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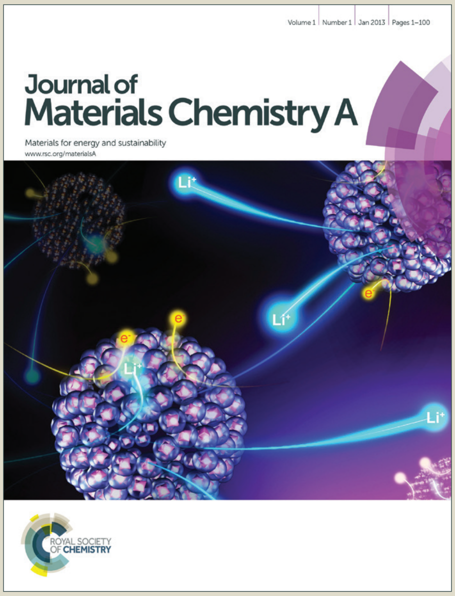

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ARTICLE TYPE

Advancing Polymers of Intrinsic Microporosity by Mechanochemistry

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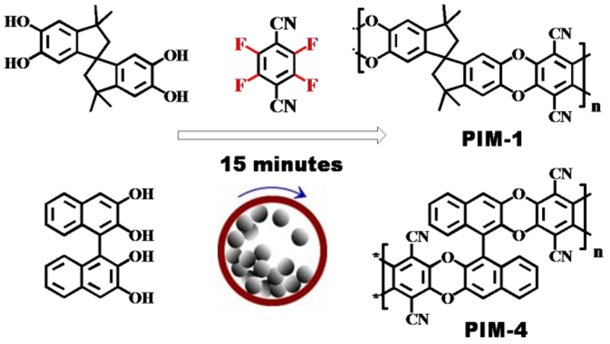
Herein, we report a fast (15 min) and solvent-free mechanochemical approach to polymers of intrinsic microporosity(PIMs) with high molecular mass and low polydipersity by solid grinding. The enhanced reaction efficiency results from the instantaneous frictional heating and continuously exposing active sites within those solid reactants.

In the field of microporous organic polymers, polymers of intrinsic microporosity (PIMs) are an exceptional family because, unlike conventional microporous materials, they are soluble in common organic solvents (e.g., tetrahydrofuran, $CHCl_3$) and can be processed readily using solvent-based techniques (e.g., membrane preparation).[1] Since their discovery in 2004, PIMs showed profound performance in many fields, such asgas separation and heterogeneous catalysis.[2] In general, PIMs with both high free volume and large surface area are fabricated on highly rigid and contorted organic monomers; for example, PIM-1, one of the most well-known PIMs, was synthesized via the dibenzodioxane-forming reaction (C-O bond construction) based on a double-aromatic nucleophilic substitution mechanism. The original method of synthesizing PIM-1 involved performing the process in dimethyl formamide (DMF) at 50–65 ℃ for 24–72 h with each monomer concentration around 3 mmol per 20 mL DMF. An alternative pathway with high-speed stirring, increased reaction temperature (155 ℃), and co-solvent toluene could shorten the reaction time to 8 minutes.[3] Actually, the initial polymerization reaction proceeded very fast; but the resulting polymer intermediates and tetraphenol salts were not soluble in DMF, which would precipitate in several minutes.[3,4] Therefore, the inhomogeneous polymerization would hinder further step-growth to a large degree, resulting in a longer reaction time and lots of branched or cross-linked chains. The question for this kind of polycondensation remains whether high-quality polymers with consistently high molecular weight, low polydispersity, and linear structure can be rapidly achieved in viscous, high concentration or solid-liquid biphasic environments.

In this contribution, we demonstrate solvent-free mechanochemical synthesis (MS) of PIMs by manual grinding in a mortar or by ball grinding. Mechanochemistry—a so called green process—is becoming a more mainstream technique for the formation of C-C and C-X bonds (X = halide), since in most cases, it can drive reactions between solids quickly and quantitatively under solvent-free conditions.[5] Herein, traditional PIM-1 and PIM-4 were rapidly fabricated by MS process (**Scheme 1**). Although the original idea for using the MS approach was only to prepare PIMs without any solvents, its unexpectedly versatile effects on accelerating the reaction rate and enhancing the molecular mass of product were quickly recognized.



Scheme 1.Synthesis of PIM-1 and PIM-4 materials by ball milling in 15 minutes.

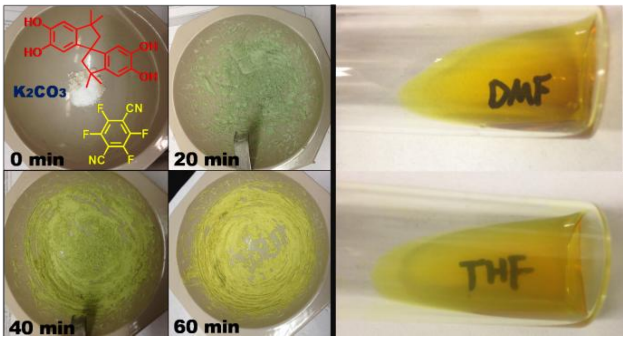


Figure 1.Left figure: MS of PIM-1 by grinding those reactants in a mortar with a pestle. Reactants: TTSBI 0.5 mmol, TFTPN 0.5 mmol, K_2CO_3 1.5 mmol. Right figure: 1 wt% PIM-1-MS solution in different solvents.

