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Short communication

A readily accessible porous organic polymer facilitates high-yielding Knoevenagel condensation at room temperature both in water and under solvent-free mechanochemical conditions

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ABSTRACT

A novel nitrogen-rich amorphous porous organic polymer has been synthesized using a microwave-assisted process. Its high chemical stability, reusability and poor solubility enable the use of the porous polymer as a metal-free heterogeneous catalyst for C—C bond formation at ambient temperature under environmentally benign conditions.

1. Introduction

The Knoevenagel condensation reaction is a fundamentally important reaction for the formation of C—C bonds in organic synthetic chemistry [1]. These condensation reactions are generally conducted in organic solvents and are facilitated by a wide range of bases (*e.g.* ammonia, amines, *etc.*) [2]. In recent years, the high utility of the Knoevenagel condensation reaction was further promoted through the development of numerous catalysts to enhance reaction yields and shorten times [3–8]. Despite the appreciable variety of available catalysts and their efficiencies [9], however, the need to develop catalysts that enable fast access to condensation products in high yields under environmentally friendly conditions still persists [10–15]. We report herein the use of a readily accessible porous organic polymer (POP) as a cost efficient, stable and reusable catalyst for fast and high-yielding Knoevenagel condensation reactions under pH-neutral conditions in water and at room temperature.

Porous organic polymers (POPs) are widely used materials for applications in gas storage [16,17], separation sciences [18–21] and optoelectronics [22]. POPs are also extensively used as heterogeneous catalysts [20,23,24] owing to their high thermal and chemical (*i.e.* hydrolytic) stability under extreme reaction conditions [25,26] and can, in terms of functionality, easily compete with other classes of emerging and established porous materials (*e.g.* metal-organic, covalent organic and zeolitic imidazolate frameworks) [27]. To enhance their catalytic properties, POPs are frequently doped with inorganic nanoparticles [28]. A recent study, for example, has shown that such doped, organic-inorganic hybrid catalysts enable Knoevenagel condensation reactions in water with remarkable efficiency [29].

2. Experimental section

2.1. Synthesis of the AmPOP catalyst

Stoichiometric amounts of melamine (252 mg, 2 mmol) and terephthaloyl chloride (609 mg, 3 mmol) in DMSO (15 ml) with catalytic amounts of triethyl amine (0.5 ml) were placed in a round bottom flask. The obtained solution was refluxed under microwave condition at 420

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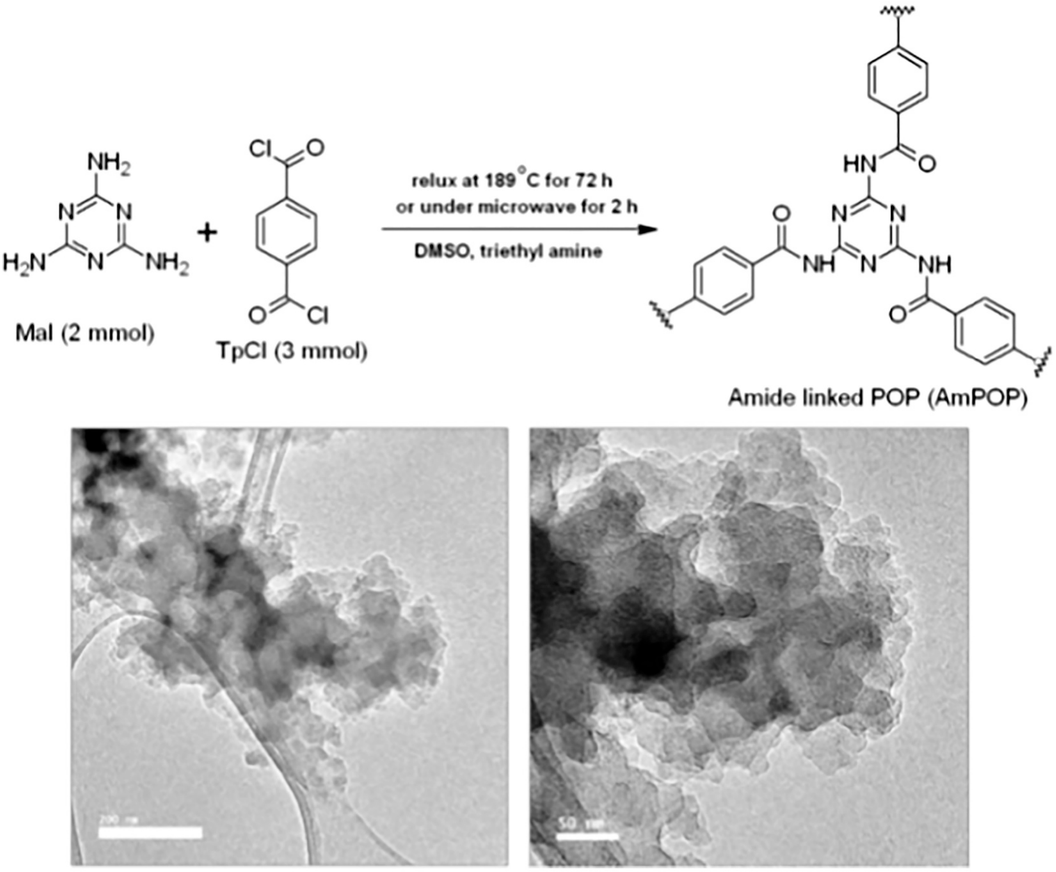


