Aromatic Polyamines Covalent Triazine Polymer as Sorbent for CO₂ Adsorption

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Abstract. A novel aromatic polyamine covalent triazine-based polymer, CPDA was obtained by the polymerization of amino group (1,4-phenylenediamine) and cyanuric chloride. CPDA was characterized with Fourier Transform Infra-red spectroscopy (FTIR) and the thermal behaviour was studied with thermal gravimetric analysis (TGA) and derivative thermal analysis (DTA). A comparison study for CO_2 adsorption capacity on covalent organic polymer 1 (COP-1) and CPDA was performed. By introducing the aromatic ring into the nitrogen fertile triazine based system, the thermal stability of the network is enhanced. Polymer structure containing secondary amine functionality was observed in this study. Besides, the suggested chemical pathway is another approach to synthesis of covalent organic materials using economic monomers and absence of expensive catalyst.

1. Introduction

Accumulation of carbon dioxide (CO_2) over the past century, one of the anthropogenic greenhouse gases (GHG), has been considered as a causative factor to global warming and its high concentration in atmosphere is a pressing environmental concern. Fossil fuel combustion for world's energy demand contributes to a great extent to these emissions. International Panel Climate Changes (IPCC) suggested that CO_2 capture from flue gas in coal gasification system is considered as a possible technology to control CO_2 emissions in atmosphere by 80-90% [1].

For post-combustion CO_2 capture from flue gas, "wet scrubbing" method by chemical absorption using amine solutions such as monoethanolamine (MEA) is implemented in worldwide power plants. However, large amount of absorbent fluids and high regeneration energy are required to treat emitted CO_2. In practice, absorption and stripping towers are expensive, large, thick wall and heavy vessel. It usually needs high maintenances to keep the absorber stripper units in good condition. Furthermore, the degradation of alkanoamine and loss due to high temperature and pressure operating condition may result negative environmental impact[2]. Obviously, high capture cost and energy consumption of current technology are the major barriers to mitigate CO_2 emission in industrial sectors.

Eco-friendly and low energy requirement adsorption system, a prominent technology in comparison to other separation processes, is recognized to be attractive to complement or replace the current absorption technology[3, 4]. Therefore, utilization of appropriate adsorbents may potentially minimize the cost associated with CO_2 separation in the overall carbon capture and storage (CCS) approach.
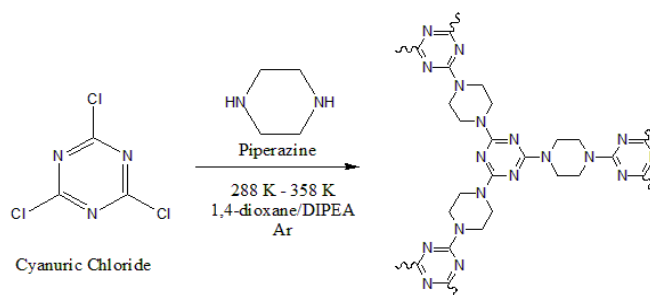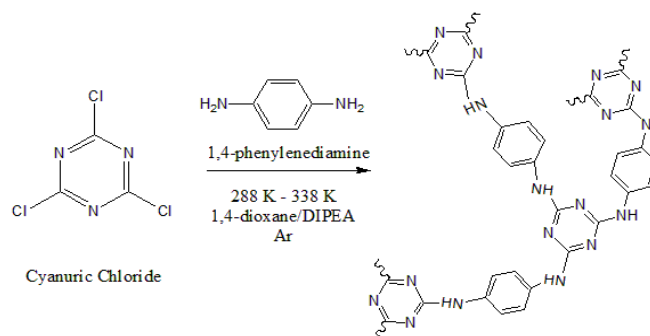
Figure 1 Chemical reaction pathways of (a) COP-1 and (b) CPDA

Different types of sorbent materials are currently under investigation for CO_2 capture. Typically, the requirements of suitable sorbents for CO_2 capture are high selective uptake of CO_2, facile regeneration of the sorbent at low-energy penalty, low cost of the sorbent material and good thermal stability. In post-combustion process, gas stream mixtures comprise a mixture of N_2 (70-75%), CO_2 (15-16%) and H_2O (5-7%) and therefore chemical stability towards H_2O is a key requisite in sorbent material design[5].

