

# Synthesis, characterization and evaluation of porous polybenzimidazole materials for CO<sub>2</sub> adsorption at high pressures

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**Abstract** Porous polybenzimidazole polymers have been under investigation for high and low pressure CO<sub>2</sub> adsorption due to the well-built stability under high pressure and at various temperatures. Pressure swing and temperature swing processes like integrated gasification combined cycle require materials which can operate efficiently at high pressure and high temperature and can remove CO<sub>2</sub>. In this manuscript we report synthesis, characterization and evaluation of two polybenzimidazole materials (PBI-1 and PBI-2), which were prepared with two different solvents and different cross-linking agents by condensation techniques. Low and high pressure CO<sub>2</sub> sorption characteristic of both the materials were evaluated at 273 and 298 K. Thermal gravimetric analysis showed high temperature stability up to 500 °C for the studied materials. PBI-1 has shown very good performance by adsorbing 3 times more (1.8025 mmol g<sup>-1</sup> of CO<sub>2</sub>) than PBI-2 at 0 °C and at low pressures. Despite low surface area results obtained via BET techniques, at 50 bars PBI-1 adsorbed up to 6.08 mmol g<sup>-1</sup> of CO<sub>2</sub>. Studied materials have shown flexible behavior under applied pressure that

leads to so-called “gate-opening” adsorption behavior and it makes these materials promising adsorbents of CO<sub>2</sub> at high pressures and it is discussed in the manuscript in detail.

**Keywords** Polybenzimidazole · CO<sub>2</sub> · Gas separation · High pressure

## 1 Introduction

Worldwide emergent demand of economically viable energy resources has compelled the nations to convert the naturally and abundantly available resources of fossil based fuels into alternative solutions that contains renewable energy sources and other various technologies that targets low CO<sub>2</sub> emission processes (Eftekhari and Van Der Kooi 2012). These energy production technologies have generated an unavoidable associated concern of CO<sub>2</sub> emission (Blok et al. 1997), which has subsequently caused various health and environmental issues (Muradov and Veziroglu 2005). Numerous techniques (Jansen et al. 1992; Farla et al. 1995; Ketzner et al. 2012) and materials (Maroño et al. 2014) have been used to capture and separate the unwanted CO<sub>2</sub> emitted at any stage during the industrial process of energy production from natural resources. Selection of material for CO<sub>2</sub> capture at different environmental and industrial conditions is still a major challenge for the energy generation sector. Large number of materials such as polymers (Du et al. 2011), co-polymers (He et al. 2014), organic/inorganic materials (Veselovskaya et al. 2013), metal organic composites (Seema et al. 2014), solids adsorbents (Krutka et al. 2013), liquid absorbents (Munoz et al. 2009), ionic liquids (Kumar et al. 2014) and various nano-composite structures have been investigated to

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capture CO<sub>2</sub> from the flue gas. Some of the major challenges that require due attention at the material selection stage are; CO<sub>2</sub> capturing efficiency, reproducibility, selectivity (Seema et al. 2014), capability (Markewitz et al. 2012), stability at various temperature and pressure conditions (Al-Khabbaz et al. 2014), multi-purpose applicability (Han et al. 2013) and economic practicability (Tzimas and Petevs 2005) of the material.

Studies have revealed that solid sorbents (Glier and Rubin 2013) are more suitable materials for CO<sub>2</sub> adsorption than the commonly used liquid sorbent systems as regeneration (Sanz et al. 2013) and CO<sub>2</sub> capture efficiency (Sanz et al. 2013) of the materials are considered. Solid materials such as activated carbon, SBA-15, metal organic frameworks (MOFs) (Liu et al. 2012) and zeolitic materials (Li et al. 2013) have been extensively investigated for CO<sub>2</sub> adsorption both at ambient and elevated temperature and pressure conditions. Although a recent study has shown that MOF-5 can behave as an efficient scrubber for CO<sub>2</sub> at elevated pressure of 225 bars, the material lost structural stability within few hours in moderate humid environment (Jung et al. 2013). Polymer based high performance membrane system utilizing various types of polymers as efficient adsorbent and porous polymer networks (PPNs) embedded with bases such as polyamines are fascinating materials and they have high efficiency and improved selectivity for CO<sub>2</sub>, though, very high post synthetic production cost is the major hindrance for the large scale applications of these materials (Lu et al. 2012). Studies on polybenzimidazole (PBI) structures and their potential applications in both gas storage and separation have also been reported (Rabbani and El-Kaderi 2012a, b; Ashourirad et al. 2015; Sekizkardes et al. 2014).

It has been suggested that materials with small mesoporous structure having pore sizes up to 3.0 nm can efficiently adsorb CO<sub>2</sub> at high pressure up to 220 bars and may have good applications in system like pressure swing adsorption (Casco et al. 2014). Incorporating various types of zeolites (Yang et al. 2011) modifies the mesoporous structure enhancing the thermal and mechanical stability of PBI, which in turn leads to increase in H<sub>2</sub> permeability and CO<sub>2</sub> selectivity at post combustion operating conditions such as temperature range of 180 and 230 °C (Yang and Chung 2013). High surface area, large pore volume and high isosteric heats of adsorption (Lu et al. 2012) were the key parameters which have effectively made solid sorbents more suitable for industrial level CO<sub>2</sub> adsorption. Additionally, in the environment containing H<sub>2</sub>S and other syngas compounds and the system operating at elevated temperature and pressure such as integrated gasification combined cycle plant (IGCC) (Li et al. 2013), lasting thermo-chemical stability is the basic necessity for CO<sub>2</sub> sorbents. Nevertheless recent studies have suggested that,

incorporating benzimidazole structure increases the selectivity, stability and efficiency of PPNs (Zhang et al. 2014). It has been demonstrated that PBIs have excellent thermal stability and possesses high CO<sub>2</sub> adsorption efficiency (Yu et al. 2013) both in dry and humid environment. The higher physicochemical stability was attributed mainly to the entire covalent bonding nature of polymers as compared to MOFs (Dawson et al. 2011) and therefore can be considered seriously for CO<sub>2</sub> adsorption at elevated pressures. PBI has been considered as one of the best HP polymers (Klaehn et al. 2011) which has very high thermal stability, mechanically robust molecular nature and tunable mesoporous structure (Lobato et al. 2010; Kumbharkar and Li 2012). Recent simulation study on pre-combustion CO<sub>2</sub> has suggested that PBI based membrane is more advantageous than commonly used Selexol™ CO<sub>2</sub> capture process due to the lower regeneration energy cost (O'Brien et al. 2009). Syngas cooling step can be excluded since PBI membrane operates at high temperature of 450 °C and pressure of 40 bars (Krishnan et al. 2009).

Based on the strong thermal and mechanical stability, suitable mesoporous structure, better CO<sub>2</sub> selectivity and affinity and economic (O'Brien et al. 2009) viability on large scale application of PBI, we investigated high pressure CO<sub>2</sub> adsorption of these materials. High pressure tests for such materials are rarely published in the open literature thus; this work addresses the limitations of PBI materials for their high pressure CO<sub>2</sub> adsorption performance.

## 2 Materials and methods

### 2.1 Materials

All chemicals were of analytical grade with 99.99 % purity and used as they are obtained from the manufacturers without any further modification. 3,3'-diaminobenzidine (DAB) and trimesic acid (TMA) were purchased from Tokyo Chemical Industry, Co. Ltd, Japan. Polyphosphoric acid (PPA), sodium carbonate (NaCO<sub>3</sub>), hydrochloric acid (HCl), nitrilotriacetic acid (NTA) and sodium chloride (NaCl) were provided by Sigma Aldrich. Gas components were also research grade with 99.99 % purity and they are obtained from Buzwair Inc., Qatar.