Because of the increasing interest in PIM-1, we initially tried the polycondensation reaction of 5,5,6,6-tetrahydroxy-3,3,3,3-tetramethyl-1,1’-spirobisindane (TTSBI) with tetrafluoroterephthalonitrile (TFTPN) in the presence of K_2CO_3. In the MS process, those solid reactants were neatly ground in a mortar with a pestle or by ball milling. As shown in **Figure 1**, the visual colour changes from white through green to yellow directly revealed the ongoing polymerization process. Compared with the solution-based method (72 h), the solid reaction between TTSBI and TFTPN by ball milling was complete in significantly less time (15 min).[3] In a typical synthesis, TTSBI (680 mg, 2mmol), TFTPN(400 mg, 2 mmol), and inorganic base (K_2CO_3 1200 mg) were added to a commercially available stainless steel reactor [4.5 cm (diameter) by 5.5 cm (height)] along with twelve stainless steel ball bearings (diameter 1.2 cm, 13.4 g × 4; diameter 0.7 cm, 3.4 g × 4; diameter 0.5 cm, 0.98 g × 4; reactant-to-ball weight ratio: ~1: 31). The reactor was placed in a high speed vibrating ball miller (300 W Motor Power, 1200 rounds min^{-1}) and the reactants were ball milled for 15 minutes. The resulting mixture was thoroughly washed with water, methanol and ethanol, affording a yellow powder at 98% yield (labelled PIM-1-MS).It should be underlined that a longer reaction time (e.g., 45 min by ball milling) would result in samples with some insoluble polymers, possibly induced by products with extremely high molecular mass. Actually, diffusion rates of molecules in the crystalline state are on the order of $10^{-15} m^2 s^{-1}$, which is at least six orders of magnitude less than in solution.[6] However, MS of PIM-1 in a solid state seems faster than synthesis by the solution-based method, and we attribute that to the mechanical action (including frictional heating)-promoted molecular collision. Certainly, the PIM-1-MS sample can be totally dissolved in organic solvents such as DMF and tetrahydrofuran, excluding the existence of cross-linked products (**Figure 1**).

Table 1. Molecular mass and BET surface area of as-made polymer materials. [a]

Sample	$M_n/10^3$ (g/mol)	$M_w/10^3$ (g/mol)	M_w/M_n	S_{BET} (m^2/g)
PIM-1[b]	96	270	2.8	850
PIM-1-MS	337	485	1.4	520
PIM-4[b]	2.6	5	1.9	440
PIM-4-MS	349	487	1.4	179

[a] Molecular mass from gel-permeation chromatography test based on polystyrene standards, BET surface area from N_2 sorption measurement at 77 K. M_n: number-average molar mass, M_w: weight-average molar mass. [b] Data of PIM-1 and PIM-4 are from references 3

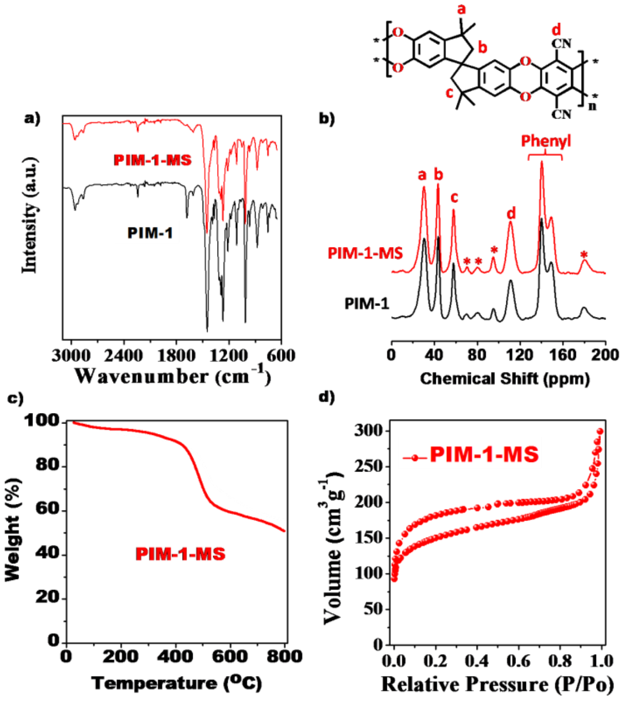


Figure 2. a) FTIR spectra of PIM-1-MS by ball grinding and PIM-1 from solution-based method; b)Solid-state ^{13}C CP/MAS NMR analysis of PIM-1-MS and PIM-1; c) TGA curve of PIM-MS in N_2 atmosphere, heating rate: 10 ℃ min^{-1}; d) N_2 sorption isotherm of PIM-1-MS sample at 77 K.