The CO_2 capture capacity of zeolite depends highly on its cation, charge density and size. Zeolites and metal-organic frameworks (MOFs) are known for their high CO_2 uptake capacity, however zeolite is hydrophilic, which causes its CO_2 adsorption to reduce greatly in the presence of moisture in gas while requiring a high regeneration temperature of around 573 K. The CO_2 adsorption performance of MOFs greatly decreases while operating with a gas mixture instead of pure CO_2[6]. Besides, MOFs tend toward chemical instability (oxidation, hydrolysis) because their dative nature of the metal–ligand bonds. As for activated carbon and ordered mesoporous silica, utilization of both materials for CO_2 capture is not practical as their CO_2 adsorption is low. It is apparent that sorbents with enhanced chemical stabilities and heats of adsorption at the borderline between strong physisorption and weak chemisorption (ca. 25–50 kJ mol^{-1}) are an attractive target to reach a good trade-off between selectivity and reversibility[5].

Recently, attention of researchers has turned to porous covalent-organic material due to applications in the fields of gas storage, gas separation, and heterogeneous catalysis[7-10]. Patel and coworkers successfully developed a series of triazine based covalent organic polymers (COPs) [11, 12] for CO_2 capture. Triazine based COPs consisting of high nitrogen content in network in particular COP-1[12] enhanced CO_2-N_2 selectivity (~25), *cf* 9 – 20 for microporous organic polymers (MOPs) [13]. In the same report, the experimental results also show that COP-1 is water resistant as the CO_2 adsorption remained stable even after boiling in water for a week at 373K. Other than that, COP-1 is highly regenerable as the CO_2 adsorption capacity remained at 100% after five cycles of compressing and decompressing. Nevertheless, the CO_2 uptake capacity of COP-1 i.e 1.38 mmol/g is below the

ordinary level. In principle, CO_2 adsorption capacity of 2–4 mmol/g should be exhibited by an optimum adsorbent for CO_2 capture in post-combustion process.

Development of amine-containing polymer is a new approach for energy efficient CO_2 capture with high CO_2 capacity and CO_2/N_2 selectivity. Among the types of amines, Sun et. al.[14] found that secondary amine functionality tailored in polymer network strike an appropriate balance between adsorption performance and energy efficient regeneration. Other than this, Ben et. al.[8] suggested that introducing aromatic ring in a building block is expected in increasing the internal surface area of a material by sufficient exposure of the faces and edges of phenyl rings. Moreover, replacement of C-C covalent bond or heterocyclic compound with rigid aromatic rings could further enhance the structural stability.

Nucleophilic substitution in COPs synthesis is a cost-efficient and simple pathway to develop porous polymers from low-cost monomers via catalyst free one-pot polycondensation. In view of the versatile organic synthesis reaction, 1,4-phenylenediamine was chosen and reacted with cyanuric chloride to form an aromatic polyamine triazine based polymers i.e CPDA in this study. A comparison of physicochemical properties and CO_2 uptake capacity of CPDA and COP-1 were also reported. A reaction scheme for COP-1 and CPDA is illustrated in Figure 1.

2. Methodology

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted. Cyanuric chloride and piperazine were purchased from Sigma Aldrich; 1,4-phenylenediamine was purchased from TCI chemical.