### 2.2 Materials preparation

Two different structures of polybenzimidazole PBI-1 and PBI-2 were prepared using two different routes. PBI-1 was prepared through already established method (Bhadra et al. 2010) with a small modification using 3,3'-diaminobenzidine, TMA and PPA, while PBI-2 was synthesized by mixing 3,3'-diaminobenzidine and nitrilotriacetic acid

without PPA. PPA was used as a polymerization solvent (Xiao et al. 2005). A typical synthesis process was used to prepare polybenzimidazole PBI-1, where, 7.5 mmol (1.6 g) of DAB and 5 mmol (1.05 g) of TMA were mixed in 25 ml of poly-phosphoric acid. After mixing and stirring at 250 °C for 12 h the product became sticky and was stacked on the container's walls. The solution was diluted and stirred vigorously to peel off from the container's walls. The solution was neutralized by adding certain amount of sodium carbonate, continuously stirred for 5 days and was filtered five times with the last one under vacuum conditions. To get rid of PPA, the filtrate was washed at least five times with sodium carbonate and was stored for further investigation as PBI-1.

Polybenzimidazole PBI-2 was prepared by mixing 7.5 mmol (1.6 g) of DAB and 5 mmol (0.956 g) of nitrilotriacetic acid (NTA) in 20 ml of 4 N HCl. The solution was continuously stirred for overnight at 200 °C, while an amount of sodium carbonate was added until the mixture changed from acidic to basic condition. A black color material was obtained by the end of procedure, which was filtered five times and washed with deionized water. After removing all of the NaCl by washing and filtration the final polymer was properly labeled (as PBI-2) and stored for further experiments.

### 2.3 Characterization and adsorption measurements

Fourier transforms infrared spectra of powder PBI materials were obtained with Bruker Vertex 80 FTIR spectrometer in the range of 4000–400  $\text{cm}^{-1}$ . Thermal stability analysis of materials was performed with Perkin Elmer Pyris 6 TGA instrument, where, samples were heated in  $\text{N}_2$  environment from 30 °C to 600 °C at the rate of 5 °C/min. Scanning electron microscopic study of samples were performed with scanning electron microscope (FE-SEM-Nova Nano-450). BET measurements were performed with Micromeritics ASAP 2420 surface and porosity analyzer. Pore volume measurement was performed with BJH analysis where average value of adsorption desorption were used in this manuscript. Prior to surface area and pore volume measurement samples were degassed at 150 °C for 5 h under vacuum. Elemental analysis was recorded with Bruker DMX400 NMR spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using solid-state cross polarization magic angle spinning (CP/MAS). Details of characterization results are given and discussed in Sect. 3.

### 2.4 High pressure adsorption and desorption study

Magnetic suspension balance (sorption apparatus) (MSB) from Rubotherm Prazisionsmess technik GmbH equipped with automated Teledyne Isco 260D pump was used to

measure the high pressure  $\text{CO}_2$  adsorption of the materials. Details of the experimental setup, apparatus description, operating principle and its schematic drawings are discussed previously by authors (Karadas et al. 2011). In a typical procedure a known amount was degassed for 5 h at 50 °C and was then kept in MSB sample holder for further evacuation at 25 °C for 5 h. The maximum set pressure (50 bars) was applied stepwise by increasing the pressure gradually from 1 bar up to 50 bars. Each pressure point took about 75 min to gain the set point of pressure and temperature, record four different sets of measurements and collect the data points. The system is fully automated and the pressure goes to next higher point after completing the previous measurement point. The system was also depressurized gradually from 50 bars to evacuation stage in order to get the desorption characteristics of the materials.

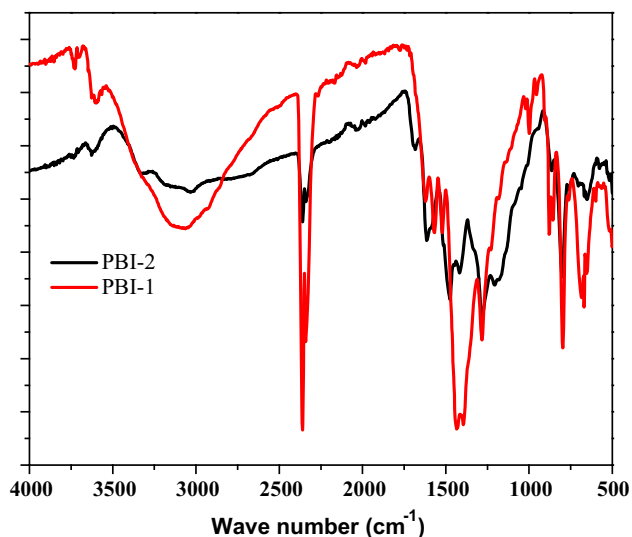
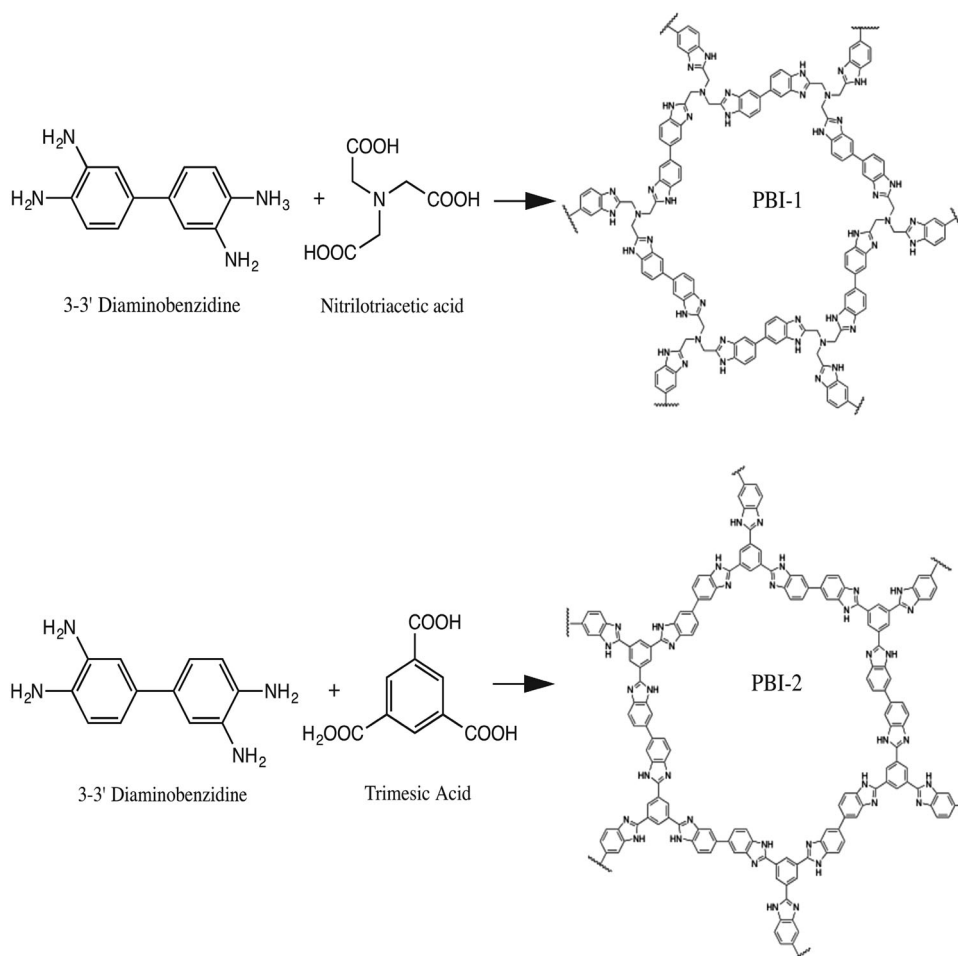
## 3 Results and discussion

