

Microporous Hypercross-linked Conjugated Quinonoid Chromophores of Anthracene: Novel Polymers for CO₂ Adsorption*

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Abstract Microporous hypercross-linked conjugated quinonoid chromophores represent a novel class of amorphous polymers, synthesized by the reaction of anthracene with dimethoxy methane in the presence of FeCl₃ catalyst. Their N₂ adsorption isotherms confirm their microporous nature. Diffuse reflectance UV-Visible (DRS UV-Vis) spectroscopy confirms their matrix built with the conjugated quinonoids by their broad light absorption characteristics extending from 1000 nm to 200 nm with the absorbance maximum close to 400 nm. The catalyst cross-linked anthracene with —CH₂— bridges and subsequently dehydrogenating them to form quinonoids. Their Fourier transform infrared (FTIR) spectra showed their characteristic quinonoid vibrations between 1600 and 1700 cm⁻¹. The synthesis of polymers was carried out at 30, 40, 50, 60, 70 and 80 °C, but the quinonoid content of the polymer obtained at 80 °C was higher than that of the others. Their scanning electron microscopy (SEM) images showed microspheres of 1 to 5 μm size built with tiny particles. Their surfaces were not smooth. The polymer synthesized at 80 °C showed 5.1 wt% CO₂ sorption at 25 °C and 0.1 MPa, but when it was re-cross-linked, the CO₂ sorption increased to 8 wt%. Hence, hypercross-linked conjugated quinonoid chromophores of anthracene are good for sorption of CO₂.

Keywords: Anthracene; Hypercross-linked polymers; CO₂ adsorption; Friedel-Crafts reaction; Quinonoid chromophores.

INTRODUCTION

Greenhouse gases absorb and emit radiation within the thermal infrared range (5.6 μm to 1.0 cm) and the primary components of greenhouse gases in the Earth's atmosphere are water vapor (H₂O), carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and ozone (O₃)^[1]. The global warming and climate changes refer to an increase in average global temperatures, caused first and foremost by an increase in “greenhouse” gases, more predominantly by CO₂. Very recently, Times of India news journal reported around 524 people died on 25th May 2013 in Andhra Pradesh, India due to heat waves. The temperature in many parts of the state crossed 47 °C and was reeling under intense heat wave throughout the day^[2].

To overcome these climatic changes and save people from the inadequate environment, the researchers around the world have been attempting to focus novel materials for CO₂ adsorption. There are different classes of materials available for sorption which include crystalline covalent organic frameworks (COFs)^[3, 4], crystalline, covalent triazine-based frameworks (CTFs)^[5, 6], metal organic framework (MOFs)^[7–9], hypercross-linked

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polymers (HCPs)^[10–12], polymers of intrinsic microporosity (PIM)^[13, 14] and porous carbons^[15]. These microporous materials have been widely studied for H₂ and CH₄ storage and show excellent uptake capacity^[16]. Among the microporous materials, HCPs gain much attention due to their excellent characteristics like physicochemical stability, large adsorption capacity, excellent selectivity and structural diversity^[17–20].