A. Synthesis of COP-1
Organic Linker: Piperazine
Cyanuric chloride (CC) (2.50 g, 13.6 mmol) was dissolved in dry 1,4 dioxane (30 mL). The solution was then added dropwise to a solution of piperazine (1.87 g, 21.7 mmol) and DIPEA (9.0 mL) in 1,4-dioxane (70 mL) with continuous stirring at 288 K under Ar atmosphere. Resulting white mixture was stirred at 288 K for 1 h and then for a further with 2 h at 298 K and then 21 h at 358 K. The off-white precipitate formed was washed with 1,4-dioxane and soaked with ethanol three times over a period of 12 h. COP-1 was obtained after the off-white slurry was dried at 393 K under vacuum for 5 h. Yield: 85%

B. Synthesis of CPDA
Organic Linker: 1,4-phenylenediamine
1,4-phenylenediamine (2.21 g, 20.3 mmol) was dissolved in 30 ml of dry 1,4-dioxane. The solution was added drop wise over a period of 1 h to a solution of 9.0 ml of N,N-diisoproylethylamine (DIPEA) and CC (2.50 g, 13.6 mol) which had been dissolved previously in 70 ml of dry 1,4-dioxane at 288 K under Ar atmosphere with continuous stirring. Light brownish mixture was stirred at 288 K for 1 h and then further with 2 h at 298 K. The system was raised to 338 K and under reflux for 21 h. The slurry was soaked with ethanol three times over a period of 12 h. CPDA was obtained after the light brownish slurry was dried at 393 K under vacuum for 5 h. Yield: 83%.

C. Material Characterization
Fourier transform infrared spectroscopy (FT-IR) spectra were recorded by Thermo Scientific Nicolet iS 10 FT-IR Spectrometer for monomers, COP-1 and CPDA using ATR technique. Thermal gravimetric analysis (TGA) was performed for COPs under nitrogen (N_2) atmosphere from 303 K to 873 K at a heating rate of 10 K/min.

D. CO₂ Adsorption and Desorption Measurement

Adsorption and desorption equilibrium measurement of CO_2 on CPDA and COP-1 was measured via volumetric method using mini BELSORP-Mini II (MicrotracBEL, Japan) at 298 K in a water bath. Both of the samples were dried at 428 K under vacuum for 5 h prior to adsorption measurement. Continuous dead volume measurement was performed in separate tube to compensate dead volume changes throughout the whole apparatus and allow high accuracy data to be collected.