### 3.1 Physical characterization

Two different types of polybenzimidazole PBI-1 and PBI-2 were prepared through one-step poly-condensation method by dissolving monomer DAB in two different solvents PPA to prepare PBI-1 and hydrochloric acid to synthesize PBI-2. Thermal and mechanical stability of polymers is related to the molecular weight, since PBIs were prepared in highly concentrated strong acid as polymerization solvents (Jouanneau et al. 2007) to obtain high molecular weight materials. TMA and NTA were used as cross linking agents to lengthen the molecular chain which subsequently increases the molecular weight, stability and tensile strength of the material (Su et al. 2012) (Fig. 1).

Figure 2 shows FTIR analysis of PBI materials cross-linked by two different cross-linking agents TMA and NTA represented as PBI-1 and PBI-2 respectively. FTIR spectra shows strong absorption in the benzimidazole ring region (1438–1631  $\text{cm}^{-1}$ ) (Valtcheva et al. 2014), which is the characteristic absorption of in-plane vibration and combined C=C, C=N ring vibration (Kumbharkar et al. 2011). The broad peak absorption between 2809 and 3450  $\text{cm}^{-1}$  is attributed to N–H asymmetric stretching (Bhadra et al. 2010), absorption at 798 and 877  $\text{cm}^{-1}$  could be assigned to C–H (Kang et al. 2013) out of plane bending and peaks at 1282  $\text{cm}^{-1}$  comes from breathing mode of benzimidazole (Suryani et al. 2011). Peak at around 3616  $\text{cm}^{-1}$  correspond to the O–H stretching which may be attributed to the presence of water in the sample since PBI is a hygroscopic materials and has high affinity for water molecules. It must be noted that two consecutive peaks at 2341 and 2360  $\text{cm}^{-1}$  represent the well complex nature and stretching mode of PBI, which is more prominent in case of

**Fig. 1** PBI-1 and PBI-2 synthesis reactions

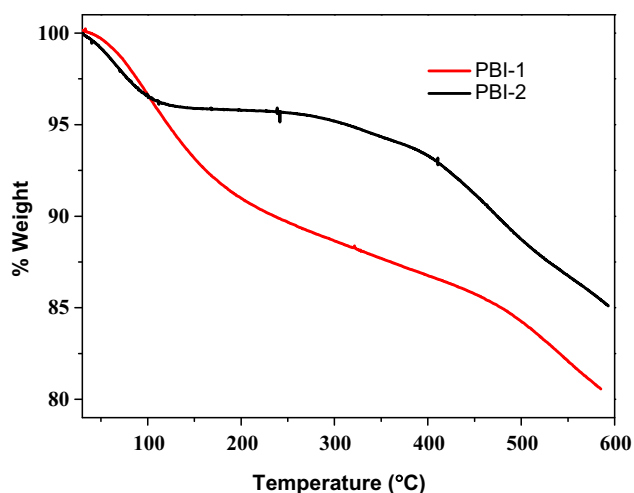


**Fig. 2** FTIR spectra of polybenzimidazole cross-linked by TMA (PBI-1) and NTA (PBI-2) (Color figure online)

PBI-1 (Cariou et al. 2010). These two peaks at 2341 and 2360 cm<sup>-1</sup> may also indicate trace amount of physisorption of ambient CO<sub>2</sub>. Most of the IR peaks are almost

similar but the two different peaks at 975 cm<sup>-1</sup> and 1585 cm<sup>-1</sup> that are observed only in PBI-1, can be associated to C-H bending and C-C in-ring stretching.

Figure 3 shows thermogravimetric analysis (TGA) of both samples, which were annealed in nitrogen environment from room temperature up to 600 °C at the rate of 5 °C min<sup>-1</sup>. The initial significant weight lost from 30 to 130 °C could be associated to the evaporation of water which was stored within the pores of materials. Various types of PBIs with dicarboxylic acids were reported in the literature and almost similar water loss for temperature at around 131 °C and similar initial decomposition temperature at around 430 °C were reported (Bhavsar et al. 2011). The middle and almost smooth weight degradation starting from 130 °C and reaches up to 430–450 °C is mainly due to burning of some un-reacted hydrocarbons such as CH<sub>2</sub>-group, cross linkers and gaseous products like ammonia and phenol (Iqbal et al. 2011; Han et al. 2011). In case of PBI-1 the middle region weight loss is larger than that of PBI-2, which can be mainly attributed to the residue of poly-phosphoric acid (PPA) retained in the porous structure after being washed few times (Asensio et al. 2004) rather



**Fig. 3** Thermo-gravimetric (TGA) analysis of polybenzimidazole PBI-1 and PBI-2 (Color figure online)

than to the polymer degradation (Musto et al. 1993). Figure 3 further reveals that PBI-2 and PBI-1 possess high thermal stability since, the initial decomposition of PBIs starts at around 490 °C. This strong and prolong thermal stability suggest that PBI can be used as an efficient CO<sub>2</sub> sorbent at high temperature up to 490 °C. This high thermal stability of PBIs can be attributed to the combined effect of aromatic ring in the molecular structure and intermolecular hydrogen bonding (Brooks et al. 1993; Kumbharkar et al. 2009).

