Synthesis and Characterization of Fluoropolymers with Intrinsic Microporosity and Their Hydrogen Adsorption Studies

Saad Makhseed, Jacob Samuel, Ali Bumajdad, Mohammed Hassan

Department of Chemistry, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait

ABSTRACT: Microporous polymers with rigid organic architecture offer a wide range of efficient on board hydrogen storage at low temperature. The fluoropolymers with intrinsic microporosity (MP1 and MP2) were synthesized and characterized. Characterization technique such as high resolution transmission electron microscopy (HRTEM) revealed that the highly stable microporous structure of MP2 was composed of nanoporous frame work which was further supported by the computational study. The high surface area and microporosity of the polymers were estimated by measuring the N_2 gas adsorption. The MP1 and MP2 exhibit BET surface areas 666 and 1050 m^2/g respectively. The micropore size distribution curves show a higher concentration of subnanometer pores. The hydrogen storage capacity of the prepared polymers are promising and the performance relative to other microporous polymers is comparable. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2591–2597, 2008

Key words: intrinsic microporosity; fluoropolymers; nanoframes; hydrogen adsorption

INTRODUCTION

Hydrogen has been considered as a potential energy carrier for the future, but the wide spread use of hydrogen as an onboard nonpolluting fuel is limited by the lack of efficient storage systems. The progress in hydrogen economy strongly depends on the development of microporous materials (diameter <2 nm) that demonstrate high hydrogen storage capacity.[1–3] Hence there has been growing demand to develop such materials which can be tailored to create a desired structure and chemical composition suitable for the efficient physisorption of hydrogen. Physisorption achieved by weak van der Waals bonding between the adsorbate (hydrogen) and adsorbent (substrate). So materials with high specific surface area and extremely small pores enhance the hydrogen adsorption to a great extent. For this purpose many materials have been explored including the carbon nanotubes (CNT),[4,5] activated carbons,[6,7] zeolites,[8,9] metal hydrides,[10] and the Metal organic frameworks (MOFs).[11–13]

Recently several attempts focused on porous polymers with intrinsic microporosity (PIMs) such as PIM1 (from the reaction between 5,5′,6,6′-tetrahydroxy-3,3,3,3′-tetramethyl-1,1′-spirobisindane and tetrafluoroterephthalonitrile), CTC-network-PIM (cyclotricatechylene and tetrafluoroterephthalonitrile) HATN-network-PIM (5,5′,6,6′-tetrahydroxy-3,3,3,3′-tetramethyl-1,1′-spirobisindane and hexachlorohexaazatrinaphthylene) and Trip-PIM (triptycene and tetrafluorophthalonitrile) were reported.[14–17] The storage capacity of PIMs is in the range of 0.95–1.63 wt % H_2 at 77 K and 1 bar. These values are generally promising for the development of microporous polymers with covalent architectures. Organic polymers offer a wide range of advantages over MOF, zeolites, and other microporous materials as an onborad storage materials. The main attaraction is due to the low intrinsic density because of their lighter constituent elemenets (e.g., C, H, N, O) where as MOFs and zeolites possess high density as they are composed of heavier elements. The other merits including good chemical, comparable thermal and structural stability (because of the strong covalent bonds), chemical homogeneity (over carbons), and synthetic reproducability.[14]

Other class of porous polymers reported are hyper crosslinked polymers (HCPs).[18,19] These are prepared by extensive crosslinking reactions which can prevent the polymer chain entanglement to give microporous material having high surface area with permanent porosity. The hydrogen adsorption of HCPs is in the range of 1.28–1.5 at 77 K and 1 bar.

Microporosity in polymers depend on the nature of bonding and their texture. Our research is focused on a novel approach to create thermally stable

Correspondence to: S. Makhseed (smakhseed@kuc01.kuniv.edu.kw).

microporous polymers composed of light elements with high surface area and volumetric capacity. In this work we present the synthesis and characterization of a microporous network polymers and their hydrogen adsorption characteristics.

