Research Article

A nanoporous organic polymer constructed from a 1,3,5-triazine derivative via ethynyl cyclotrimerization reaction: Synthesis and carbon dioxide capture

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ABSTRACT

Ethynyl cyclotrimerization reaction of 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine (2) results in a nanoporous organic polymer. The structure of the resulting polymer, TNOP is characterized by FT-TR, solid-state ^{13}C NMR spectroscopy and elemental analysis. TNOP shows high thermal stability and is highly porous with Brunauer-Emmett-Teller specific surface area (S_{BET}) of 755 m^2 g^{-1}, total pore volume of 0.43 cm^3 g^{-1} and relatively narrow pore size distribution. For applications, TNOP possesses a moderate carbon dioxide uptake of 1.02 mmol g^{-1} (4.49 wt%) at 298 K and at 1.03 bar, suggesting its potential application in storing and capturing carbon dioxide.

Keywords: Nanoporous organic polymers; Microporous polymers; Triazine; Carbon dioxide capture
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INTRODUCTION

Nanoporous organic polymers (NOPs) have attracted increasing interests because of their potential applications in extensive areas including gas storage, gas separation, and heterogeneous catalysis, *etc*[1-4]. Compared with the traditional porous materials such as silica, zeolites, and metal-organic frameworks (MOFs)[5-7], NOPs have intriguing advantages in terms of the combining wide synthetic diversity with chemical and thermal stability, and low skeletal density. Therefore, various NOPs have been developed including polymers of intrinsic microporosity (PIMs), hypercrosslinked polymers (HCPs), covalent organic frameworks (COFs), and conjugated microporous polymers (CMPs)[1-2].

NOPs are often synthesized through the direct synthesis methodology by selecting proper monomers and polymerization reactions because this strategy has characteristic advantages: a high utilization of the starting materials and easy formation of micropores[1]. The monomers are generally selected to have multifunctional reaction sites and rigid structures to form crosslinking networks with stable pores[2]. To provide reaction sites and rigidity, aromatic compounds are commonly utilized as the monomers. The chemical reactions are required to efficiently link the monomers together. Various polymerization reactions have been developed, such as Sonogashira coupling, Yamamoto coupling, Heck coupling and cyclotrimerization reaction[1-2].

Triazine-containing NOPs materials have attracted specific interests because introduction of thermally stable and electron-withdrawing triazine units into NOPs systems could be advantageous for stability and also in terms of electronic state manipulation of the polymers[8-9]. Most of this kind of porous materials are prepared by nitrile cyclotrimerization reaction, while the triazine units and crosslinking networks are simultaneously formed, but the formation commonly needs high reaction temperature[1-2, 10]. It is apparently easier to construct them based on triazine derivatives containing other reactive groups, such as vinyl and ethynyl by the mild polycondensation techniques. Ethynyl cyclotrimerization reaction is an ideal polymerization method to construct porous polymers because no functional groups were remained after the reaction and the resulting materials possess high thermal and chemical stability[11-12].

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One important potential application for NOPs materials is the capture and separation of CO_2. Efficient CO_2 adsorption depends not only on the surface area of the materials, but also on the chemical functionality. As previous reports, the introduction of functional groups such as amines or carboxylic acids can improve CO_2 adsorption. For example, it has demonstrated that nitrogen-rich triazine units could be advantageous for CO_2 adsorption in porous polymers[13].

Herein, we select a triazine derivative, i. e., 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine (**2**) as the starting monomer and synthesize a novel nanoporous organic polymer, TNOP, via ethynyl cyclotrimerization reaction (see Figure 1). Moreover, its application in capturing CO_2 was explored.

EXPERIMENTAL SECTION

Materials: Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was dried by distillation over sodium metal prior to use. Dioxane and *i*-Pr$_2$NH anhydrous solvents were distilled from their respective mixture with CaH$_2$. 2,4,6-Tris(4-bromophenyl)-1,3,5-triazine (**1**) was synthesized as the previous report[14].