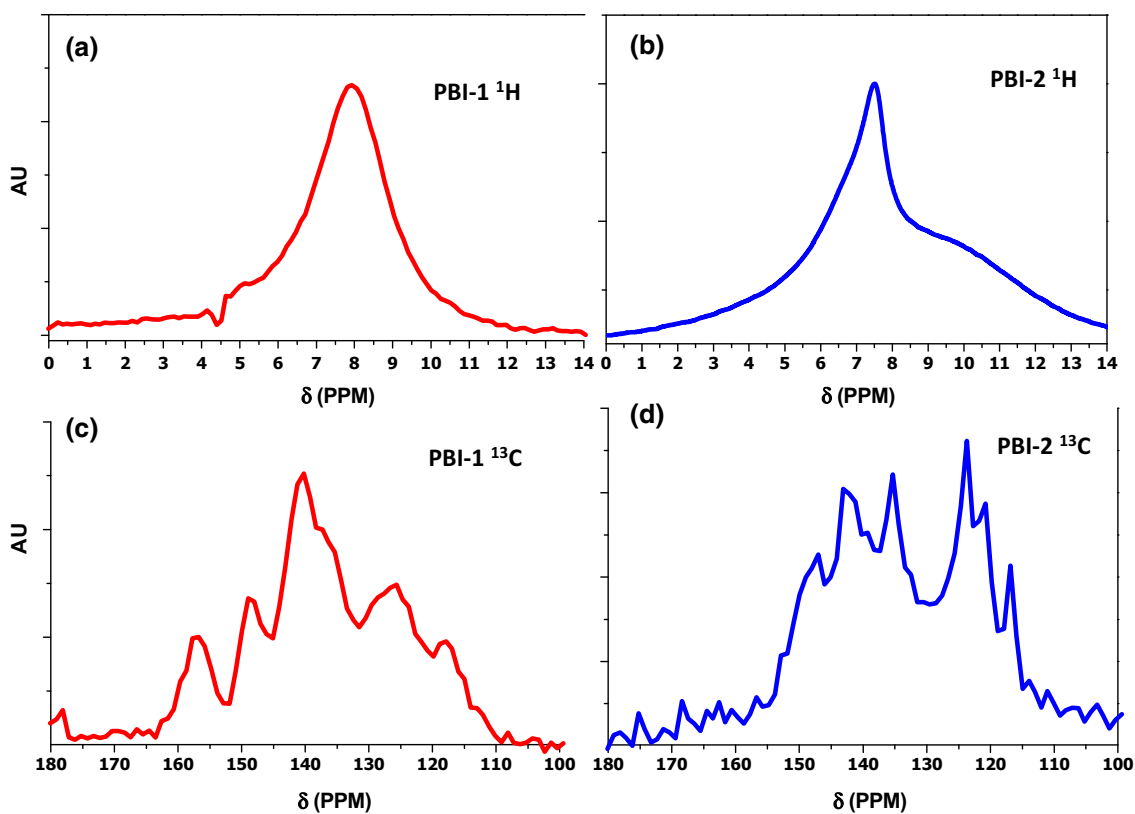
Figure 4 shows <sup>1</sup>H and <sup>13</sup>C NMR spectra of PBI-2 and PBI-1, indicating formation of cross linked PBI with two different cross linking agents and two different solvents (Su et al. 2012). Conti et al. have critically investigated the polymer–solvent interaction and has observed almost similar <sup>1</sup>H (at  $\delta = 7.94$ ) and <sup>13</sup>C (at  $\delta = 114$  and 116) NMR peaks with a minute variation, which can be attributed to the difference in cross linking agent (Conti et al. 2013). In our case <sup>1</sup>H NMR peaks were observed at chemical shift  $\delta = 7.9$  ppm and  $\delta = 7.65$  ppm in PBI-1 and PBI-2 respectively. The small shoulder between 9 ppm and 12 ppm in case of PBI-2 (Fig. 4b) can be associated to the presence of un-bonded water molecule (Brooks et al. 1993), where TGA analysis between 30 and 130 °C also indicated that PBI-2 has more water content than PBI-1. The fundamental <sup>13</sup>C NMR peaks of PBI were detected at  $\delta$  114 ppm, 117 ppm, 139/140 ppm, 147 ppm and 156 ppm for both PBI-2 and PBI-1 with very minor differences. These small variations in the peaks values of <sup>1</sup>H and <sup>13</sup>C in case of PBI-2 and PBI-1 can be attributed mainly to the difference in chemical environment surrounding the benzimidazole ring (Sannigrahi et al. 2010). Upon comparing <sup>13</sup>C NMR data of PBI-1 and PBI-2 at 156 ppm, 140/139 ppm it can be realized that the former has broader

peaks than PBI-2. This effect of peaks broadening in case of PBI-1 can be the reason of the protons associated with polymer backbone in the dried condition, where mobility of the water molecules narrows NMR peaks in PBI-2 (Guenther et al. 2013).

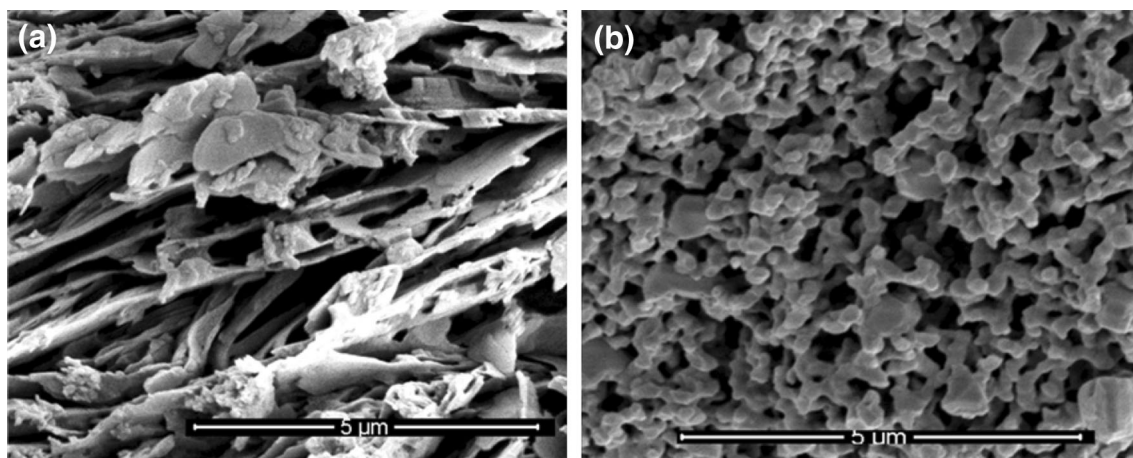
Figure 5 shows the SEM images of the PBI materials studied in this work. PBI-2 and PBI-1 cross-linked with different cross-linking agents have different morphological structures. PBI-2 has “plate-like” structure with large micrographs stacked upon each other with irregular and unoccupied space in between the plates. PBI-1 were synthesized with TMA has very small size particulates agglomerated with each other making a “sponge-like” arrangement. The significant variation in morphology of the two polymers may be attributed to the solvents effect on the nucleation and agglomeration of the materials. Since PPA is more viscous than concentrated HCl, thus it may slow down the agglomeration and coagulation process during synthesis (Wang and Chung 2006; Kumbharkar et al. 2011).

Figure 6 shows nitrogen up take isotherms of PBI-2 and PBI-1 materials having type-III characteristics with a visible hysteresis suggesting macro-porosity and amorphous nature of these materials (Zhang et al. 2014). Upon comparing the isotherms, it can be deduced that, PBI-1 has very weak hysteresis suggesting almost collapsed structure with very low porosity. Additionally, unlike PBI-2 nitrogen isotherm, PBI-1 nitrogen up take isotherms (Fig. 6b) do not coincide but remain open at the lower partial pressure values. Weber et al. also indicated such open ended nitrogen isotherm of PBI, which was mainly attributed to the filling of pores with doping agent (Weber et al. 2008a, b). PBI-1 was prepared with poly-phosphoric acid as a solvent and washed properly with de-ionized to remove the un-used reactants. Nevertheless, hysteresis begins at the very low relative pressure of (p/p<sub>0</sub>) 0.25 in case of PBI-1(6b) while it start at the relative pressure of about (p/p<sub>0</sub>) 0.7 for PBI-2. This clearly indicates that, PBI-1 may have more open head and irregular porous structure while PBI-2 pores probably have narrower openings. BJH pore volume distribution of PBI-2 and PBI-1 spread between 1.70 nm and 300.0 nm indicate that both the materials have mesoporous as well as macro-porous cages.