EXPERIMENTAL

Materials and methods

All the chemicals were of reagent grade purity and used without further purification. The dry solvent Dimethylformamide (DMF) with water content less than 0.005% was purchased from Aldrich. The finely grounded anhydrous potassium carbonate was used after further drying at 200°C. ^{1}H-NMR spectra (400 MHz) were recorded using Bruker DPX 400. IR spectra were recorded on a Perkin–Elmer System 2000 FTIR. Elemental analyses were carried out using LECO Elemental Analyzer CHNS 932. Mass analyses were done on a VG Autospec-Q. Solid state NMR measurement was carried out on a Bruker Avance 300 spectrometer equipped with a cross polarization magic angle spinning (CP/MAS) probe and a fully automated pneumatic unit for sample spinning. Average molecular weights of MP1 were calculated with Knauer Gel Permeation Chromatograph fitted with a refractive index detector. Microscopic techniques employed are Scanning Electron Microscopy (SEM: JEOL Model 6300) and High Resolution Transmission Electron Microscopy (HRTEM: JEOL Model JEM-3010). X-ray diffraction measurements were conducted using Bruker XRD, D 5000. TGA and DSC analyses were carried out on Shimadzu TGA-50 and Shimadzu DSC-50. Molecular structures were created using the Spartan program and the Semiemperical molecular orbital methods (PM3 and MNDO) were used to simulate molecular structure. Surface area analysis was carried out at liquid nitrogen temperature using ASAP 2010 Micromeritics Sorptometer equipped with an outgassing platform, an online data acquisition and handling system. Hydrogen sorption measurements were done using the Micromeritics ASAP 2020.

Synthesis of monomers (1 and 3) and microporous fluoropolymers (MP1 and MP2)

2,3,6,7-Tetramethoxy-9,10-bis(pentaflurophenyl)-9,10-dihydroanthracene (1)

To a solution of veratrole (19.6 g, 100 mmol) and pentafluorobenzaldhyde (13.8 g, 100 mmol) in chloroform (50 mL), 75% sulfuric acid (100 mL) was added dropwise while the temperature was kept at 0°C. After the addition was completed the suspension was stirred for 24 h at room temperature. The reaction mixture was cooled and poured onto ice

and neutralized with aqueous ammonia. The resulting precipitate was collected by filtration and washed several times with water and methanol. The crude product was crystallized from chloroform to afford **1** as a white powder (yield 60%), Mp. 261°C; MS (EI): m/z (%): 632 (100) (M^+). ^{1}H-NMR (CDCl$_3$): δ 3.67 (s, 12H), 5.74 (s, 2H) and 6.36 (s, 4H). IR/cm^{-1} (KBr) 1225 (C—O), 1006 (C-F). Elemental analysis (%) calculated for C$_{30}$H$_{18}$F$_{10}$O$_4$: gives C, 56.97; H, 2.87. Found: C, 56.96; H, 2.75.

#### 9,10-Bis(pentafluorophenyl)-9,10-dihydroanthracene-2,3,6,7-tetraol (3)

To a stirred solution of **1** (6.3 g, 10 mmol) in dry dichloromethane (300 mL) kept in an ice bath borontribromide (5.7 mL, 60 mmol) was added slowly. After the completion of addition of borontribromide the reaction mixture was further stirred for 12 h at room temperature. The reaction mixture was then poured into ice and the organic layer was collected and evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: 1: 4 methanol/chloroform) to afford **3** as a pale brown powder (yield: 88%), Mp. 244°C; MS (EI): m/z (%) 576 (100) (M^+). ^{1}H-NMR (DMSO-d_6): δ 5.52 (s, 2H), 6.26 (s, 4H) and 8.77 (s, 4H). IR/cm^{-1} (KBr) 3440 (C—OH). Elemental analysis (%) calculated for C$_{26}$H$_{10}$F$_{10}$O$_4$: gives C, 54.18; H, 1.75. Found: C, 53.80; H, 1.86.

Synthesis of MP1

To a solution of **1** (6.3 g, 10 mmol) and 5,5′,6,6′-tetra-hydroxy-3,3,3,3′-tetramethyl-1,1′-spirobisindane (**2**) (3.40 g, 10 mmol) in dry DMF (100 mL) K$_2$CO$_3$ (8.28 g, 60 mmol)was added and heated at 80°C for 24 h. Then the reaction mixture was allowed to cool and precipitated in acidified water. The precipitate was filtered off and washed with deionized water and then with methanol. The purification was done by reprecipitating two times from THF into methanol. The resulting polymer is off white solid and dried in vacuum at 80°C for 12 h (yield 90%). The weight-average molecular weight and number-average molecular weight are 131,037 and 24,680 g/mol respectively. ^{1}H-NMR (CDCl$_3$): δ 1.32 (s, 12H), 2.19 (s, 4H), 3.77 (s, 12H), 5.77 (s, 2H), and 6.41–6.91 (m, 8H). IR/cm^{-1} (KBr) 1250 (C—O), 1006 (C—F). Elemental analysis (%) calculated for the proposed repeat unit C$_{51}$H$_{38}$F$_6$O$_8$: gives C, 68.61; H, 4.29. Found: C, 67.39; H, 4.30.