Characterizations: Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor27 spectrophotometer. Elemental analyses were conducted using an Elementar vario EL III elemental analyzer. Field-emission scanning electron microscopy (FE-SEM) experiment was performed by using HITACHI S4800 Spectrometer. The high-resolution transmission electron microscopy (HR-TEM) experiment was performed by using a JEM 2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Thermogravimetric analyses (TGA) was performed with a MettlerToledo SDTA-854 TGA system in N_2 at a heating rate of 10 ℃ min^{-1} to 800 ℃. Nitrogen sorption isotherm measurement was performed on a Micro Meritics surface area and pore size analyzer. Before measurement, the samples was degassed at 100 ℃ for least 12 h. Nonlocal density functional theory (NL-DFT) pore size distributions were determined using the carbon/slit-cylindrical pore mode of the Quadrawin software. Carbon dioxide (CO_2) adsorption isotherms at 298 K were measured on a Micrometrics ASAP 2020. Before measurement, the sample was degassed at 150 ℃ for at least 15 h.

Synthesis of 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine (2): 2,4,6-Tris(4-bromophenyl)-1,3,5- triazine (**1**, 1.64 g, 3 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.13 g, 0.18 mmol), CuI (0.017 g, 0.09 mmol), and PPh$_3$ (0.094 g, 0.36 mmol) were placed in a three-bottled flask; anhydrous *i*-Pr$_2$NH (40 mL) and trimethylsilylacetylene (1.18g, 12 mmol) were added via a syringe. The reaction mixture was reflux overnight and then cooled down to room temperature. Then the mixture was filtrated and concentrated in vacuum. CH_2Cl_2 was added to dissolve the residue and filtered through a pad of Celite. The solvent was removed in vacuum and yellow solid was afforded.

Then the solid was dissolved in a mixture of THF/CH$_3$OH and K$_2$CO$_3$ was added. The resulting mixture was stirred for 24 h at room temperature, washed with water, and the aqueous phase was extracted with CH_2Cl_2 thrice. The organic layers were combined, washed with brine, and then dried over MgSO$_4$. The solution was filtrated, concentrated and the crude product was afforded. Pure white product (0.98g, 86% yield) was obtained by column chromatography. IR (KBr pellet cm^{-1}): 3284, 3060, 3014, 1633, 1591, 1536, 1489, 1383, 1270, 825, 766, 728, 646, 598, 532, 443. ^{1}H NMR (CDCl$_3$, δ, ppm): 3.11 (s, 3H, C≡CH), 7.56 (dd, 12H, Ar-H), 7.85 (dd, 12H, Ar-H). HRMS (FAB) calcd for $C_{27}H_{15}N_3$ (MH$^+$): 382.4386, found 382.4376.

Synthesis of TNOP: Compound **2** (0.76 g, 2 mmol) and Co$_2$(CO)$_8$ (0.10 g, 0.3 mmol) were dissolved in anhydrous dioxane (15 mL) under argon. The mixture was stirred and bubbled by argon under stirring for 0.5 h at room temperature. The resulting solution was then heated at 115 ℃ for 2 h and cooled to room temperature. The mixture was filterated and washed with dioxane, THF, water, CH$_3$OH and acetone. Further purification was performed by exaction with THF for 24 h. The solid was dried in vacuum at 80 ℃ for 48 h. The product (0.8 g, ~100% yield) was obtained as a brown solid. IR (KBr pellet cm^{-1}): 3282, 3059, 3016, 1635, 1592, 1538, 1492, 1385, 1265, 826, 763, 726, 644, 595, 532, 443. Elemental analysis calc. (wt.%) for $C_{27}H_{12}N_3$: C 85.70, H 3.20, N 11.10; Found C 84.82, H 3.45, N 11.55.