Table 1 represents the BET analysis and physical parameters of PBI-2 and PBI-1 along with low and high pressure CO<sub>2</sub> uptake at 273 K and ambient conditions. PBI-2 has comparatively larger BET surface area (of 12.07 m<sup>2</sup>/g), and larger pore volume, but, have smaller pore diameter than that of PBI-1. Although, surface area and pore volume of these materials are much smaller than the PBI prepared with tris(4-carboxyphenyl) amine (Yu et al. 2013), and Suzuki coupling polymerization techniques (Zhang et al. 2012) which have much higher surface



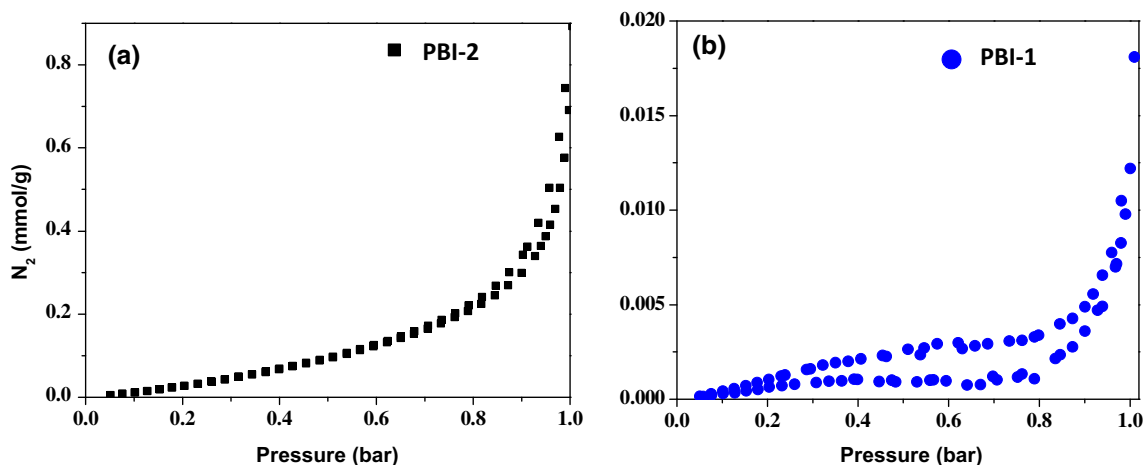
**Fig. 4**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polybenzimidazole. **a**  $^1\text{H}$  NMR peak for PBI-1, **b**  $^1\text{H}$  NMR peak for PBI-2, **c**  $^{13}\text{C}$  NMR peaks for PBI-1 and **d**  $^{13}\text{C}$  NMR peaks for PBI-2



**Fig. 5** Scanning electron micrographs of **a** BPI-2 and **b** PBI-1

areas of  $358\text{ m}^2/\text{g}$  and  $158\text{ m}^2/\text{g}$  and pore volume of  $0.316$  and  $0.159\text{ cm}^3/\text{g}$  respectively. PBI-2 and PBI-1 have higher pore diameters of  $12.38$  and  $18.59\text{ nm}$  respectively as compared to the  $10\text{ nm}$  pore size of commercial (Ogunlaja et al. 2014) PBIs materials and those synthesized with silica hard template (Weber et al. 2007). These significant

differences in physical parameters (such as surface area and pore volume) of PBIs materials in literature to the present work may be related to the synthesize routes, chemical nature of the monomers (Han et al. 2010), linking agents (Zhao et al. 2012) and network structure (Weber et al. 2008a, b).



**Fig. 6** Nitrogen adsorption-desorption isotherms of PBI-2 **a** and PBI-1 **b** after degassing at 120 °C for 5 h. Isotherm of PBI-1 **b** is with more refined y-axis values indicating very weak hysteresis with even open head starting from relative pressure of (p/p<sub>0</sub>) 0.25

**Table 1** A summary of PBI materials for their surface area, pore volume, pore size via BET measurements

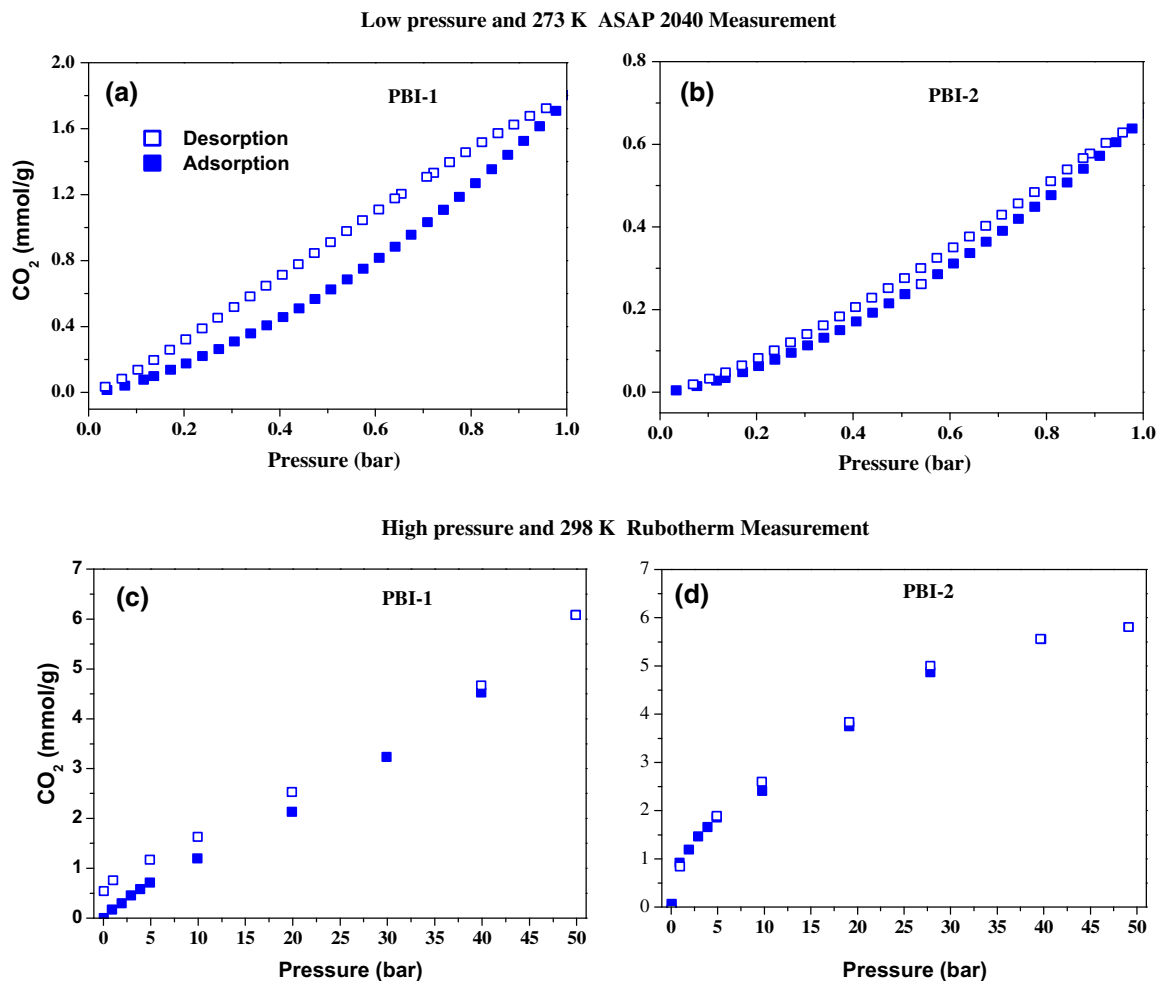
Material	Surface area (m <sup>2</sup> /g)		BJH Pore volume (cm <sup>3</sup> /g)	Average pore size (nm)	Adsorbed CO <sub>2</sub> (mmol/g)		
	BET	Langmuir			1 bar (273 K)	50 bars (298 K)	250 bars (323 K)
PBI-1	0.33	0.41	0.001	18.59	1.80	6.08	9.14
PBI-2	12.07	16.77	0.034	12.38	0.67	5.98	27.04