Synthesis of MP2

A solution of 9,10-bis(pentaflurophenyl)-9,10-dihydroanthracene-2,3,6,7-tetraol (**3**) (5.76 g, 10 mmol) in
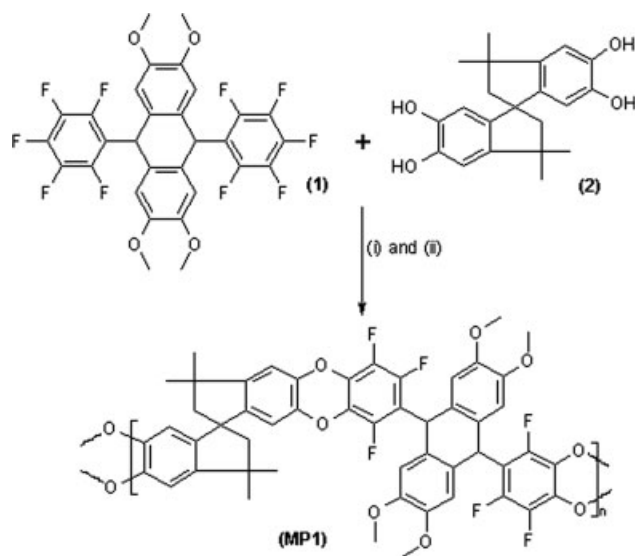
Scheme 1 Synthesis of microporous polymer (**MP1**). Reagents and conditions: (i) Dry DMF, Anhydrous K_2CO_3, (ii) 80°C, 24 h.

anhydrous DMF (100 mL) containing K_2CO_3 (5.52 g, 40 mmol) was heated at 120°C with vigorous stirring for 72 h. Upon cooling, the reaction mixture was transferred to deionized water followed by neutralization with 1M HCl and filtered through a sintered funnel. The insoluble product was washed with deionized water and methanol. Further purification was done using soxhlet extraction in methanol, ethanol, acetone and THF. The resulting pale brown powder was dried under vacuum at 100°C for 12 h (yield 80%). IR/cm^{-1} (KBr) 1226 (C—O), 1113 (C—F). Elemental analysis (%) calculated for the proposed repeat unit $C_{26}H_{14}F_6O_4$: gives C, 61.91; H, 2.8. Found: C, 60.27; H, 2.10.

RESULTS AND DISCUSSION

The microporous polymer **MP1** was prepared in good yield (90%) by the dibenzodioxane formation reaction between the corresponding tetra functional monomers (**1** and **2**) having the nonplanar architecture which is composed of wholly fused ring subunits (ladder type) as illustrated in Scheme 1. The **MP1** was soluble in polar aprotic solvent such as THF. The solution processable **MP1** was precipitated as pale yellow amorphous powder and can be cast in to membrane which can be used as a separation membrane, selectively removing one component either from liquid or gas mixture. MP1 shows a number average molecular weight 24,680 g/mol using the GPC as calibrated against standard Polystyrene. Other characterizations like IR, NMR, and elemental analyses confirmed the proposed structure. The second polymer **MP2** was synthesized by the self-poly-

condensation of the bifunctional monomer **3** and it forms a three dimensional network structure also exhibiting nonlinearity (Scheme 2). The insoluble polymer **MP2** was also characterized by IR spectroscopy, elemental analysis, and the results were consistent with the proposed structure. The proposed structure of the MP2 was further confirmed by the solid-state ^{13}C-NMR spectroscopy (Fig. 1). The peak at 40 ppm is arised from the carbons of the corresponding aliphatic ring. Three strong signals in between 100 and 150 (B, C, and D) attributed to the carbons of the aromatic units. The presence of fluorine was confirmed by using EDS analysis and the result was comparable with the estimated value and calculated value of the repeat units. The % weight changes as a function of temperature are shown in Figure 2. From the thermograms it was found that the both materials exhibit 10% degradation in the temperature range of 400°C. Considering the other high surface area material, in particular high temperature applications these materials exhibit good thermal stability. SEM images (Fig. 3) of the samples show the presence of irregular particles of different sizes. The high resolution transmission electron microscopy (HRTEM) operating at 300 kV was used to confirm the microstructure of the MP2 and the presence of nanopores observed at the area of investigation. The network polymer structure composed of nanoframes arranged in an ordered manner and show well defined microstructure (Fig. 4). Like other microporous carbons the synthesized network polymer MP2 was found to be stable under the experimental condition (300 kV) which is another indication of the high stability of such materials. Wide-angle X-ray diffraction measurements revealed that these polymers were amorphous.