Thus, it can be seen that hypercross-linked polymers, microporous polymers and heteroatom-rich microporous organic polymers (MOPs) are supposed to play a vital role in the CO₂ adsorption in future as evidenced by the ample reports that are available^[21–29]. For example, Buyi Li *et al.*^[30] reported a series of microporous polymers obtained by knitting rigid aromatic building blocks, such as benzene, biphenyl, 1,3,5-triphenyl benzene, methyl benzene, chlorobenzene and phenol using an external cross-linker for CO₂ adsorption in the presence of FeCl₃ catalyst. They reported that the aromatic blocks were linked by —CH₂— bridges. Li *et al.* synthesized polymers by Friedel-Crafts type hypercross-linking of poly(vinylbenzyl chloride and divinylbenzene). They were uniform microporous polymers with high surface area (1500 m²/g) for hydrogen storage applications^[31]. Also, Luo *et al.*^[32] published hypercross-linked aromatic heterocyclic microporous polymers from thiophene using an external cross-linker, formaldehyde dimethyl acetal, through Friedel Crafts reaction. The synthesized polymers exhibited a significant adsorption capacity for H₂ (1.11 wt%, 77 K and 0.113 MPa) and CO₂ (12.7 wt%, 273 K and 0.1 MPa). Weigang Lu *et al.*^[33] synthesized porous polymers grafted with sulfonic acid. Its lithium salt exhibited a significant increase in isosteric heats of CO₂ adsorption capacities. However, up to now, systematic studies of the effect of synthesis conditions of microporous polymers on the adsorption of CO₂ have not been attempted to the best of our knowledge. As rigid building blocks are the essential requirements for the formation of microporous polymers^[34], in this study we have attempted to synthesize hypercross-linked conjugated anthracene polymers at different temperatures with FeCl₃ catalyst with dimethoxymethane as the cross-linker for CO₂ sorption. As FeCl₃ was used in most of the previous reports and in this study, dehydrogenation of the cross-linking is expected in all to form hypercross-linked conjugated quinonoid chromophores. The dehydrogenation characteristic of FeCl₃ was also reported in the literature^[20].

Anthracene is a solid polycyclic aromatic hydrocarbon consisting of three fused benzene rings. As it is a rigid building block, organization of it by cross-linking can generate micropores. Hence we chose this monomer as a better starting material to synthesize hypercross-linked polymers than mono cyclic benzene, toluene, phenol and aniline. We have been involved in the synthesis of novel hypercross-linked microporous polymers with high surface area for selective CO₂ sorption for more than five years. We expected colorless polymers since the reaction mainly involved cross-linking of colorless aromatic monomers with —CH₂ bridges, but unexpectedly the resultant product was intense brown. The brown color is quite unusual and unexpected. It is this color which becomes the potential cause of hypercross-linked conjugated quinonoids. Also, we are reporting for the first time the effect of re-cross-linking of hypercross-linked polymer on CO₂ sorption. The synthesized polymers were characterized by FTIR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), DRS-UV, Brunauer-Emmett-Teller (BET) and SEM techniques.

EXPERIMENTAL

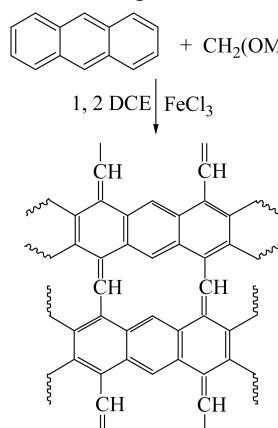
Materials

Anthracene (CAS No. 120-12-7, 97%) was purchased from Alfa Aesar. Dimethoxymethane (CAS No. 109-87-5) was purchased from Sigma-Aldrich (USA). Anhydrous iron (III) chloride (CAS. No. 16010-02) was purchased from Kanto Chemicals Co., Inc. Tokyo. Other chemicals like acetone, conc. HCl, 1, 2-dichloroethane and methanol were purchased from Daejung Chemicals, South Korea.

Synthesis of Hypercross-linked Polymers

In a typical procedure, 1 g of anthracene and 2.4 g of dimethoxy methane were dissolved in 40 mL of 1,2-dichloroethane in a 100 mL round bottom flask, and the mixture was vigorously stirred using a magnetic stirrer. Then 3.0 g of anhydrous ferric chloride was added to it, and the flask was attached to a reflux condenser carrying a calcium chloride guard tube. The synthesis of polymers was carried out by stirring the mixtures at 10 °C for 5 h

and then raising the temperature to 30, 40, 50, 60, 70 and 80 °C. The reaction was continued for 24 h, and then the reaction mixture was cooled and filtered under suction. The residue was washed with 5% HCl in water, methanol and acetone mixture in the ratio 3:1:1 for four times, then with water and finally acetone, and dried in the oven at 100 °C for 12 h. The schematic representation of synthesis procedure is shown in Scheme 1. The experimental procedure for all the characterizations is given in electronic supplementary information.



