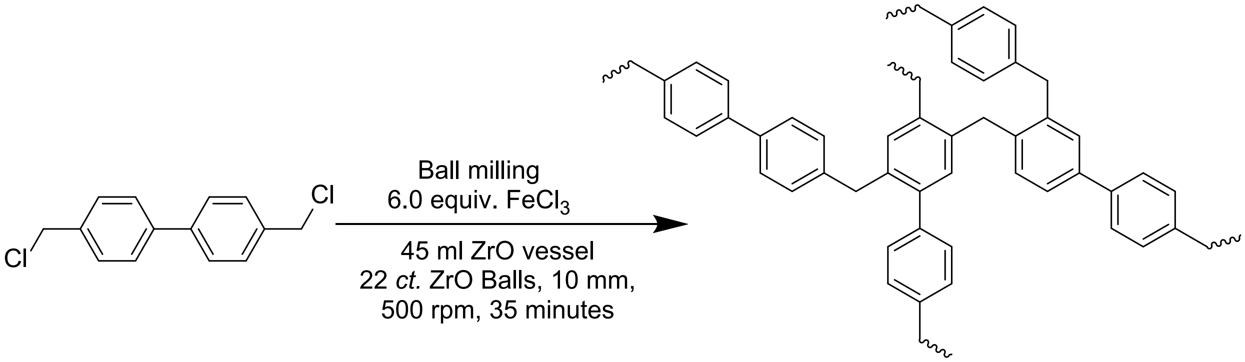
Park and Kim reported a mechanochemical polymerization of trimethylene carbonate using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as organ catalysts through solvent-free ball milling conditions [27]. The traditional solvent-mediated synthesis of this polymer showed a low reaction rate, which was found be enhanced under ball milling conditions. The use of DBU resulted in an outstanding efficiency of polymerization and decent control of the length of the polymer chain. TBD also displayed an excellent efficacy in boosting the rate, with all polymerizations being complete in 5 minutes. The only drawback of this process was that it suffered from degradation, therefore restricting the molecular weight to 10,000 g/mol. Other examples of polymer synthesis in this area include the synthesis of poly (lactic acid) [28,29], polystyrenes [30] and poly (ethylene oxide) (Scheme 1) [31].



Scheme 1: Trimethylene carbonate polymerization using solvent-free ball-milling.

Hyper-Crosslinked Polymers

Grätz S, et al. [32] developed a rapid solvent-free Friedel-Crafts alkylation (Scheme 2) that resulted in a porous polymer which not only had a much narrower pore size distribution compared to solvent-based analogues, but also had surface areas of up to 1720 m^2g^{-1} and pore volumes of up to 1.55 cm^3g^{-1}. The conventional synthesis of this polymer uses 1,2-dichloroethane (a chlorinated solvent). It was also observed that LAG (liquid-assisted grinding) had a huge impact on the texture of the polymer produced.



Scheme 2: Mechanochemical polymerization of 4, 4'-bis ((chloromethyl)-1, 1'-biphenyl) to form a porous hyper-crosslinked polymer.