3. Results and Discussion

The FTIR spectra in Figure 2 (a) and Figure 3 (a) show the functional groups of piperazine and 1,4-phenylenediamine, the organic linkers in this study. For Figure 2 (b) and Figure 3 (b), FTIR spectra reveal the functional groups of COP-1 and CPDA. Typically, the stretching vibration band of C-Cl of CC is assigned near to 850 cm⁻¹. Disappearance of C-Cl bond together with N-H band of amines at about 1630 cm⁻¹ as shown in Figure 2 (b) and Figure 3 (b) indicated formation of C-N linkage by substitution of amine group from piperazine and 1,4-phenylenediamine. It is noticeable that CPDA gives different IR spectrum with COP-1. Due to insertion of amine functionality in polymeric network, the IR spectrum of CPDA show the band at 3380 cm⁻¹ which is assigned to N-H stretching vibrations. Additionally, the presence of both benzene rings and triazine rings in a polymer network resulted a broad trough in the 1200 – 1600 cm⁻¹.
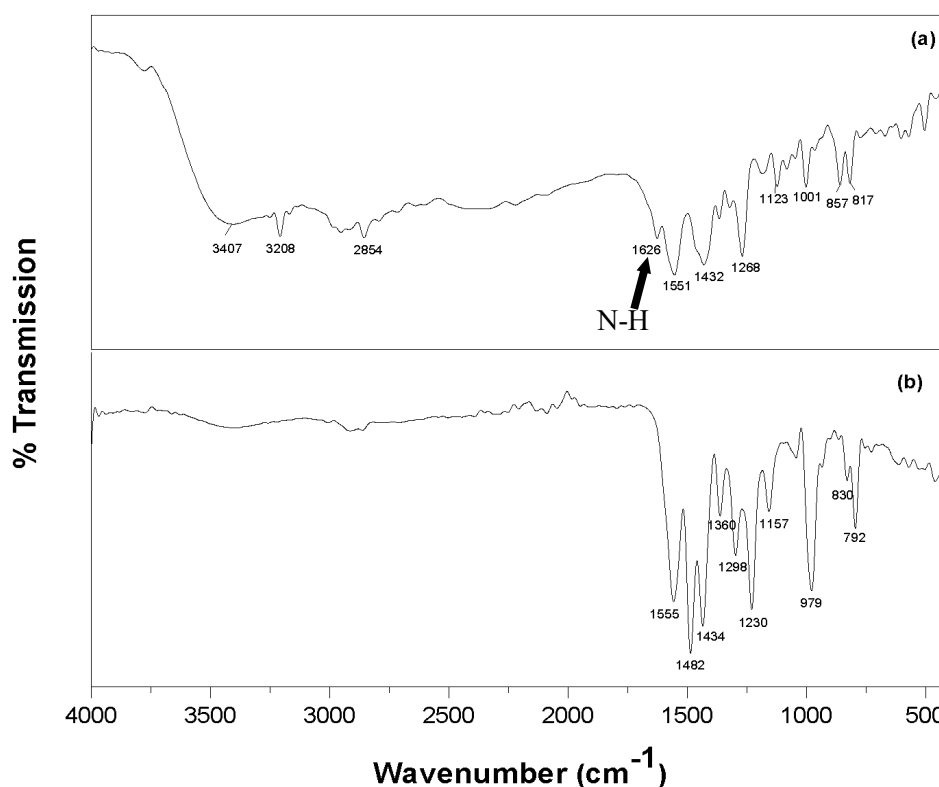

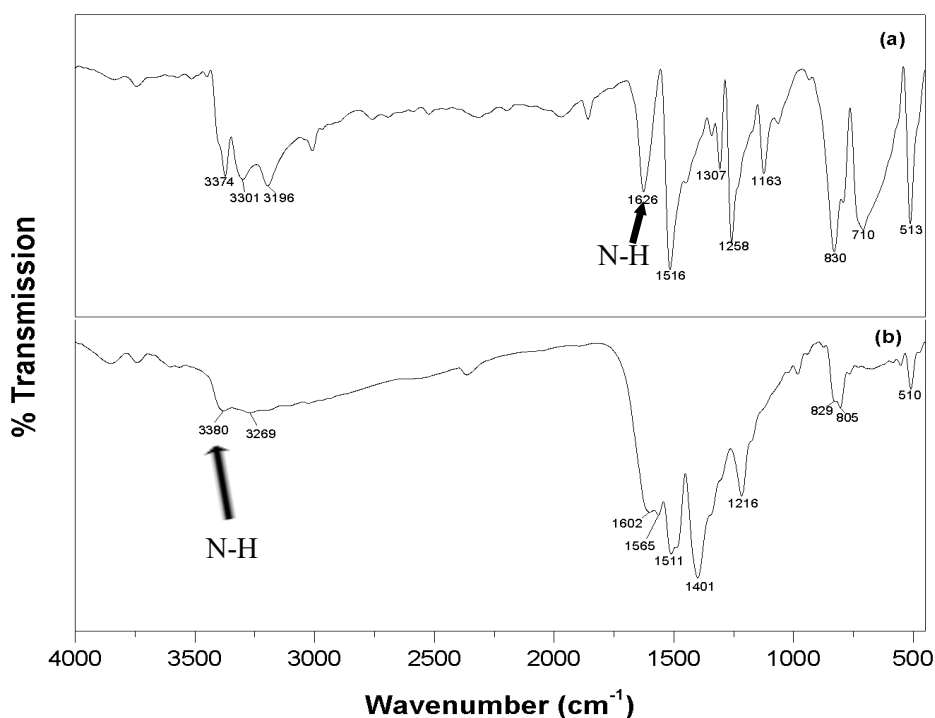Figure 2 FTIR spectra of (a) piperazine (b) COP-1