Scheme 1 Schematic representation for the synthesis of hypercross-linked polymers

The yield of polymers synthesized at various temperatures is presented in Table 1. In the calculation, complete alkylation was considered and dehydrogenation was ignored. The percentage yield of the polymers synthesized at 30 and 40 °C was slightly lower than that at other temperatures, as multi cross-linking is a high activation energy demanding one. The portion of unreacted reactants and soluble products are not considered in the calculation. Increase in substitution in an aromatic ring demands a gradual increase in temperature compared to fewer substitution. Dehydrogenation also affects yield, but it is not considered, as it cannot be quantified. Because of different levels of alkylation and dehydrogenation at each temperature, the experimental yield is lower than the theoretical yield.

Table 1. Yield percentage of hypercross-linked anthracene at various temperatures

Hypercross-linked anthracene synthesized temperature (°C)	Actual yield (g)	Theoretical yield (g)	Yield (%)
30	1.46	1.63	89.6
40	1.40	1.63	85.9
50	1.53	1.63	93.9
60	1.49	1.63	91.4
70	1.57	1.63	96.3
80	1.56	1.63	95.7

Characterizations

Ultraviolet-Visible diffuse reflectance (DRS UV-Vis) spectra were recorded on a SCINCO Neosys 2000 spectrometer. The Fourier transform infrared (FTIR) spectra were recorded at room temperature with 4 cm⁻¹ resolution between 4000 and 400 cm⁻¹ in an FTIR spectrometer (Nicolet IR 200). The solid state ¹³C-NMR spectra were recorded using a CP/TOSS NMR instrument with 4 mm probe and 5 kHz spinning. The nitrogen adsorption-desorption isotherms were measured at -196 °C with a Belsorp mini II sorption analyzer. Prior to each adsorption measurement the samples were degassed at 150 °C under vacuum ($p < 10^{-9}$ MPa) in the de-gas port. The surface area was determined from the linear part of the Brunauer-Emmett-Teller (BET) equation. CO₂ adsorption-desorption measurements using high purity CO₂ (99.999%) and N₂ for the samples were performed using a thermogravimetric analyzer (Scinco TGA N1000). A sample weight of ~10 mg was loaded into a platinum sample pan in a TG unit and the initial activation was carried out at 150 °C for 1 h under nitrogen atmosphere. Then the temperature of the sample was brought down to 25 °C for CO₂ adsorption. Desorption was

conducted by gradually raising the temperature from 25 °C to 150 °C by passing N₂. CO₂ and N₂ were passed through an automatic valve, assisted with a timer, for continuous adsorption and desorption profile, respectively. The morphologies of the sample were studied by scanning electron microscopy after gold coating using a JOEL instrument operating at 30 kV and equipped with an EDAX detector. The TGA thermal analysis was carried out using a SCINCO TGA N-100 instrument. The measurements were conducted by heating from room temperature to 800 °C at a heating rate of 10 K/min under nitrogen atmosphere. Differential scanning calorimetry was conducted on a DSC N-650 thermal analyzer. Measurements were performed in helium atmosphere at a heating rate of 10 K/min.

RESULTS AND DISCUSSION

FTIR

The FTIR spectra of anthracene and hypercross-linked anthracene synthesized at different temperatures are shown in Fig. 1. The spectrum of anthracene showed its peaks of C—H stretching vibrations just above 3000 cm⁻¹. The aromatic ring vibrations generally are observed between 1600 and 1400 cm⁻¹, but they were nearly absent in this spectrum, as anthracene is centrosymmetric.