Fourier transform infrared (FTIR) spectroscopy of PIM-1-MS showed the vanishing of the –OH group of TTSBI and those characteristic sorption bonds of PIM-1 (**Figure 2a**). The successful formation of a PIM-1network was then confirmed by these aliphatic and aromatic hydrogen signals of PIM-1-MS in ^1H NMR spectra (Experimental Section in Supporting Information) and solid state ^{13}C NMR analysis (**Figure 2b**). Peaks a-c should be induced by the carbon atoms in the aliphatic section of the indane ring. The signal at approximately $\delta = 111$ ppm can be assigned to the carbon atom of benzylic nitrile group, while peaks from $\delta = 140\text{-}160$ ppm are attributed to the phenyl carbons. There is no difference in the ^{13}C NMR spectra for the PIM-1-MS and PIM-1 sample. Thermogravimetric analysis (TGA) of PIM-1-MS in N_2 showed that it was quite stable up to 400 ℃ (**Figure 2c**). The glass transition of those polymers was studied by differential scanning calorimetry analysis. Upon heating from -90 ℃, an exothermic transition for PIM-1-MS sample at -88.9 ℃ is observed (**Figure S1**), which corresponds to the glass transition (*T*g); and it is close to the *T*g of PIM-1 (-89.0 ℃).

Further analysis by gel-permeation chromatography illustrated the sufficiently high molar mass of PIM-1-MS (number-average molar mass, $M_n = 337000$ g mol^{-1}; weight-average molar mass, $M_w = 485000$ g mol^{-1}), and the corresponding polydispersity (M_w/M_n) can be calculated to be 1.4 (**Table 1**). Note that the PIM-1-MS sample holds a higher molar weight and narrower molar weight distribution than the PIM-1 counterpart from solution synthesis ($M_n = 96000$ g mol^{-1}, $M_w = 270000$ g mol^{-1}, $M_w/M_n = 2.8$); and no oligomers or cyclic polymers were found on GPC curve.[3] We observed that the initial polymer product would rapidly precipitate out from the reaction mixture in the wet synthesis of PIM-1 using DMF solvent at 60°C. At this point, it was not easy for the common step-growth polymerization reaction to proceed in a fast manner. Therefore, the enhanced molar weight of this ladder polymer by MS might be induced by the physical effect of mechanical action that is continually breaking down particles to smaller sizes and breaking up any product coating layers to expose fresh active sites, thereby keeping the rapid chain-growth and overcoming premature chain-termination in the inhomogeneous polycondensation.

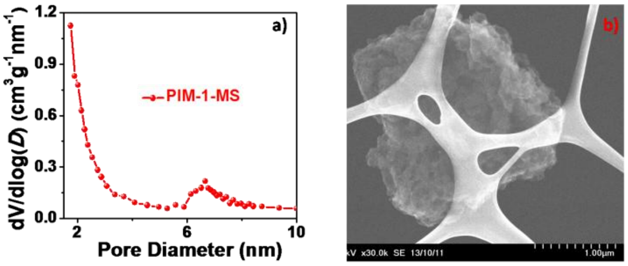


Figure 3. a) Pore size distribution and b) SEM image of PIM-1-MS.

Furthermore, the mechanochemistry-derived PIM-1-MS polymer is highly porous ($S_{BET} = 520\ m^2 g^{-1}$), and the significant N_2 uptake at low relative pressure indicates its rich microporosity

(**Figure 2d**). The pore size distribution plot also shows a smooth peak at ~7 nm, suggesting the existence of some mesopores in the polymer (**Figure 3a**). The hierarchical pores of PIM-1-MS are also suggested by the scanning electron microscopy image (**Figure 3b**). Compared with PIM-1 (S_{BET} = 720–875 m^2g^{-1}), the slightly decreased surface area of PIM-1-MS might be the consequence of enhanced polymer cohesion and packing during solid state grinding.[3,5] In an endeavour to expand the scope of this MS method, the polymerization between2,2',3,3'-tetrahydroxy-1,1'-binaphthyl (THBN) and TFTPN (the synthetic route to PIM-4) was carried out by ball grinding (labelledPIM-4-MS).[3] As expected, the PIM-4 framework formed in 15 min, and the PIM-4-MS product possessed a BET specific surface area of 179 m^2g^{-1} with high mass weight (M_n=349000; M_w=487000).

Conclusions

In summary, high-quality PIMs with consistently high molecular weight and low polydispersity are rapidly achieved by mechanochemistry, providing an effective and sustainable strategy for controlling this kind of polycondensation that is running in viscous, high-concentration, or solid-liquid biphasic environments. The current finding moves the scope of laboratory mechanosynthesis towards porous organic polymers, and once again highlights advantages of MS, including greater efficiency with regard to time, materials and energy usage, as well as the discovery of new or improved reactivity and products. It is expected that such integration will, ultimately, lead to a highly efficient system for materials synthesis and screening completely independent of solvents and waste byproducts.

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Notes and references

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