RESULTS AND DISCUSSION

As shown in Figure 1, the starting monomer, 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine (**2**), was synthesized from 2,4,6-Tris(4-bromophenyl)-1,3,5-triazine (**1**) by Sonogashira coupling reaction with trimethylsilylacetylene and deprotection of trimethylsilyl groups. Then the nanoporous polymer, TNOP, was synthesized by ethynyl cyclotrimerization base on compound **2** catalyzed by Co$_2$(CO)$_8$ in dioxane at 115 ℃ for 2 h[11]. The product was recovered by filtration and washed with several solvents. An exhaustive Soxhlet extraction was performed using

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THF for further purification. The resulting polymer was insoluble in common solvents, such as THF, CH_3OH, H_2O and *N,N*-dimethyl formamide (DMF).
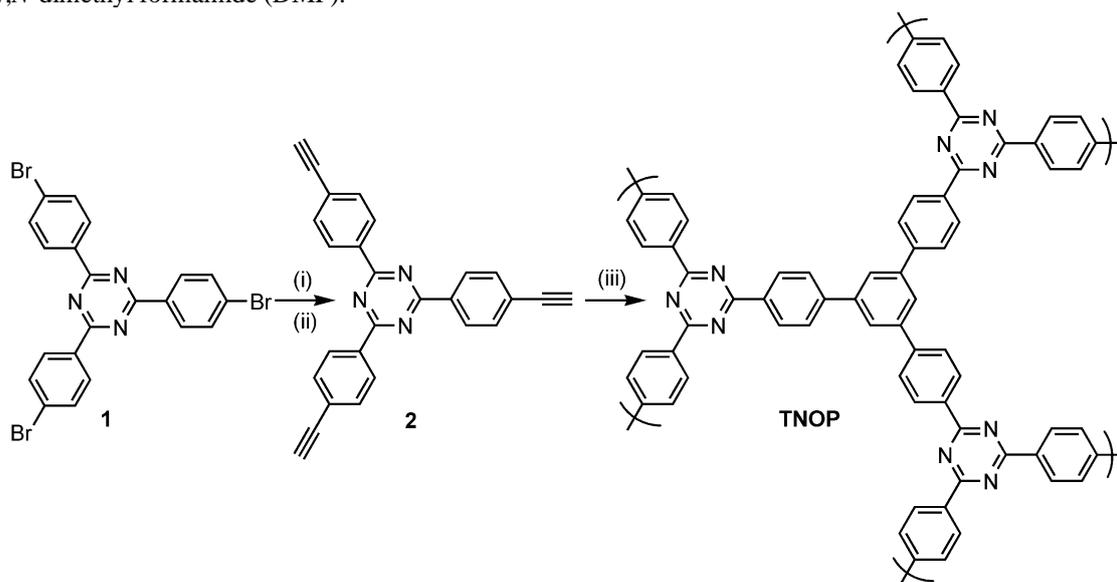

Figure 1. Synthesis of compound 2 and polymer TNOP. (i) $Me_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$/CuI, PPh_3, *i*-Pr_2NH, reflux overnight; (ii) THF/CH_3OH, K_2CO_3, R.T., 24h; (iii) $Co_2(CO)_8$, dioxane, 115 °C, 2 h

The structure of the polymer was characterized by FT-IR spectroscopy (Figure 2a). The peaks from 1640 to 1450 cm^{-1} with moderate intensity can be assigned to the C=C and C=N stretching vibrations from the triazine and phenyl groups. The intensity of the alkynyl C-H stretching vibration at ~3285 cm^{-1} obviously decreased compared with that of compound **2**, indicating that the trimerization reaction successfully occurred. The residual ethynyl groups suggested that higher surface area could be probably achieved after the trimerization reaction completely occurred. TGA result revealed that the polymer was stable up to 350 °C (decomposition temperature at 5% mass loss) (Figure 2b), thereby indicating the polymer possessed high thermal stability.
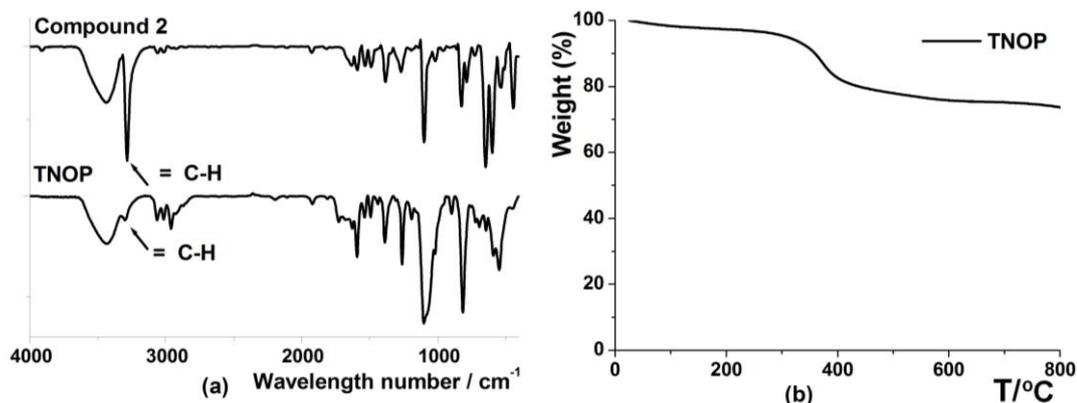