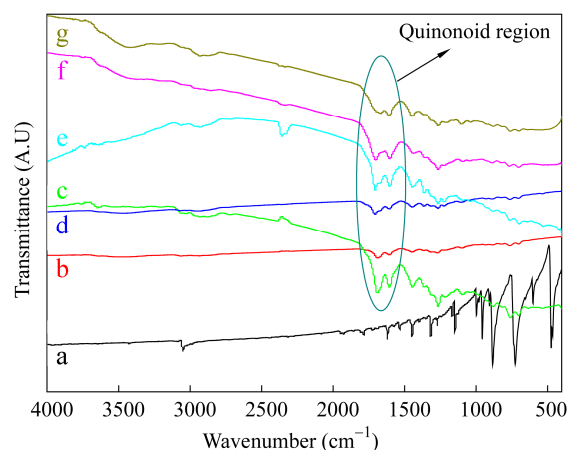


Fig. 1 FTIR spectra of (a) anthracene and hypercross-linked anthracene synthesized at (b) 30, (c) 40, (d) 50, (e) 60, (f) 70 and (g) 80 °C

The peaks of C—H bending vibrations appeared below 1000 cm⁻¹. All the spectra of hypercross-linked anthracene showed nearly similar features but different from that of anthracene. The ring C—H vibrations were nearly absent, hence the rings might almost be completely substituted. This view is also supported by absence of almost C—H bending vibrations of the ring below 1000 cm⁻¹. They showed intense peaks between 1700 and 1600 cm⁻¹, they are the characteristic ones of quinonoid skeleton^[35]. Its formation is evident even at 30 °C. The quinonoid arises as a result of dehydrogenation of —CH₂— bridges between the rings by FeCl₃ catalyst. The intensity of quinonoid peaks increased with the increase in temperature, as dehydrogenation is an endothermic process. As the peaks due to —CH₂— vibrations just below 3000 cm⁻¹ were nearly weak or absent, nearly all the bridges are suggested to be dehydrogenated. Though polymerization was run in non-polar 1,2-dichloroethane, protons release from electrophilic substitution might abstract a hydride ion from one —CH₂— bridge, and facilitate release of a proton from neighboring —CH₂— bridge to form a quinonoid.

Solid State ¹³C-NMR

The solid state ¹³C-NMR spectra of hypercross-linked anthracene synthesized at 30, 60 and 80 °C are shown in Fig. 2. The intense broad signal at $\delta = 129.49$ includes the signals due to quinonoid ring carbons and anthracene ring carbons. The un-dehydrogenated, residual —CH₂ bridges yielded a signal at $\delta = 45.6$. As its intensity is very low, it is expected that most of the —CH₂ bridges might be dehydrogenated to form quinonoids. Comparison of

the spectra of the hypercross-linked quinonoids synthesized at 30, 60 and 80 °C illustrates a gradual decrease in the intensity of the peak due to residual $-\text{CH}_2-$ bridges with increase in temperature. Hence, formation of quinonoids is more favored at 80 °C than at 30 and 60 °C. So, formation of quinonoid is well established by these spectra. All the other spinning side bands are indicated as asterisk (*).