### Nitrogen adsorption and pore size distribution

Physical adsorption (physisorption) considered as the most common type of adsorption and it is the important phenomena for studying pore characteristics of solid materials. Many applications related to the microporous materials require a good knowledge of its porosity. The relevant parameters which characterize a microporous system are the specific surface area of pore walls, the total pore volume, and the micropore size distribution. The most common technique used for screening the porosity involves the fitting of Brunauer–Emmett–Teller (BET) equation[20] to the data obtained from the nitrogen adsorption/desorption isotherms at 77 K. Analysis of the isotherms using BET theory results in spatial maps of the specific surface area, and the pore size distribution. Figure 5 shows the nitrogen adsorption isotherms for the polymers (MP1 and MP2) giving the BET surface areas 678 and 1050 m^2/g respectively,
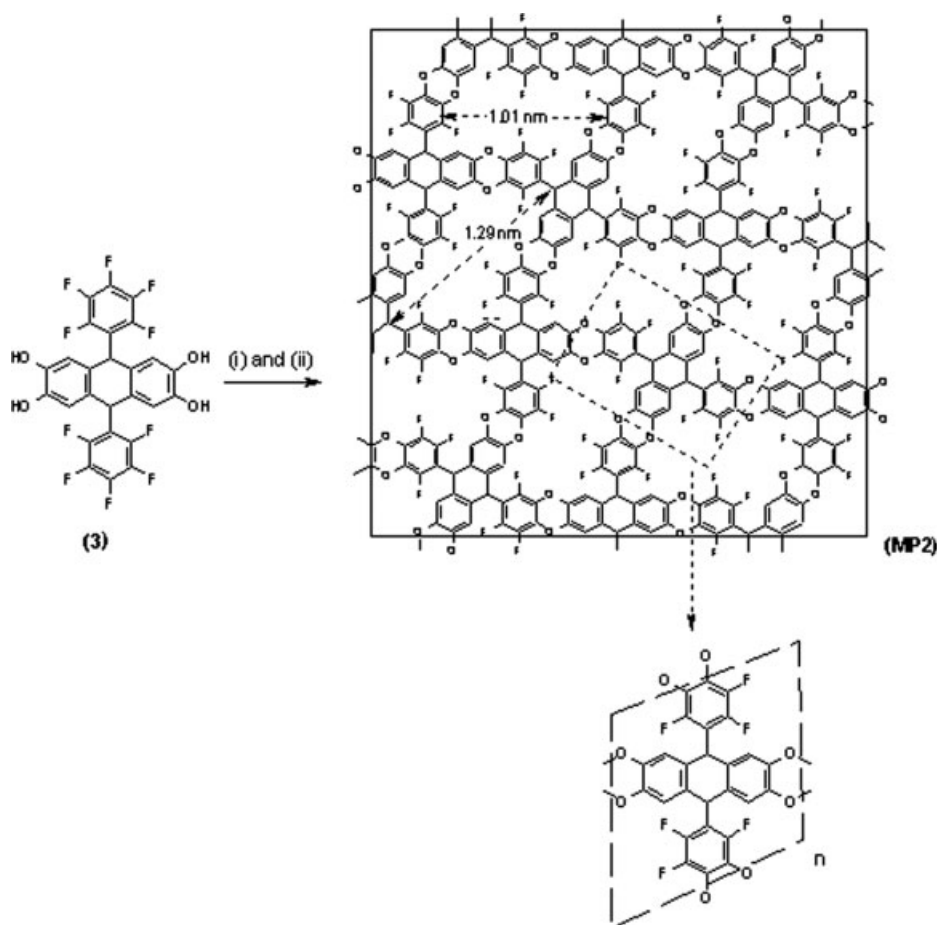
Scheme 2 Synthesis of the proposed microporous network polymer (**MP2**). Reagents and conditions: (i) Dry DMF, and Anhydrous K_2CO_3, (ii) 120°C, 72 h.