### 3.2 CO<sub>2</sub> adsorption: desorption measurements

Both low pressure and high-pressure adsorption-desorption measurements were conducted for PBI-2 and PBI-1 materials. We modified one of the six ports of Micromeritics ASAP 2420 surface and porosity analyzer for low-pressure CO<sub>2</sub> adsorption measurements. On the other hand, as mentioned previously, we used Rubotherm<sup>®</sup> fully automated MSB for the high-pressure adsorption data collections. Figure 7a, b show the low pressure sorption performance and Fig. 7c, d show the high pressure sorption performance for both the PBI-1 and PBI-2 materials respectively. The larger pore diameter of PBI-1 than PBI-2 shows that, PBI-1 has favorable mesoporous structure with wider pore channels. These wider channels may facilitate transport of gas molecules (N<sub>2</sub>/CO<sub>2</sub>) to the inner-stacked layers of capillaries during adsorption. Conversely, during desorption we believe that capillary condensation (Mulfort et al. 2010) might take place and thus leads to a blocking and eventually resulting in hysteresis. The small hysteresis effect observed in PBI was attributed to the powdery nature of the material (Rabbani and El-Kaderi 2012a, b) and the relatively higher hysteresis in PBI-1 than PBI-2 (Fig. 7a, b) can be attributed to the blockage of capillaries after being occupied by CO<sub>2</sub> adsorption. Since, mesoporous structures

have the tendency of hysteresis due to the channels condensation (Li et al. 2011), where both BET and SEM analysis suggested that PBI-1 has more mesoporous structure than PBI-2. Obviously this material has more channel condensation resulting in relatively larger hysteresis. As shown in Fig. 7c, d, almost similar trend of more hysteresis effect in PBI-1 than PBI-2 was observed up to the pressure range of 40 bars. On the other hand beyond 40 bars both the materials desorbed entire CO<sub>2</sub>, representing complete regeneration of the adsorbents at high pressure. This complete removal of CO<sub>2</sub> at high pressure can be attributed to two reasons; (i) opening/swelling (Kumbharkar et al. 2009) of pore channels at higher pressure, which allow CO<sub>2</sub> movement toward and away from the closed pores and voids and (ii) loss of quadruple interaction between polarized CO<sub>2</sub> molecules and imidazole ring.

It must be noted that both of the materials have almost similar adsorption isotherms behavior at first glance, when low-pressure sorption data is considered. It seems like based on the low-pressure sorption data, both the materials show typical type-III adsorption behavior. However, when the high-pressure sorption data is considered, PBI-2 reaches to equilibrium (or saturation) around 40 bars and adsorption measurements levels of around 50 bars, which



**Fig. 7** Low (a and b) and high pressure (c and d) CO<sub>2</sub> adsorption/desorption behavior of polybenzimidazole, **a** low pressure CO<sub>2</sub> uptake by PBI-1, **b** low pressure CO<sub>2</sub> uptake by PBI-2, **c** high pressure CO<sub>2</sub> uptake by PBI-1 and **d** high pressure CO<sub>2</sub> uptake by PBI-2

exhibits type-1 adsorption behavior. On the other hand, when PBI-1 is considered, since the CO<sub>2</sub> uptake has not been levelled off and it shows monotonic increase at 50 bars, its adsorption type behavior cannot be classified. In order to classify it, higher-pressure sorption data is required. As shown in Table 1, PBI-2 and PBI-1 adsorbed significantly large quantities of CO<sub>2</sub> at lower pressure of 1 bar and 273 K. PBI-1 adsorbed comparatively more CO<sub>2</sub> at 273 K and 1 bar than 1.0 mmol/g reported in the literature (Yu et al. 2013; Zhang et al. 2014) with PBI materials.

At higher pressure of 50 bars and room temperature PBI-1 adsorbed 6.08 mmol g<sup>-1</sup>, while PBI-2 adsorbed 5.98 mmol g<sup>-1</sup> CO<sub>2</sub> under the same pressure and temperature conditions. It is evident from Fig. 7 that, adsorption–desorption behavior of both the materials at higher pressure is different than that at lower pressure, since, saturation was observed in case of PBI-2, whereas PBI-1 seemed to have

more CO<sub>2</sub> capture capacity if the higher pressures beyond 50 bars is observed. This non-saturable adsorption–desorption performance of PBI-1 at relatively high pressure indicates the capturing capability at very high pressure and further suggest that material is strong enough and flexible (Bhavsar et al. 2011) to be utilized in high pressure environment like IGCC. The existence of covalent bonding in the structure of cross-linked PBI (PBI-1) strengthens the material and makes it capable of accommodating high pressure. In addition, hydrogen bonding due to cross linking agents and N–H group (Kumbharkar et al. 2009) make the material elastic where pore volume increases due to swelling under high pressure (Weber et al. 2008a, b). In case of PBI-2, the pore volume remains stable by increasing CO<sub>2</sub> pressure, where all the available free space becomes occupied resulting in the material saturation. The non-swelling effect which causes saturation in NTA linked PBI-2 may be related to the lower content of hydrogen bonding



and less mesoporous structure of the material. Importantly, PBI-1 has lower surface area than that of PBI-2, whereas the former has almost three times more pore volume and relatively larger pore diameter. These physical parameters contribute very limitedly in the adsorption performance of materials (Chen et al. 2013), though, effect of larger pore volume and pore diameter must not be excluded at all (Rabbani and El-Kaderi 2012a, b). Various PBI materials with different surface areas and pore volumes were tested in the literature for low and high pressure CO<sub>2</sub> adsorption without any co-relation between adsorption performance and physical parameters, except, material with higher pore size, have shown higher CO<sub>2</sub> uptake (Rabbani and El-Kaderi 2012a, b). Physical parameters such as pore size and pore volume may have some contribution in CO<sub>2</sub> uptake at relatively high pressure but elasticity of PBI-1 plays a significant role in higher, stable and non-saturable CO<sub>2</sub> adsorption. Mechanical stress may be introduced in molecular structure of PBI-1 due to modifications in bonds strength caused increasing/decreasing pressure during adsorption/desorption process. This molecular mechanical stress can effectively squeeze the pores (from higher pressure up to 40 bars) allowing complete removal of CO<sub>2</sub>, however, at lower pressure (less than 40 bars), squeezing of pores may not occurs due to less bonding stress resulting in hysteresis effect at lower pressure.