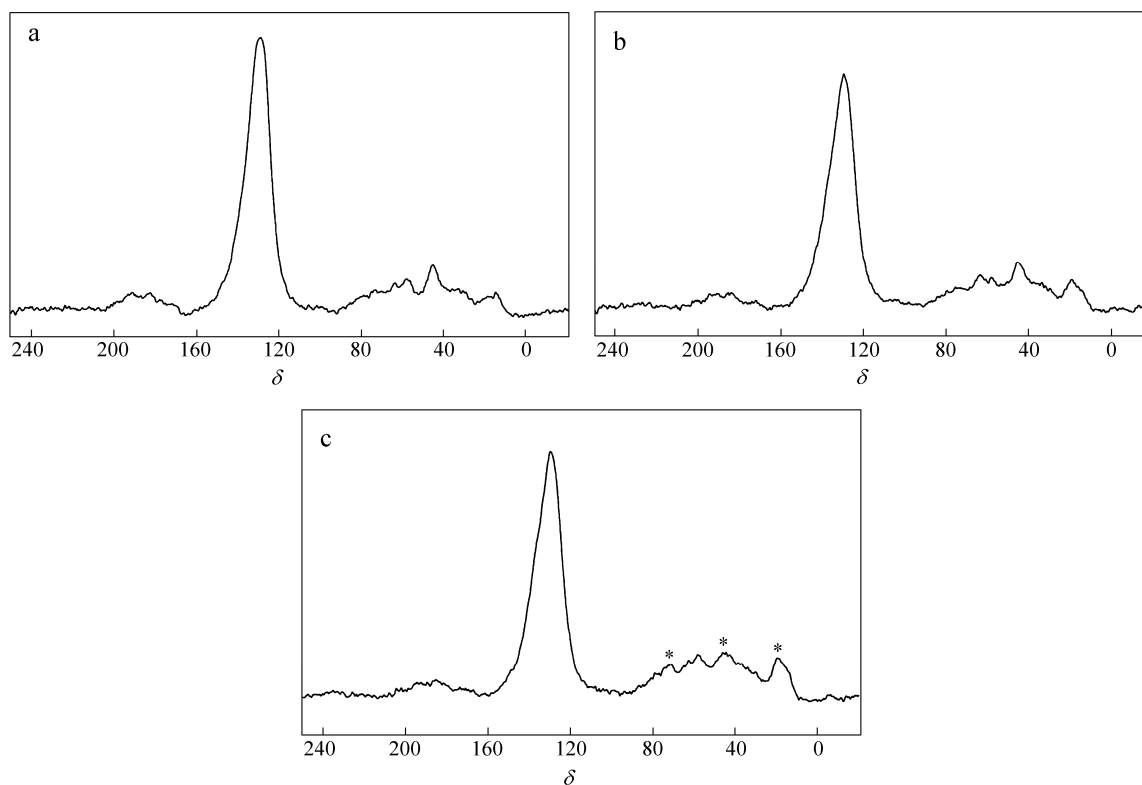


Fig. 2 Solid state ^{13}C -NMR spectra of hypercross-linked anthracene synthesized at (a) 30, (b) 60 and (c) 80 °C

N₂ Adsorption-Desorption Isotherm

The nitrogen adsorption and desorption isotherms and pore size distribution curves of hypercross-linked anthracene synthesized at different temperatures between 30 and 80 °C are shown in Fig. 3 and Fig. 4, respectively. The sharp increase in nitrogen sorption at low relative pressure ($p/p_0 < 0.05$) proves the existence of micropores in all the hypercross-linked polymers. According to IUPAC classification, all of the HCPs are typical adsorbents with large amount of micropores in the polymer matrix. The height of condensation increased with the increase in temperature. As the micropores are due to organization of rigid building blocks of cross-linked quinonoid chromophores, their optimum temperature for formation is important. From the results it is inferred that its formation increased with the increase in temperature. The formation of quinonoid has to occur by endothermic dehydrogenation of $-\text{CH}_2-$ bridges; hence, an increase in polymerization temperature increased quinonoid formation and their organization to form micropores. The isotherm of the polymer obtained at 30 °C deviated much from the others: unlike the others the condensation of nitrogen in micropores varied from $p/p_0 = 0.0$ to 0.1 and the curve corresponding to multilayer formation failed to reach $p/p_0 = 1.0$. Both these observations confirm low level of quinonoid formation. The polymer matrix carries large number of aromatic rings and $-\text{CH}_2-$ bridges, and interaction of them leads to pile them up with negligible amount of micropores. It is the cause for such a low capillary condensation and reduced multilayer formation. The surface area and pore volume were also lower than others in support of our view. The desorption isotherms do not trace their respective adsorption isotherms for the polymers synthesized above 30 °C due to heat of adsorption. It has to be low but

significant. Hence, the delocalized electronic cloud of the polymer might have some amount of $\pi\pi$ - $n\pi$ interaction with nitrogen at low temperatures and they are not desorbed at low pressures. It was also verified that at room temperature nitrogen was not absorbed.