and it shows type I isotherms and the corresponding single point micropore volumes are 0.43 and 0.67 cm^3/g. The adsorption/desorption isotherms clearly exhibit remarkable hysteresis up to low partial pressure which is typically observed for microporous materials.[15] Figure 6 shows the micropore size distribution (MPSD) for **MP1** and **MP2** as calculated by the Horvath–Kawazoe (HK) method. The HK method is suitable for microporous materials and this equation relates the adsorption potential with the micropore size and allows each amount adsorbed at a relative pressure to be expressed in terms of the width of a slit shape pore.[21] Our MPSD analysis is strongly shifted towards subnanometer pores in the range of 0.5–0.6 nm.
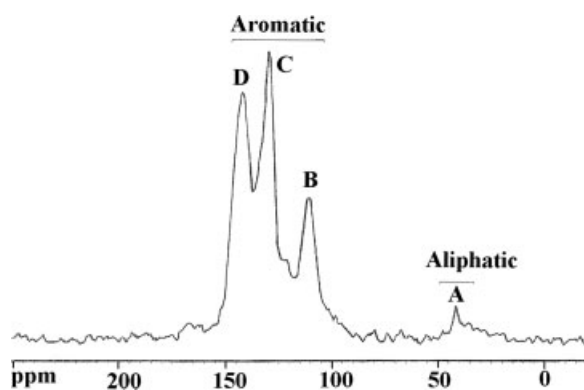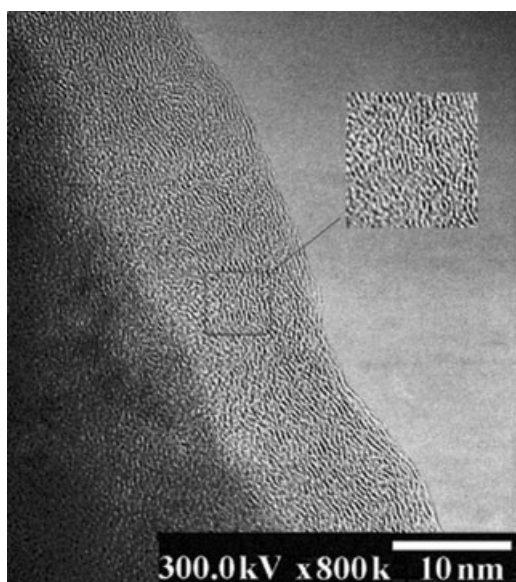

Figure 1 Solid-state ^{13}C-NMR spectrum of **MP2**.
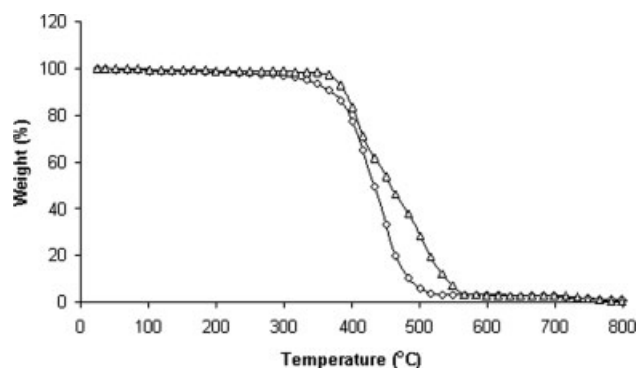
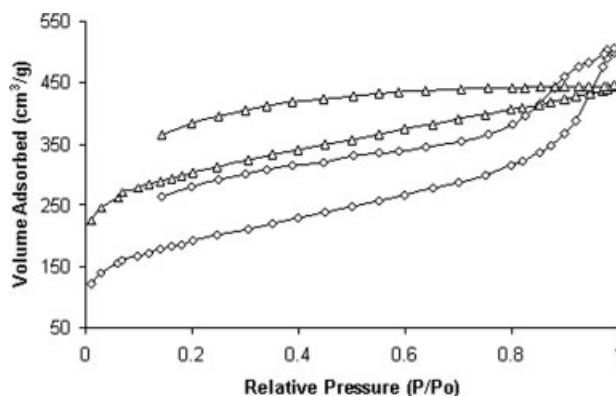**Figure 2** Thermogravimetric curves for **MP1**(-◇-) and **MP2** (-△-) at a heating rate of 20°C/min.
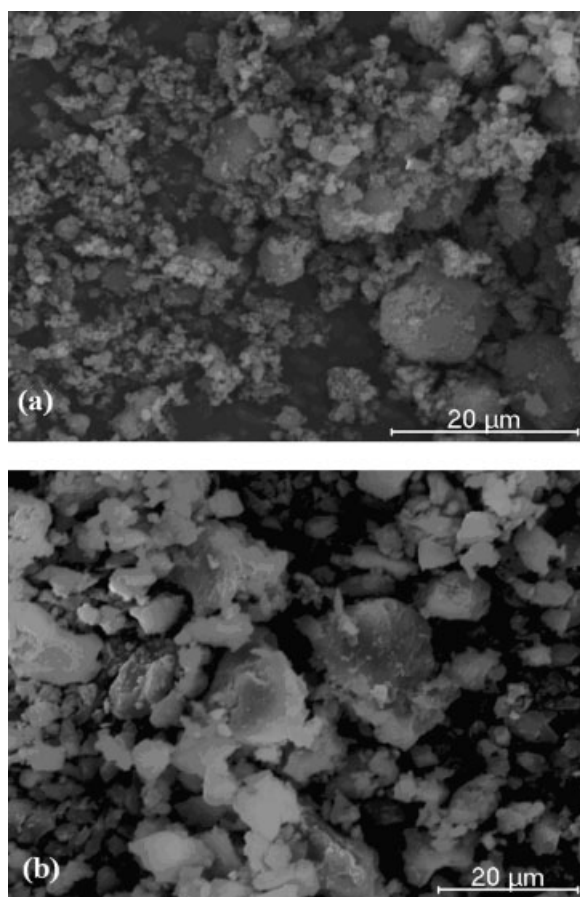
Figure 3 SEM images of microporous polymers: (a) **MP1** and (b) **MP2**.