Figure 2. (a) FT-IR spectra of compound 2 and TNOP; (b) TGA curve of TNOP

The porosity of the polymer, TNOP was investigated by the nitrogen adsorption-desorption isotherm measured at 77 K. As shown in Figure 3a, TNOP showed a sharp uptake at low relative pressure and a gradually increasing uptake at higher relative pressure with hysteresis, suggesting the presence of micropore and mesopore within the structure. The specific surface area determined using the Brunauer- Emmett-Teller (BET) equation was 755 m^2 g^{-1} and total pore volume was 0.43 cm^3 g^{-1} calculated at P/P_0=0.99. The micropore pore volume and the micropore area were 0.26 cm^3 g^{-1} and 430 m^2 g^{-1}, respectively, using the *t*-plot method based on the Halsey thickness equation. The pore size distribution (PSD) was evaluated by nonlocal density functional theory (NL-DFT) (Figure 3b). TNOP network showed relatively narrow PSD with major micropores with micropore diameter centered at 1.7 nm and a broad distribution of mesopore from 2~4 nm. This result was consistent with the shape of the N_2 sorption isotherm, indicating that this material possessed both micropore and mesopore. The polymer exhibited apparent BET surface area and pore volume, which was comparable to those of other porous polymers such as CMPs materials[15-16]. These results demonstrated that TNOP was highly porous.
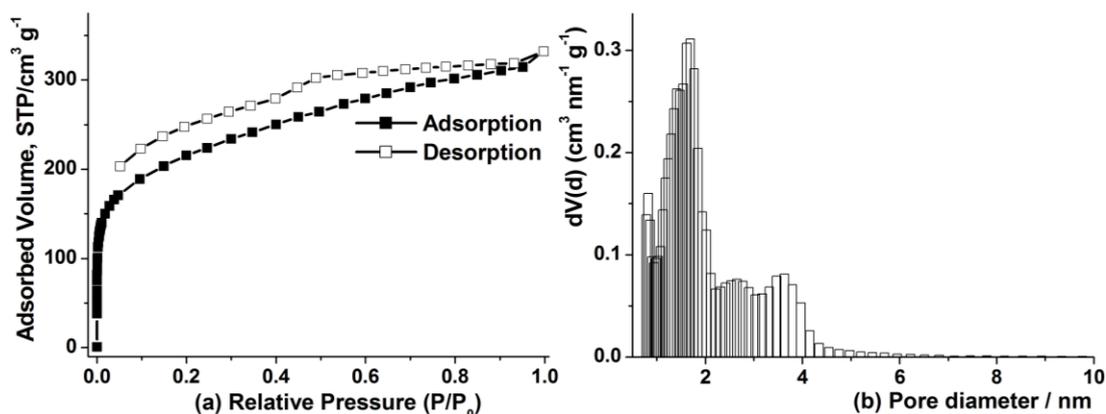
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Figure 3. (a) Nitrogen sorption isotherm of TNOP; (b) pore size distribution curve of TNOP