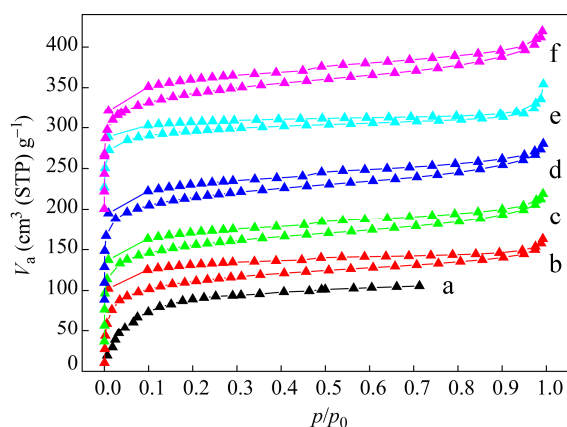


Fig. 3 N_2 adsorption-desorption isotherms of hypercross-linked anthracene synthesized at (a) 30, (b) 40, (c) 50, (d) 60, (e) 70 and (f) 80 °C

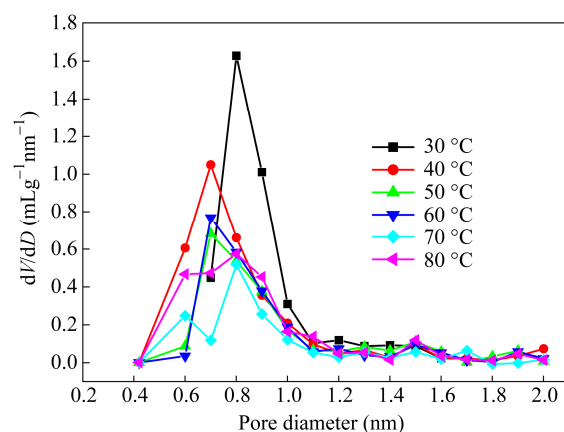


Fig. 4 The pore size distribution of hypercross-linked anthracene at varying temperatures

The results of textural properties of the polymers are presented in Table 2. The surface area increased with the increase in the synthesis temperature. The micropore volume also increased in a similar manner. The pore diameter was in the micropore region. At low temperature the degree of cross-linking has to be low, and as the additional cross-linking (alkylation) is an activation energy demanding, the degree of cross-linking has to increase with the increase in temperature. Origin of micropores also depends on degree of cross-linking and quinonoid formation and all are favored at high temperatures. Hence, higher reaction temperature is better than lower reaction temperatures for high micropore volume and surface area.

Table 2. Textural properties of hypercross-linked anthracene

Hypercross-linked anthracene synthesized at different temperatures (°C)	Surface area (m ² /g)	Micropore volume, V_p (cm ³ /g)	Total pore volume, V_p (cm ³ /g)	Pore diameter, d_p (nm)
30	135.1	0.1436	0.1633	0.8
40	383.6	0.1512	0.2130	0.7
50	451.1	0.2064	0.2646	0.7
60	585.3	0.2263	0.3122	0.7
70	612.6	0.2361	0.3260	0.8
80	704.1	0.2597	0.3709	0.8
Re-crosslinked at 80 °C	572.5	0.1916	0.2278	0.8

Thermogravimetric Analysis

The results of thermogravimetric analysis of anthracene and hypercross-linked anthracene are illustrated in Fig. 5(a). Anthracene shows an intense weight loss around 190 °C due to volatilization. All the hypercross-linked polymers showed an initial weight loss due to desorption of adsorbed gases. All showed gradual increase in weight loss above 200 °C. From the nature of the weight loss it could be depicted that it is due to carbonization to graphene or graphite *via* dehydrogenation over a range of temperatures until 800 °C. The thermograms were nearly the same showing increase in weight loss with the increase in temperature, but the percent weight loss for the polymer synthesized at 30 °C is higher than the other polymers. Though the difference is not very high, even at 30 °C, there might be quinonoid content to form micropores in the polymer structure. The polymer synthesized at 80 °C was subjected to thermal analysis in air to ascertain its

decomposition temperature. Selection of this polymer is based on its high quinonoid content, microporosity and CO₂ sorption. The results are illustrated in Fig. 5(b). The decomposition starts close to 350 °C in air and ends at 550 °C. The entire polymer is oxidized in one step without any carbonaceous residue. The analysis was started at 50 °C, and so the weight loss of about 7% is due to adsorbed solvents.