Fig. 1. Base-catalysed condensation of melamine (triaminotriazine) and terephthaloyl chloride to prepare the AmPOP catalyst under various reaction conditions (top); TEM images of AmPOP showing irregularly shaped particles under different magnifications (scale length 200 nm for bottom left; 50 nm for bottom right).

W for about 2 h. The solid obtained was filtered and slurried in 30 ml MeOH, filtered and dried under vacuum.

2.2. *Mechanochemical Knoevenagel condensation reactions*

A mixture of an aromatic (or a heteroaromatic) aldehyde (1 mmol) and an active methylene compound (1 mmol) were added to a mortar along with the AmPOP catalyst (2.4 mol%). The mixture was ground at room temperature for the lengths of time shown in Schemes 2 and 3. Progress of the reaction was monitored by TLC, using an *n*-hexane:ethyl acetate (5:1) solvent mixture as eluent. The reaction mixture was then washed with ethanol and purified by recrystalisation from ethanol.

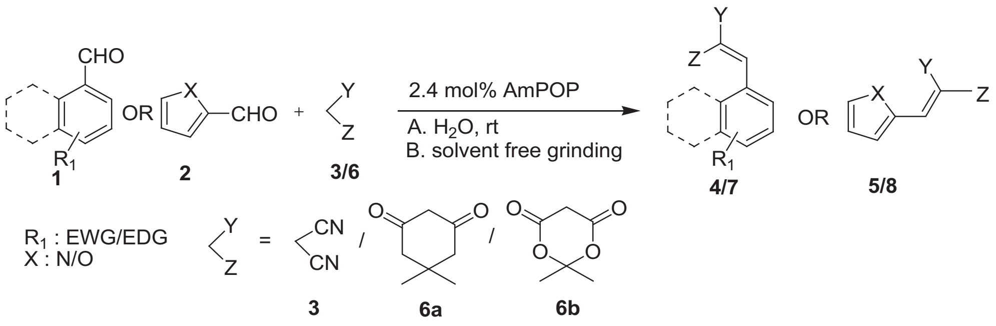
2.3. *Knoevenagel condensation reactions in an aqueous medium*

A mixture of an aromatic (or a heteroaromatic) aldehyde (1 mmol), an active methylene compound (1 mmol) and the AmPOP catalyst (2.4 mol%) was added to a mixture of 5 ml of distilled water. The suspension was stirred at room temperature for the lengths of time shown in Schemes 2 and 3. The reaction progress was monitored by thin-layer chromatography using the above-mentioned eluent. After completion of the reaction, the aqueous solution was filtered and the solid was dissolved in ethanol. Again, the solution was filtered for removal of the catalyst from the reaction mixture, and purified by recrystalisation from ethanol to obtain the pure product. The characterization of products was performed using ^{1}H NMR, ^{13}C NMR, MS, powder and single-crystal X-ray diffraction.