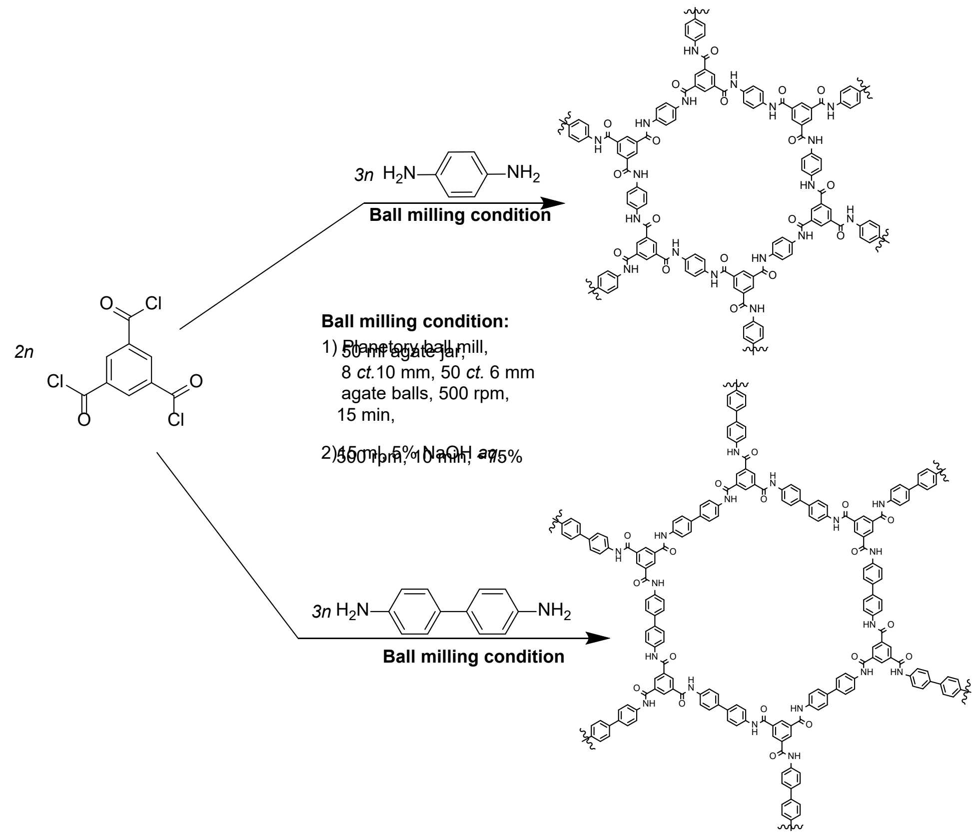
Hyper-Crosslinked Cyclodextrin Polymers

Jicsinszky L, et al. [33,34] used planetary ball mill to synthesize cyclodextrin (CD) derivatives. CDs have reactive hydroxy groups, which can be used to form nanostructured crosslinked polymers known as cyclodextrin nanosponges (CD-NS). The conventional synthesis of nanosponges involves dissolving the use of organic solvents such as DMF/DMSO. Pedrazzo AR, et al. [35] reported ball milling conditions for the synthesis of biodegradable CD-NS using 1, 1-carbonyldiimidazole as the crosslinker. α, β, and γ-cyclodextrins were used in the following molar ratios of the cyclodextrin and the crosslinker, 1:2, 1:4 and 1:8. The resulting product had identical properties to that synthesized by traditional solvent-mediated methods.

2-D Aromatic Polyamides

2D aromatic polymers have extensive applications as Nanoporous membranes in drug delivery and photocurrent generators on account of their excellent mechanical and thermal properties [36-39]. However, there is a scarcity of scalable procedures to synthesize these polymers. Xu Y, et al. [39] reported the first ball milling solvent-free synthesis of 2D aromatic polyamides (2DAPAs) in room temperature. The resulting polymers had high crystallinity, were ultrathin (like graphene), dispersible in solvents and had extraordinary thermal stability (up to 400˚C). 1,3,5-benzenetricarbonyl chloride and 1,4-phenylenediamine or 4,4-diaminobiphenyl were used as monomers for the polymerization (Scheme 3) and the products were designated as 2DAPA-1 and 2DAPA-2, respectively. While the solvent-mediated methods took several days to complete [36,40], this reaction was generally over in 15 minutes, with an overall yield of 75%.

In order to probe why it was imperative to have solvent-free conditions for the synthesis of 2D planar polyamides, the authors subjected 1,3,5-benzenetricarbonyl chloride and 1,4-phenylenediamine to polymerization under ball milling conditions with a small amount *N*-methylpyrrolidone (NMP) a solvent. This resulted in an amorphous product, unlike the highly crystalline sheet-like product obtained under solvent-free conditions. It was thus concluded that since the bonds can rotate easily in a solution, the polymerization did not happen in the 2D plane. In contrast, rotation of the bonds is restricted in the solid phase, resulting in polymerization in a 2D plane.



Scheme 3: Mechanochemical ball-milling synthesis of 2DAPAs.

Representative Procedure

The starting materials 1,3,5-benzenetricarbonyl chloride (2.00mmol) and 1,4-phenylenediamine (3.00mmol) were taken in a 50ml agate jar. The ball milling process was performed at room temperature in a planetary ball milling instrument (QM-3SP04, Nanjing University Instrument Co. Ltd) with the aid of eight count 10mm diameter agate balls and fifty count 6mm diameter agate balls. Under this condition milling was performed for 15mins followed by milling with

50 ml 5% NaOH aq. at 500rpm for 10min. The polymer was purified by filtration through 0.22μm membrane, washing with water and ethanol and drying at 80°C for overnight to obtain ~75% isolated yield of the polymer.

Conclusion

Ball milling (BM) is an eco-friendly technique that holds high potential in the cost-effective and efficient synthesis of polymers with a variety of desired characteristics. It is appropriate for both continuous and batch operations and can be used for both open and closed circuit grinding. Interestingly, mechanochemistry often leads to results unforeseen in solvent-mediated synthesis, thus opening a new avenue in the concept of bond cleavage and formation [31]. While numerous developments have been attained in this field in the last few years, there is no doubt that a lot more will be achieved in the ensuing years.

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