Figure 3 FTIR spectra of (a) 1,4-phenylenediamine (b) CPDA

Table 1 Mass loss in different degradation steps and temperature of half weight loss ($T_{50\%}$) in COP-1 and CPDA

COPs	Stage 1	Stage 2	Stage 3	$T_{50\%}$ (K)
COP-1	8.4	17.0	54.6	740
CPDA	9.3	11.6	49.3	905

Figure 4 (a) and (b) present thermal gravimetric analysis (TGA) for COP-1 and CPDA under N_2 atmosphere with a heating rate 10 K/min. The TGA curves shows that there is a gradual reduction weight when temperature increases, reaching 80% and 70% of weight loss from COP-1 and CPDA, respectively. The thermogram for COPs shows three weight loss stages representing three different polymer structures generated from stepwise polymerization. As shown in Table 1, similar weight loss i.e 8.4% and 9.3% were found in stage 1 for COP-1 and CPDA. In stage 2 and 3, about 6.4% and 5.3% higher reduction were found on COP-1 than CPDA as polymer chains breakdown begin. Moreover, the temperature at which 50% of weight loss has occurred ($T_{50\%}$) for the polymeric network with aromatic ring, CPDA, increases up to 165 K as compared to the COP-1 (740 K). As expected, the planar aromatic ring attributes to greater effect in thermal stability of a structure at higher temperature.

The results of derivative thermal analyses (DTA) of the COPs are shown in Figure 4 (b). In COP-1, three endothermic sharp peaks are observed at 339 K, 542 K and 732 K. Contrary, the endothermic peaks of CPDA are relatively broad than COP-1 which shows that the rate of decomposition in CPDA polymer is slower. A drastic change in DTA curve of CPDA at 873 K corresponds to the decomposition of main polymer chains while the degradation of polymer chain of COP-1 begins at 732 K.
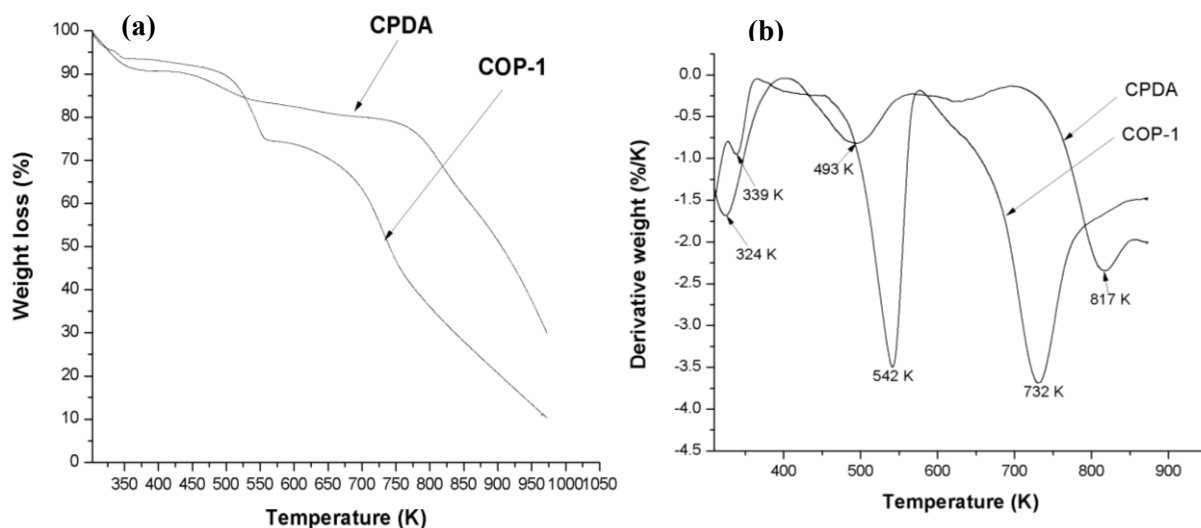
Figure 4 (a) TGA curves and (b) DTA curves for thermal decomposition of COP-1 and CPDA at a heating rate of 10 K/min in N_2