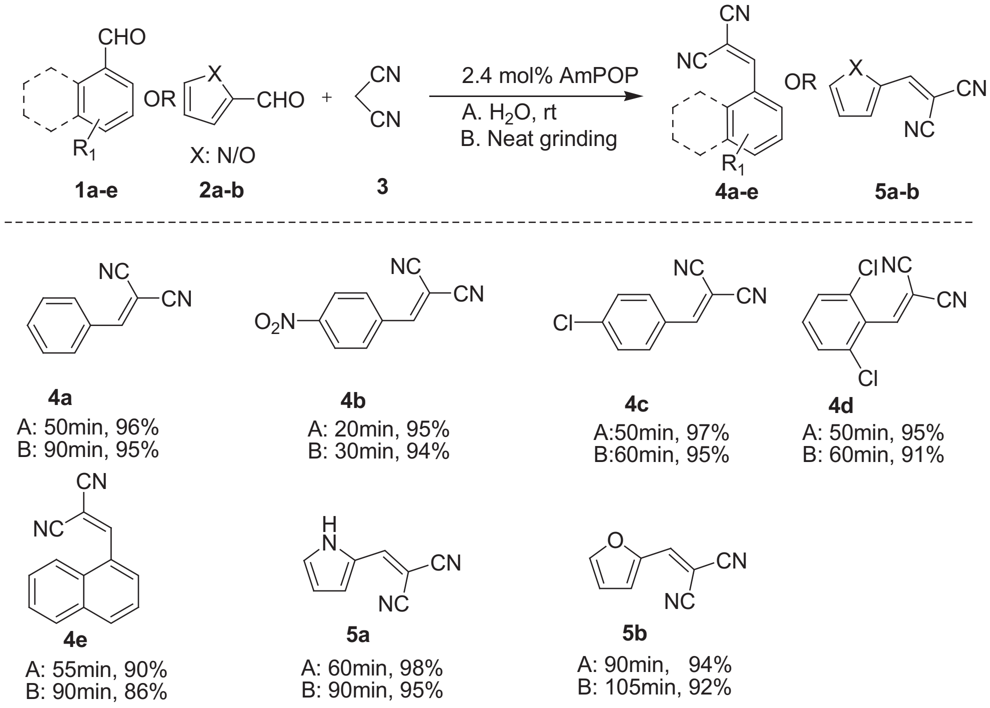
3. Result and discussion

Our recent interest in porous organic materials led to the discovery of an amorphous POP that is decorated with amide functional groups (hereafter abbreviated with AmPOP). The AmPOP can be efficiently and rapidly synthesized in a condensation reaction involving melamine and terephthaloyl chloride under reflux conditions or through a microwave-assisted reflux process (see Supplementary Information, SI). Popular mechanochemical methods [26], such as neat grinding or liquid-assisted grinding, on the other hand, enabled the formation of the AmPOP, but the reactions did not reach completion even after four hours of manual milling. Powder X-ray diffraction and transmission small-angle X-ray scattering (SAXS) revealed that the AmPOP material consists of amorphous particles that are 20 nm small, with radial size distributions (RSD) of 38.5%. Results of transmission electron microscopy (TEM) studies of the particle properties were also consistent with the results of the SAXS studies (Fig. 1) and revealed that the particles exhibit irregular morphologies. Surface area measurements, using the Barrett−Joyner−Halenda method, showed that the material exhibits pore sizes in the 15–70 Å diameter range and surface areas of 66–96 $m^2\ g^{-1}$ (or 100–133 $m^2\ g^{-1}$, as determined by the Brunauer–Emmett–Teller method). The activated AmPOP was also shown to exhibit outstanding chemical stability upon exposure to a range of commonly utilized solvents (including water), as well as under acidic conditions (see SI, Fig. S7). The synthesis and the characterization of the AmPOP are detailed in the SI document.