Intrinsic microporosity

The high surface areas of **MP1** and **MP2** can be illustrated by its rigid nonlinear architecture. The rigidity


Figure 4 HRTEM image of **MP2**. Inset is the enlarged version of the selected area.

Figure 5 Nitrogen adsorption/desorption isotherms at 77K for **MP1** (-◇-) and **MP2** (-△-).

arises because of the restricted rotation as a result of the dioxane-ladder linkage. Though **MP1** is a linear polymer yet it is microporous polymer. It is believed that non linear polymers can possess large amount of void space, which is usually defined as the free volume. The presence of these interconnected voids enhances the intrinsic microporosity of the polymer even without the network structure. The spirocenter present in the 5,5′,6,6′-tetrahydroxy-3,3,3,3′-tetramethyl-1,1′-spirobisindane (2) creates the nonlinearity by propagating the polymer chain in three dimensional irregular fashion producing a polymer chain that can also prevent the dense packing which provides enough internal surface area.[22,23] It is interesting to note that the presence of four methoxy groups per repeat units can be easily demethylated to produce polymer with reactive sites. So using these potential sites it is possible to graft catalytic moieties without changing much of its porosity.[24] In the case of **MP2** the structure itself is considered as a network system built on nanoporous frame work held by strong covalent bonds (Scheme 2). Thus the possibility of efficient packing of polymer chains is
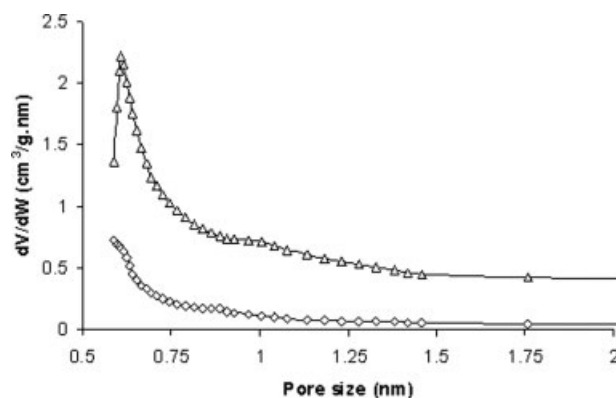
Figure 6 Apparent micropore size distributions (MPSD) from the Horvath–Kawazoe analysis of nitrogen adsorption data for **MP1** (-◇-) and **MP2** (-△-).
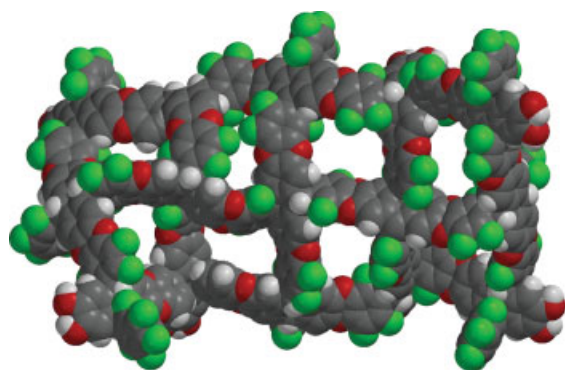
Figure 7 Space filling molecular model of **MP2**.

Figure 8 Hydrogen adsorption/desorption isotherm for **MP1** at 77 K.

prohibited. It is very important to note that high surface area cannot always be created from network structures and many network polymers show predominantly very low surface area.[25] The dihydroanthracene unit itself creates a polynuclear ring system and clearly provides a nonplanar random structure. The irregular or random in and out of plane of the phenyl groups at 9,10 position containing five F atoms further enhances the nonlinearity by catenation with the highly active hydroxyl groups forming network structure (which prevents the dense packing of the each polymer layer) essential for the microporosity. Moreover fluorinated polymers (**MP1** and **MP2**) are a class of materials that attract greater attention because of high thermal stability, oil and water repellence, flame retardant, and good resistance to chemical and physical treatments.[26]

Semiemperical molecular orbital methods (**PM3** and **MNDO**) were used to simulate microporous structure of the **MP2**. The molecular structure was created (Fig. 7) using the Spartan program and the semiemperical calculations were performed to optimize the molecular geometry at **PM3** and **MNDO** levels and the geometries were reoptimized using G03 program. The optimized geometry of MP2 suggests nonspherical pores with dimensions 1.01 nm (shortest width) and 1.29 nm longest width) as represented in the Scheme 2. On the basis of the 3D structure drawn by using the program the calculated pore volume of a single framework is 2.281 nm[3]. These computational results suggest that MP2 was constructed with nanometer size frame works as depicted in the Figure 7. The pore dimensions calculated from the computational method as well as from the HK method further support the nanometer scale frame works.