To evaluate the particle size and morphology of TNOP, field-emission scanning electron microscopy (FE-SEM) was performed. As expected, the material exhibited the irregular shape with a wide range of size distribution from 100 nm to several tens of micrometers (Figure 4a). The texture and ordering of the material was evaluated by high-resolution transmission electron microscopy (HR-TEM). The TEM image showed that TNOP exhibited the characteristics of porous materials, but no long-range ordering was observed (Figure 4b). In addition, the polymer was stable under the electron beam.
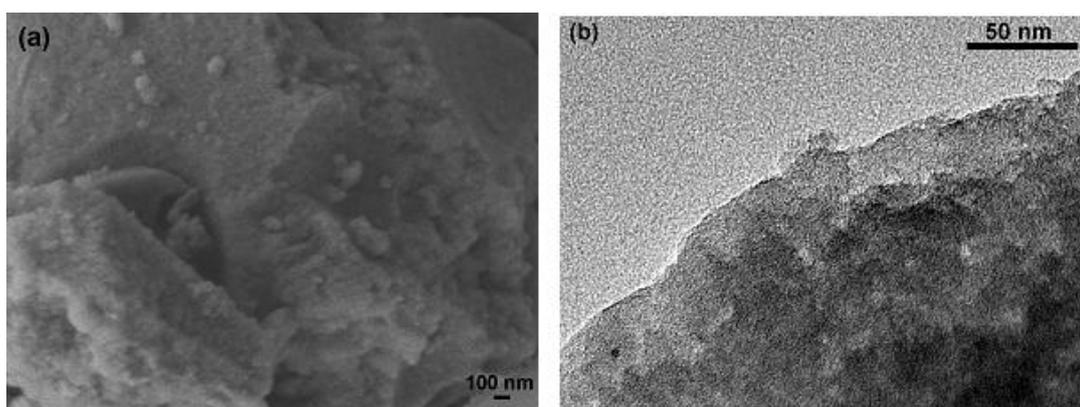

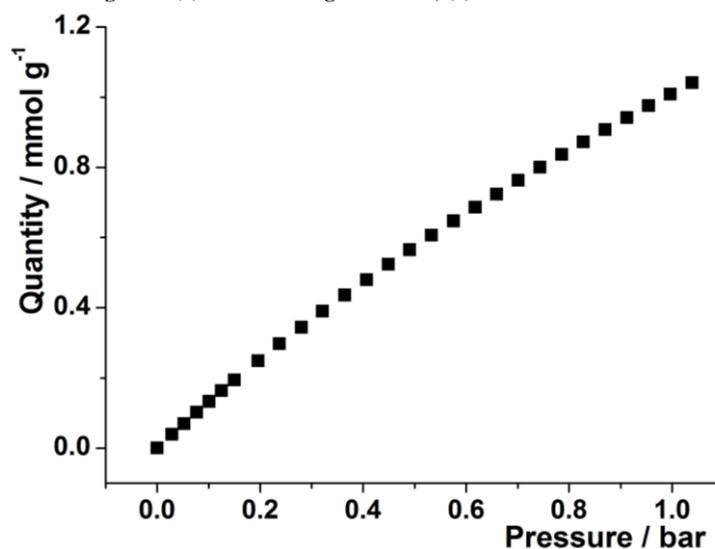**Figure 4. (a) FE-SEM image of TNOP; (b) HR-TEM of TNOP**

Figure 5. Carbon dioxide adsorption isotherm of TNOP at 298 K

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To investigate the potential application in carbon dioxide capture, the CO_2 adsorption isotherm for TNOP at 298 K was performed. As shown in Figure 5, the CO_2 capacity of TNOP was found to be 1.02 mmol g^{-1} (4.49 wt%) at 298 K and at 1.03 bar. This value was comparable to some porous materials such as MOFs material [17] and COFs material[18]. This result suggested that this material could be applied as the promising candidate for storing and capturing CO_2.

CONCLUSION

In conclusion, we have synthesized a novel nanoporous polymer based on a triazine derivative, 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine by using ethynyl cyclotrimerization reaction. The resulting polymer was highly porous with BET specific surface area of 755 m^2 g^{-1}, total pore volume of 0.43 cm^3 g^{-1}, as well as relatively narrow pore size distribution. Moreover, this material could be potentially applied in carbon dioxide capture and storage.

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