Further studies showed that the AmPOP can be used as metal-free heterogeneous catalyst with relatively low catalytic loadings (2.4 mol %) to facilitate Knoevenagel condensation reactions both in water and in solvent-free mechanochemical reactions. To the best of our knowledge,



Scheme 1. General scheme for the AmPOP-catalysed Knoevenagel condensation reaction.



Scheme 2. Synthetic targets (top) and the obtained yields (an average of two runs) for compounds **4** and **5** using two different synthetic methods (bottom): stirring of the reactants in a round bottom flask at room temperature (**A**) and milling under solvent-free conditions (**B**). Method **A**: Aldehyde (1 mmol), malononitrile (1 mmol), AmPOP catalyst (2.4 mol%), H_2O (5 ml), room temperature stirring. Method **B**: aldehyde (1 mmol), malononitrile (1 mmol), catalyst AmPOP (2.4 mol%), in an agate mortar and pestle for the above-mentioned times and in the absence of liquid additives. The percentage yields are given for the isolated products.

Table 1

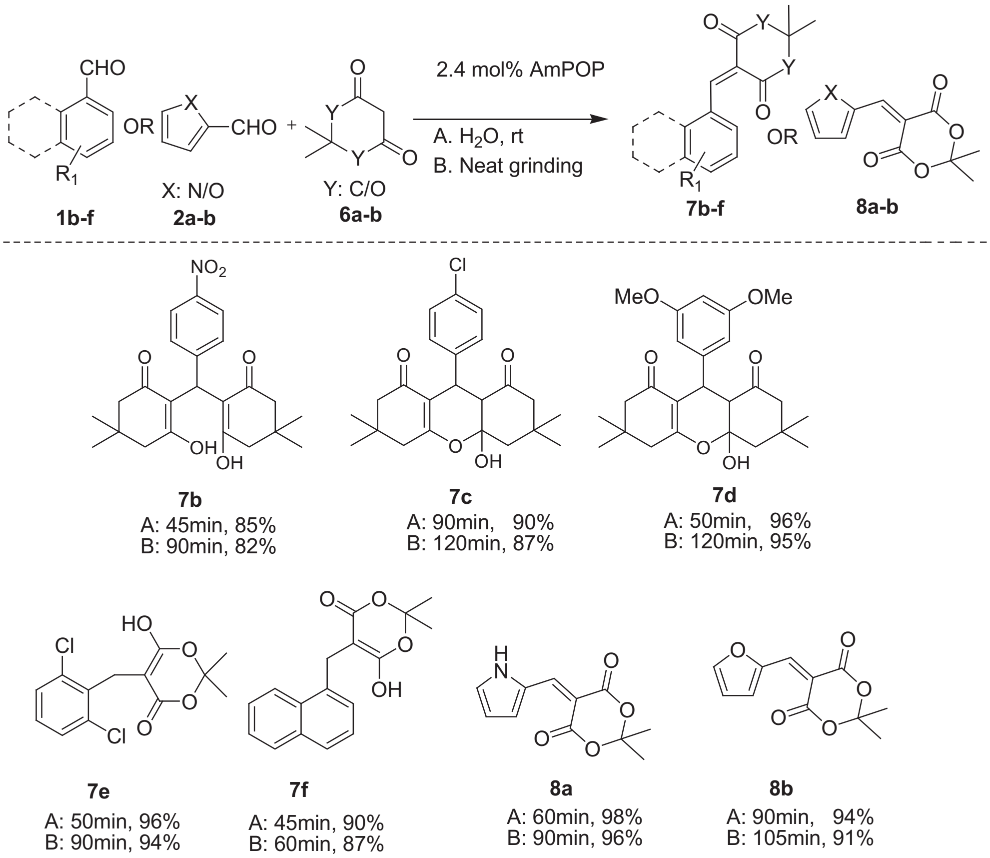
Screening of optimal reaction conditions (catalyst loading, solvent and reaction time). Reaction conditions unless specified otherwise: 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), in each solvent (5 ml), room-temperature stirring. Yields are given for isolated materials.