Hydrogen adsorption

Hydrogen sorption measurements were carried out by using the isothermal volumetric method over the pressure range (0–1) bar. The storage of hydrogen is achieved via physical or chemical adsorption of hydrogen on to the surface of the material. It is very
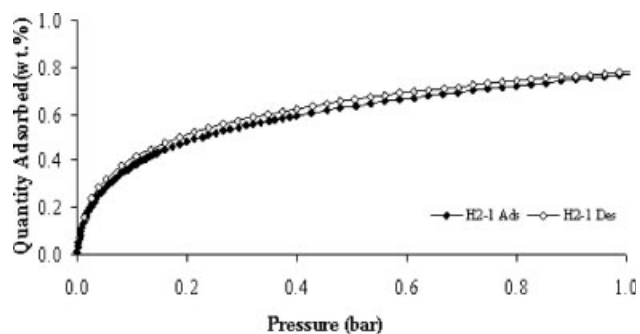
important to note that the hydrogen physisorption is completely reversible and this behavior is always consistent with microporous materials. Therefore, materials of high specific surface area and of subnanometer pore size are preferable.[17] Figures 8 and 9 show the hydrogen adsorption/desorption isotherms of MP1 and **MP2**. There is a much difference in the weight percentage of hydrogen stored in the two polymers and the difference is largely based on the difference in the specific surface areas. The uptake of hydrogen at 1 bar for the **MP1** and **MP2** is 0.8 and 1.3 wt % respectively, and the isotherms does not reach a plateau which is a promising observation to continue the hydrogen adsorption measurements at high pressure and this work is under progress. The significant increase in the amount of hydrogen in **MP2** is due to the microporous architecture which was confirmed by the high surface area and the large proportion of subnanometer pores. Generally the hydrogen sorption capacity of materials can be enhanced by increasing surface area as well as by maintaining the microporosity. In addition the adsorption is completely reversible and there is no significant hysteresis which can be correlated with the physisorption of hydrogen on a microporous material. The mechanism of hydrogen adsorption
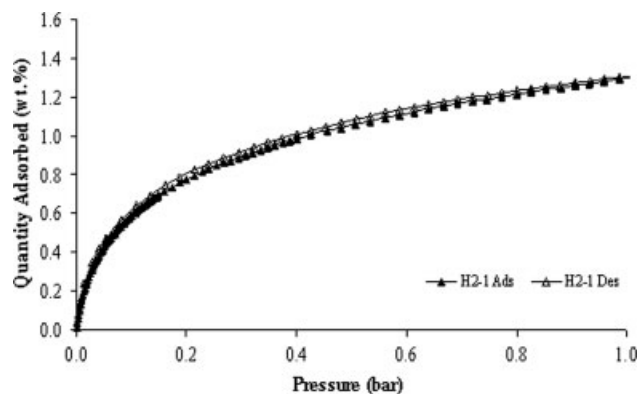

Figure 9 Hydrogen adsorption/desorption isotherm for **MP2** at 77 K.

TABLE I
Comparison of Hydrogen Storage Capacity of Microporous Polymers with the Reported Polymers

Polymer	BET SA (m^2/g)	H_2 (wt %) 1 bar	Ref.
MP1	678	0.80	
MP2	1050	1.30	
PIM1	760	1.04	14
HATN-network-PIM	820	1.37	14
CTC-network-PIM	830	1.43	14
Trip- PIM	1065	1.65	15
HCP	1466	1.28	18
HCP	1930	1.40	19

within rigid micropores behaves like monolayer and the adsorption is enhanced through multiwall interactions. However we cannot ignore the effect due to adsorption on open solid surface (multilayer). Our material is almost rigid due to the structural features and which is reflected in the adsorption characteristics. So it is worth mentioning that storage capacity of a physisorption based carrier is the sum of the capacity due to adsorption on open solid surface and capacity due to compression in the nanovoid (monolayer). The repeatability of the hydrogen adsorption was also checked and found to be constant. The comparison of hydrogen adsorption in other microporous polymers is summarized in Table I. The results show that these microporous polymers can store H_2 in comparable amounts to that of the commercial resins and other microporous polymers. However to attain good storage capacity it will be necessary to design materials with accessible high surface areas and microporosity.