### 3.3 Selectivity measurements

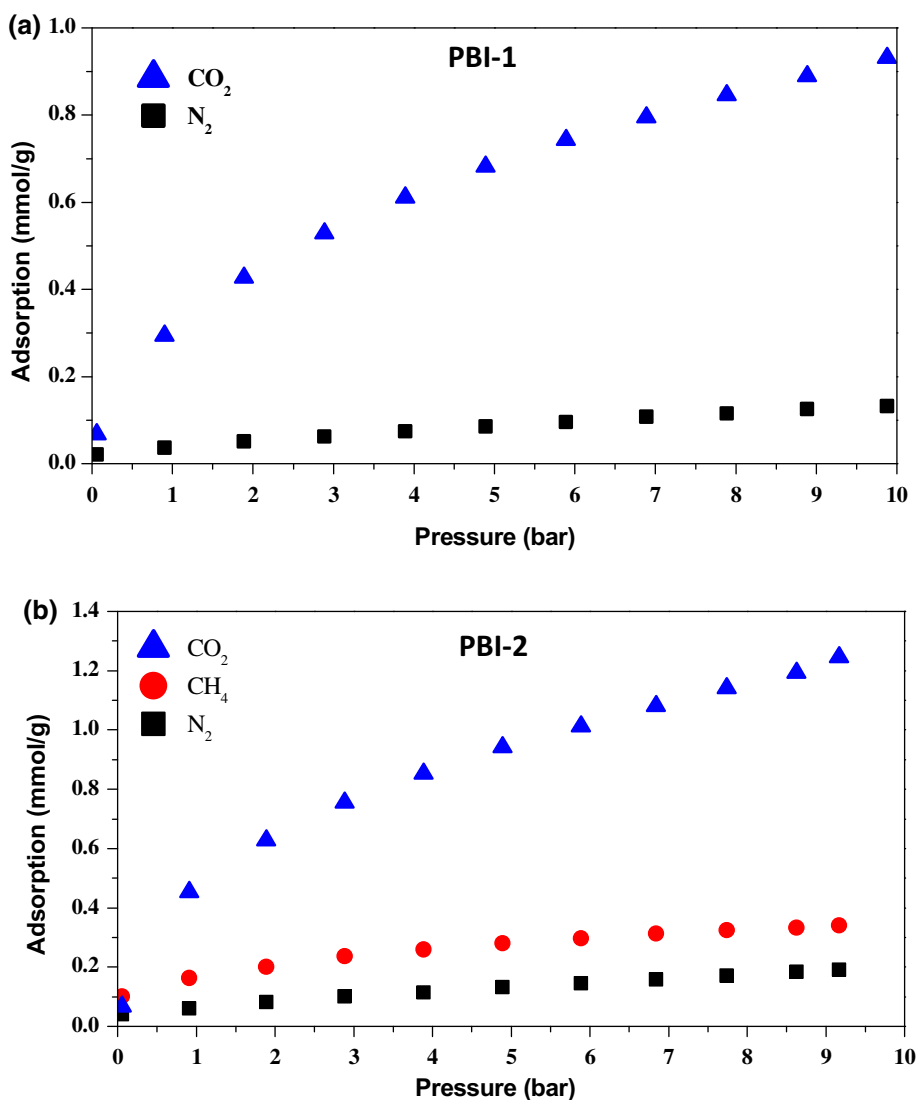
Selectivity studies for PBI-2 and PBI-1 materials based on single gas adsorption was also carried out for CO<sub>2</sub>, nitrogen (N<sub>2</sub>) and methane (CH<sub>4</sub>). Figure 8a shows the selectivity data for PBI-1 and Fig. 8b shows the similar data for PBI-2 material up to 10 bars. It is noted that for PBI-2 material selectivity based on single gas adsorption for CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> calculated as 6.55:1.78:1 respectively. On the other hand PBI-1 shows good selectivity between CO<sub>2</sub> and N<sub>2</sub> as 7.15:1 as showed in Fig. 8a. Selectivity of PBI-1 is comparatively less than that measured by Patel et al. (2013) for nitrogen phobic covalent organic polymers, since, by inserting nitrogen function group in the structure CO<sub>2</sub>/N<sub>2</sub> selectivity was significantly increased. Porous benzimidazole-linked polymers have also shown good selective for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> at 1 bar and different temperatures, but these materials were not tested for adsorption and selectivity at high pressure such as in this article (Rabbani and El-Kaderi 2012). It is important to note that, CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivity of PBI-1 and PBI-2 (showed in Table 2) are found to be comparatively better than other covalent organic polymers (COPs) which were also measured at lower pressure and different temperatures (Xiang et al. 2012). Binary selectivity given in Table 2 was obtained from the data of single gas adsorption.

### 3.4 High pressure CO<sub>2</sub> adsorption

Depending on the selection of the linker groups for porous coordinate on polymers, mechanical flexibility of the materials can be adjusted. Starting material of the both presented PBI-1 and PBI-2 materials are same, 3-3'-Di-aminobenzidine and it is polymerized by using two different linkers, nitrilo triacetic acid (NTA) and trimesic acid (TMA) respectively. Depending on the selection of the linker, molecular flexibility can be controlled through modulating the pore size upon adsorption of gas molecules especially at high pressures. Connecting the starting material with so-called slim aliphatic based linkers allow the cage structure to expand with the presence of gas, thus leads to a phenomena called gate-opening adsorption. Such behavior leads structural transformation from non-porous (or low-porous) structure to a porous structure under certain gas pressures, which enables materials for utilization of pressure-swing adsorption applications. Such reversible “swelling” effect increases the unit volume of the amorphous cells of the parent structure remarkably depending on the length and the structure of the used linker, without any apparent bond breaking. At low pressures, PBI-1 and PBI-2 had shown a CO<sub>2</sub> uptake capacity of 0.6724 and 1.8025 mmol/g of sorbent respectively. When their BET surface area is considered (0.325 and 12.07 m<sup>2</sup>/g) they showed remarkable CO<sub>2</sub> uptake potentially at low pressures. More interestingly, when high pressure CO<sub>2</sub> adsorption experiments for these materials were conducted, PBI-2 material showed type I adsorption behavior with no swelling or gate-opening adsorption. On the other hand, PBI-1 material showed a remarkable jump on pressure vs CO<sub>2</sub> uptake plot (Fig. 9) beyond critical pressure of CO<sub>2</sub> and it showed type IV adsorption behavior. This jump should not be attributed to the capillary condensation and increased density of CO<sub>2</sub> beyond critical point, since, under the similar circumstances, PBI-2 CO<sub>2</sub> uptake curve followed a monotonic slope in Fig. 9. Due to “slim” carbon-based linker behavior of nitrilo triacetic acid, PBI-1 had gone through structural cage expansion, which enabled the material to adsorb more CO<sub>2</sub> under high pressures. It is also observed that at around 225 bars, PBI-1 had reached to its limits and pressure vs CO<sub>2</sub> uptake plot levelled off reaching to a plateau.

Generally speaking, high surface area porous materials also have a high CO<sub>2</sub> uptake performance. Nevertheless, there is no vigorous linear (or non-linear) functional relationship between the surface area and the adsorption capacity/performance of CO<sub>2</sub> at a given pressure range (Xu and Hedin 2013). Vishnyakov et al. showed that the type of CO<sub>2</sub> capture isotherm is mainly dominated by the pore size and small pores leads to abrupt CO<sub>2</sub> uptake at low partial pressures, which is a desired condition for post-combustion

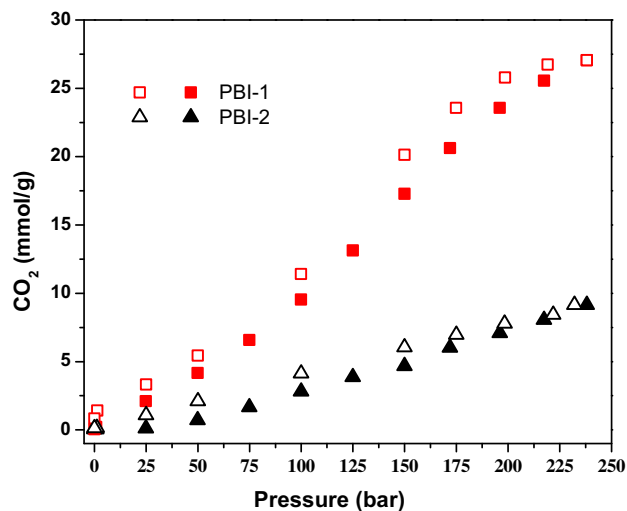
**Fig. 8** CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> selectivity data at 298 K for **a** PBI-1 and **b** PBI-2