Entry	Catalyst (mol%)	Solvent	Stirring time	Yield of **4c** (%)[b]
1	0	H_2O	5 h	10
2	0.1	H_2O	5 h	30
3	2.0	H_2O	2 h	80
4	**2.4**	$\mathbf{H_2O}$	**50 min**	**97**
5	3.8	H_2O	50 min	97
6	2.4	H_2O	30 min	82
7	2.4	H_2O	40 min	87
8	2.4	H_2O	1.5 h	97
9	2.4	THF	2.5 h	32
10	2.4	CH_3CN	2.5 h	10
11	2.4	CH_2Cl_2	2.5 h	23
12	2.4	$CHCl_3$	2.5 h	22
13	2.4	MeOH	2 h	65
14	2.4	EtOH	1 h	93

this study describes the first example of a metal-free amorphous organic polymer that acts as a highly efficient heterogeneous catalyst for C − C bond formation under solvent-free conditions.

The general scheme for the studied Knoevenagel condensations in water, as well as under solvent-free manual grinding conditions, using AmPOP as catalyst is shown in Scheme 1. To establish the optimal reaction condition, an initial catalyst screen was conducted using an equimolar mixture of 4-chlorobenzaldehyde **1c** and malononitrile **3** in water at neutral pH. Product **4c** (Scheme 2) was obtained in 97% yield in presence of 2.4 mol% AmPOP after 50 min (Table 1, entry 4). Notably, the product was isolated in poor yields (10%) in the absence of catalyst (Table 1, entry 1) (see SI, Fig. S19). Further investigations showed that the use of smaller amounts of the catalyst (0.1–2.0 mol%) yields less product, while increasing the amount of the catalyst (to 3.8 mol%) did not further improve the yields. Using the optimal catalytic loadings of 2.4 mol%, a subsequent solvent study showed that water is the most effective solvent for the Knoevenagel condensation at room temperature using the same model reaction (Table 1, entry 4, 9–14). The model reaction was then further studied to compare the effect of reaction time on the product yield. It was found that stirring at room temperature for 50 min in water affords the best yields (Table 1, entry 4, 6–8).

Once the most effective reaction conditions have been determined for the formation of compound **4c** (Scheme 2), the scope and generality of the developed protocol was further tested by subjecting various reactants in form of substituted aromatic and heteroaromatic aldehydes and active methylene compounds (*viz.* malononitrile, 5,5-



Scheme 3. Synthetic targets (above) and the obtained yields (an average of two runs) for compounds **7** and **8** using two different synthetic methods: stirring of the reactants in a round bottom flask at room temperature (**A**) and milling under solvent-free conditions (**B**). Method **A**: Aldehyde (1 mmol), cyclic active methylene compound (1 mmol for **7e-f**, **8a-b**; 2 mmol for **7b-d**), catalyst AmPOP (2.4 mol%), H_2O (5 ml), room temperature stirring; method **B**: Aldehyde (1 mmol), cyclic active methylene compound (1 mmol for **7e-f**, **8a-b**; 2 mmol for **7b-d**), catalyst AmPOP (2.4 mol%), in agate mortar & pestle for above mentioned time period in absence of added liquid. The percentage yields are given for isolated products.

dimethylcyclohexane-1,3-dione and 2,2-dimethyl-1,3-dioxane-4,6-dione) to the same reaction conditions (yields: 82–97%). Knoevenagel condensation reactions involving heterocyclic aldehydes (2a-2b) also gave excellent yields (yields for 5a and 5b: 92–98%) whereby no occurrence of a polymerization reaction was observed (Scheme 2) [30,31]. Reactions involving malononitrile and aryl aldehydes bearing electron-withdrawing or donating groups completed within 105 min to give the alkene product in high yields.