CONCLUSIONS

In this work we have demonstrated synthesis and characterization of microporous polymers. The fluoropolymers (**MP1** and **MP2**) attract greater attention due to their high surface area and the presence of subnanometer pores which is essential for the gas separation and gas storage applications. The hydrogen adsorption results indicate that the microporous polymer MP2 can store hydrogen up to 1.3 wt %. The microporous fluoropolymer MP2 contains nanoporous framework structure which was confirmed by HRTEM. Molecular simulations also suggested the existence of such frame works. It is concluded that the microporous polymer with rigid architecture therefore act as a good storage system for H_2, through the increase in microporosity.

References

1. Service, R. F. Science 2004, 305, 958.
2. Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs; National Research Council and National Academy of Engineering; National Academies Press; Washington, DC, 2004.
3. Zuttel, A. Mater Today 2003, 6, 24.
4. Anson, A.; Callejas, M. A.; Benito, A. M.; Maser, W. K.; Izquierdo, M. T.; Rubio, B.; Jagiello, J.; Thommes, M.; Parra, J. B.; Martınez, M. T. Carbon 2004, 42, 1243.
5. Anson, A.; Benham, M.; Jagiello, J.; Callejas, M. A.; Benito, A. M.; Maser, W. K.; Züttel, A.; Sudan, P.; Martínez, M. T. Nanotechnology 2004, 15, 1503.
6. Kajiura, H.; Tsutsui, S.; Kadono, K.; Kakuta, M.; Ata, M.; Murakami, Y. Appl Phys Lett 2003, 82, 1105.
7. Kadono, K.; Kajiura, H.; Shiraishi, M. Appl Phys Lett 2003, 83, 3392.
8. Weitkamp, J.; Fritz, M.; Ernst, S. Int J Hydrogen Energ 1995, 20, 967.
9. Langmi, H. W.; Walton, A.; Al-Mamouri, M. M.; Johnson, S. R.; Book, D.; Speight, J. D.; Edwards, P. P.; Gameson, I.; Anderson, P. A.; Harris, I. R. J Alloy Comp 2003, 356/357, 710.
10. Bogdanovi, B.; Schwickardi, M. J Alloy Comp 1997, 1, 253.
11. Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. Science 2003, 300, 1127.
12. Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. Angew Chem In Ed 2005, 44, 4745.
13. Lee, J. Y.; Pan, L.; Kelly, S. P.; Jagiello, J.; Emge, T. J.; Li, J. Adv Mater 2005, 17, 2703.
14. McKeown, N. B.; Ghanem, B.; Msayib, K. J.; Budd, P. M.; Tattershall, C. E.; Mahmood, K.; Tan, S.; Book, D.; Langmi, H. W.; Walton, A. Angew Chem Int Ed 2006, 45, 1804.
15. Ghanem, B.; McKeown, N. B.; Harris, K. D. M.; Pan, Z.; Budd, P. M.; Butler, A.; Selbie, J.; Book, D.; Walton, A. Chem Commun 2007, 67.
16. McKeown, N. B.; Budd, P. M.; Book, D. Macromol Rapid Commun 2007, 28, 995.
17. Budd, P. M.; Butler, A.; Selbie, J.; Mahmood, K; McKeown, N. B.; Ghanem, B.; Msayib, K.; Book, D.; Walton, A. Phys Chem Chem Phys 2007, 9, 1802.
18. Lee, J. Y.; Wood, C. D.; Bradshaw, D.; Rosseinsky, M. J.; Cooper, A. I. Chem Commun 2006, 2670.
19. Germain, J.; Hradil, J.; Frechet, J. M. J.; Svec, F. Chem Mater 2006, 18, 4430.
20. Brunauer, S.; Emmett, P. H.; Teller, E. J Am Chem Soc 1938, 60, 309.
21. Horvath, G.; Kawazoe, J. J Chem Eng Jpn 1983, 16, 470.
22. McKeown, N. B.; Makhseed, S.; Budd, P. M. Chem Commun 2002, 2780.
23. Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. Chem Commun 2004, 230.
24. Makhseed, S.; Bumajdad, A.; Ghanem, B.; Msayib, K.; McKeown, N. B. Tetra Lett 2004, 45, 4865.
25. Makhseed, S. The synthesis of novel phthalocyanine containing polymers and soluble spiro polymers, Ph. D. Thesis, Manchester University, UK.
26. Cassidy, P. E.; Aminabhavi, T. M.; Reddy, V. S.; Fitch, J. W. Eur Polym J 1995, 31, 353.