Low pressure CO_2 adsorption isotherms for COP-1 and CPDA at 298 K are graphically presented in Figure 5. The amount of CO_2 adsorbed in COP-1 (0.85 mmol/g) is slightly higher than CPDA (0.67 mmol/g) with the increase of relative pressure to 1. The conjugated effect of π electron from aromatic ring may weaken the N-H affinity towards CO_2 moieties. However, the CO_2 uptake for phenyl diamine linkers shows better performance than the polymer synthesized with aliphatic diamine linkers in our previous work[14]. In comparison to COP-1, CPDA shows saturation tendency as the relative pressure increases. However, the adsorption and desorption branches of CPDA are not reversible well which results small degree of hysteresis. The presence of amine functionality in CPDA is capable of chemisorption of CO_2 and therefore adsorbed CO_2 is not desorbed completely from the active sites. Similar adsorption isotherms were also illustrated in some of the reports with amine-containing adsorbents[15].
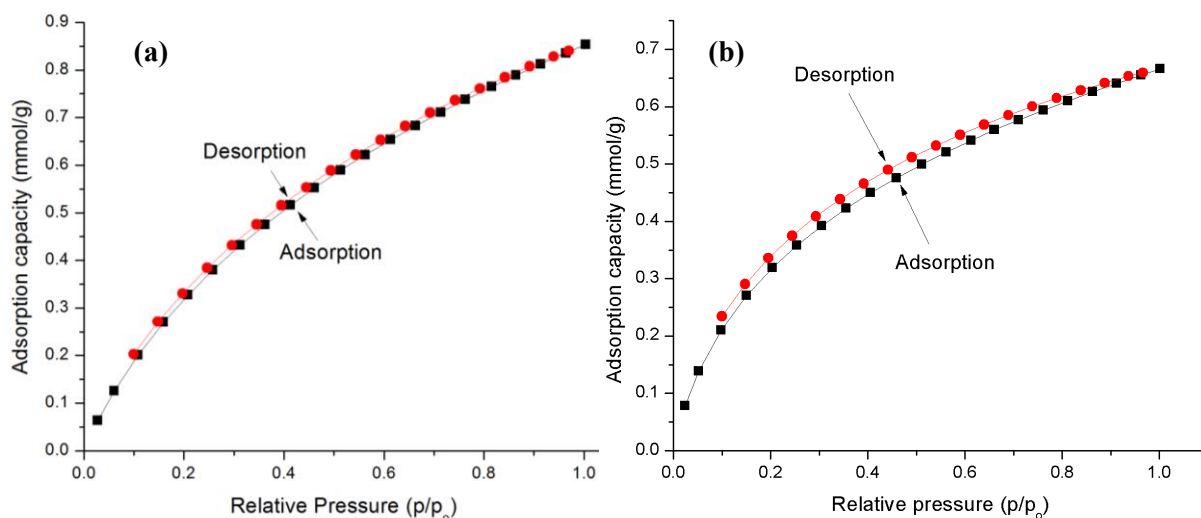

Figure 5 CO_2 adsorption desorption isotherms at 298 K for (a) COP-1 and (b) CPDA

4. Conclusion

In summary, triazine ring is covalently linked with aromatic diamine to form a novel organic polymer through catalyst free nucleophilic substitution approach. The polyamine network contributes a mild chemisorption towards CO_2 molecules. Still, low CO_2 uptake is observed as compared to COP-1. Enhancement of thermal stability of a network because of aromatic ring insertion is verified in this study.

Acknowledgements

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