The versatility of the investigated AmPOP-assisted Knoevenagel condensation reactions was further examined by expanding the range of suitable reactants to cyclic methylene derivatives (Scheme 3). The Knoevenagel condensation reaction was pursued under mild experimental conditions, namely through stirring of the reactants in water at room temperature and through solvent-free milling. All products were obtained under both reaction conditions in high yields (82–98%) and in short reaction times (45–120 min). In addition, the reaction of one mole equivalent of aldehydes (4-nitrobenzaldehyde **1b**, 4-chlorobenzaldehyde **1c** and 3,5-dimethoxy benzaldehyde **1d**) with a two mole equivalent of dimedone **6a** resulted in the formation of Knoevenagel-Michael addition products (Scheme 3, **7b**: 85%, **7c**: 90% and **7d**: 96%), similar to those reported by Rostamizadeh *et. al* [32], while reactions involving substituted aldehydes and Meldrum's acid resulted in the formation of arylidene products with good to excellent yields (**7e-7f** & **8a-8b**; 87–98%). It is noteworthy that reactions pursued in stirred aqueous suspensions reached completion faster than those conducted under solvent-free mechanochemical conditions. This may be attributed to the faster diffusion rates of the reactants into the AmPOP in water, as compared to the diffusion of molecules through the AmPOP under solvent-free conditions. All products were characterized using ^{1}H and ^{13}C NMR spectroscopy, MS (SI document, Fig. S19) and crystallographic methods (either single crystal or powder X-ray diffraction, PXRD) (SI document, Figs. S20-S29 and Table S2). In addition to the examples discussed above a few more Knoevenagel condensation products have been synthesized using AmPOP and discussed elsewhere [33]. PXRD was used as a characterizing tool to compare the products obtained using solvent-free milling with the respective products obtained from room temperature stirring (SI document, Figs. S21-S29).

After completion of the reaction, the AmPOP catalyst was recovered quantitatively by dissolving the reaction mixture in ethanol and through subsequent separation of the virtually insoluble catalyst by filtration. The re-activation of the catalyst is achieved by soaking the recovered material in methanol, followed by drying under reduced pressure for one hour. The catalyst was shown to exhibit a slight decrease in surface area once recycled although no signs of chemical decomposition were detected (see SI, Fig. S14 and Table S1), thus indicating that the recycling procedure needs to be further optimised. The recyclability of AmPOP was evaluated using the standard reaction condition in presence of 4-chlorobenzaldehyde and malononitrile. The recycled AmPOP catalyst yielded compound **4c** in no less than 85% within 60 mins once it was recycled up to five times (see SI, Fig. S18).

4. Conclusions

In conclusion, we have described the synthesis of a chemically stable porous organic polymer that effectively catalyses Knoevenagel condensation reactions of various substituted aromatic/ heteroaromatic aldehydes in very mild and environmentally benign experimental conditions in water and at room temperature. To the best of our knowledge, only a few reports [34,35] are available for porous organic polymer that catalyses Knoevenagel condensation reaction under metal-free and pH-neutral conditions in water. We also demonstrated that the condensation reaction can be effectively catalysed with the polymer under solvent-free mechanochemical conditions. The high relevance and broad applicability of the Knoevenagel condensation reactions and the high catalytic efficiency and recyclability of the polymeric catalyst offers the development of environmentally-friendly industrial processes relying in such type of chemical transformation.

Dedication

We dedicate this work in memory of Prof. Israel Goldberg on his sudden demise.

Declaration of Competing Interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

The Supporting Information is available online at the Elsevier Publications website. General Information about synthesis and characterization of the AmPOP (ss-NMR, PXRD, Electron microscopy analysis, Spectroscopic analysis, Thermal analysis, Gas adsorption analysis); Catalysis Study of AmPOP and characterization of the Knoevenagel products (NMR spectroscopic analysis, GC–MS, HR-MS analysis, SC-XRD analysis, PXRD analysis of representative products prepared using NG). Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2021.106304.

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