**Table 2** Binary selectivity of PBI-1 and PBI-2 at 298 K and 10 bars

	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	CH <sub>4</sub> /N <sub>2</sub>
PBI-1	7:1	∞	∞
PBI-2	6.56:1	3.68	1.8:1

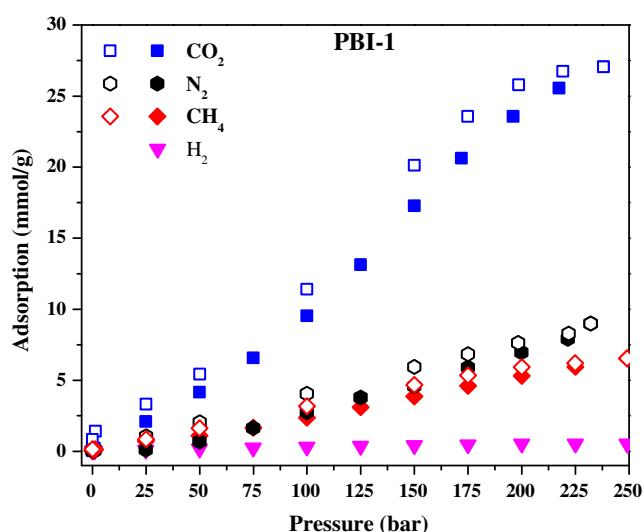
capture applications (Vishnyakov et al. 1999). On the other hand, porous coordination polymers with improved surface area have not posed much higher adsorption of CO<sub>2</sub> at high pressures, which is relevant conditions for CCS, than those with moderate surface areas. Interestingly, in several cases, the CO<sub>2</sub> uptake performance has observed to be even lower; PAF-1 with an ultra-high surface area of 5600 m<sup>2</sup>/g had a modest CO<sub>2</sub> adsorption capacity of 1.09 mmol/g at 1 bar and 298 K, 2.05 mmol/g at 1 bar and 273 K, which is lower than many less porous polymers. On the other hand, due to high CO<sub>2</sub> adsorption capacity of 29.6 mmol/g



**Fig. 9** Adsorption-desorption isotherms of PBI-1 and PBI-2 for CO<sub>2</sub> at very high pressure of 250 bars and 323 K

at elevated pressures of 40 bar and at 298 K, this polymer appears to be more suitable for the pre-combustion CO<sub>2</sub> separation and mitigation applications and can be used for “temporary gas storage” (Ben et al. 2009). Similar conclusion can also be made for PBI-1 material due to its improved CO<sub>2</sub> uptake capacity and it can be used to employ as pre-combustion CO<sub>2</sub> separation and gas storage material. Another supporting data for utilization of PBI-1 at high pressures at pre-combustion CO<sub>2</sub> separation is that the selectivity data, which is obtained through the single gas adsorption at 250 bars. In this manuscript the performance of the presented materials at various processing conditions and their suitability at above processes were targeted; thus, both of the materials were tested at wide pressure (and temperature) conditions to observe the capacities of materials at low, moderate and high pressures.

PBI-1 has much better adsorption capacity at 250 bars than PBI-2, therefore, its suitability for separation of CO<sub>2</sub> from other gases like N<sub>2</sub>, CH<sub>4</sub> and particularly H<sub>2</sub> was further investigated. As shown in Fig. 10, PBI-1 was also tested for adsorption of gases other than CO<sub>2</sub> at high pressure and results indicated that its CO<sub>2</sub> adsorption capacity is interestingly better than the other gases. Figure 10 further shows a promisingly distinct selectivity of CO<sub>2</sub> over N<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. It can be deduce from Fig. 10 that adsorption of N<sub>2</sub> and CH<sub>4</sub> is almost similar up to the pressure of 125 bars, whereas a small increase in N<sub>2</sub> over CH<sub>4</sub> can be observed at high pressure of 225 bars. Importantly, PBI-1 has shown negligible affinity toward H<sub>2</sub>, since; even at high pressure up to 250 bars very nominal amount (less than half a mmol/g) of H<sub>2</sub> was captured. It must be noted that unlike other physical sorbets, PBI-1 has maximum to infinity selectivity for CO<sub>2</sub>



**Fig. 10** Adsorption-desorption isotherms of PBI-1 for CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> at very high pressure of 250 bars and 323 K

over H<sub>2</sub>, which indicates the suitability of this material for pre-combustion CO<sub>2</sub>. Based on its exceptionally high CO<sub>2</sub> capturing capability and negligible H<sub>2</sub> up take capacity at high pressure, PBI-1 may be considered for further investigation to be used on large scale for CO<sub>2</sub>/H<sub>2</sub> separation.

## 4 Conclusions

Two PBI materials PBI-2 and PBI-1 were prepared using DAB as fundamental monomer with two different solvents and two different cross linking agents. PBI-2 was found to have higher surface area but, smaller pore size and smaller pore volume than PBI-1. FTIR peaks between 1438 and 1631 cm<sup>-1</sup> confirmed formation of PBI in both the samples. SEM analysis showed that, PBI-1 has more mesoporous structure than PBI-2, but, the former has very smaller agglomerates than the later confirming the suitability of this material for gases adsorption. Both the materials have very stable CO<sub>2</sub> adsorption characteristic at partial pressure relatively lower than 1 bar. PBI-2 adsorbed about 0.6724 mmol g<sup>-1</sup> of CO<sub>2</sub> at 273 K and low pressure, while it adsorbed 5.98 mmol g<sup>-1</sup> at 298 K and high pressure of 50 bars. PBI-2 exhibited saturation at high pressure, has steeper adsorption at around 50 bars and has shown negligible hysteresis in adsorption/desorption performance. PBI-1 has displayed very good performance by adsorbing 3 times more (1.8025 mmol g<sup>-1</sup>) CO<sub>2</sub> than PBI-2 at 0 °C and lower pressure, while, at high pressure (of 50 bars) PBI-1 adsorbed up to 6.08 mmol g<sup>-1</sup>. Unlike PBI-2, PBI-1 has shown relatively more hysteresis effect both at low pressure and high pressure of CO<sub>2</sub>, however, this effect was not detected after 40 bars. The imperfect removal of CO<sub>2</sub> at lower pressure (> 40 bars) was mainly attributed to the capillary condensation of mesoporous structure in PBI-1. In case of PBI-1, at higher pressure of 40 bars and above, swelling and squeezing effects were detected in PBI-1, indicating a non-saturable adsorption of CO<sub>2</sub>. This elastic behavior of PBI (PBI-1) was primarily attributed to the readjustment of the molecular bonds caused by the stress, which was subsequently introduced by the adsorbed gas pressure. The linear relationship of adsorption with pressure indicates that, PBI-1 can uptake significantly large amount of CO<sub>2</sub> at high pressure and room temperature. As compared to other adsorbents and PBI materials prepared with different techniques, PBI-1 (prepared with TMA as cross linking agent and PPA as solvent) has shown relatively high CO<sub>2</sub> adsorption at lower and high pressure without any saturation tendency. Since, TGA analysis indicated that PBI material has excellent stability at higher temperature (up to 490 °C), thus, further investigation of the material at high temperature and high pressure would give interesting results. Moreover, advance level

investigation is required to critically assess the swelling/squeezing effect of PBI-1 at pressure above than 50 bars and higher temperature.

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