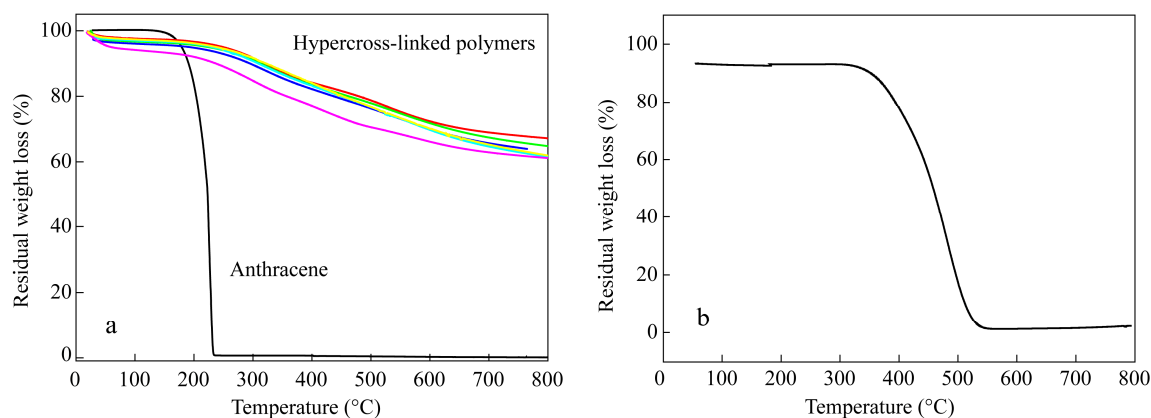


Fig. 5 (a) Thermogravimetric curves of anthracene and hypercross-linked anthracenes synthesized at 30, 40, 50, 60, 70 and 80 °C in N₂ atmosphere and (b) hypercross-linked polymer synthesized at 80 °C in air atmosphere

Differential Scanning Calorimetry

The DSC results are illustrated in Fig. 6. Anthracene shows an endotherm at about 220 °C due to its melting, and the same accompanying it is due to its volatilization. The DSC traces of all the hypercross-linked polymers of anthracene showed shallow endotherms from 200 to 600 °C, and it is in support of desorption of solvents in their thermograms. Absence of sharp endotherms in all the polymers from 200 to 600 °C precludes the possibility of any major chemical transformation. In order to confirm it once again, the polymer synthesized at 80 °C was heated to 600 °C in helium, and the resultant dark powder was analyzed by DRS UV-Vis spectroscopy. The spectrum is depicted in Fig. 7. The spectrum of as-synthesized polymer is also presented and compared.

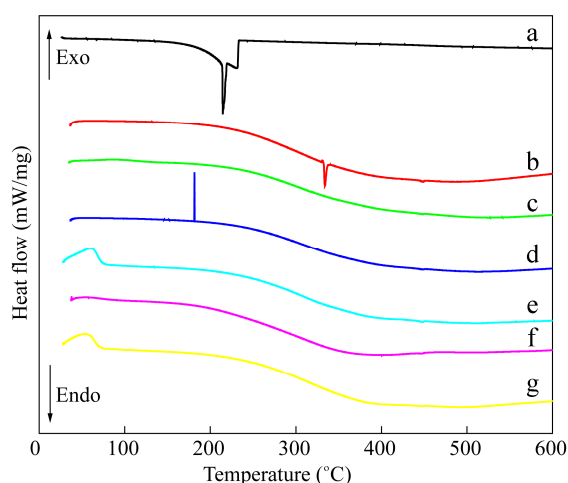


Fig. 6 DSC traces of (a) anthracene and hypercross-linked anthracene synthesized at (b) 30, (c) 40, (d) 50, (e) 60, (f) 70 and (g) 80 °C

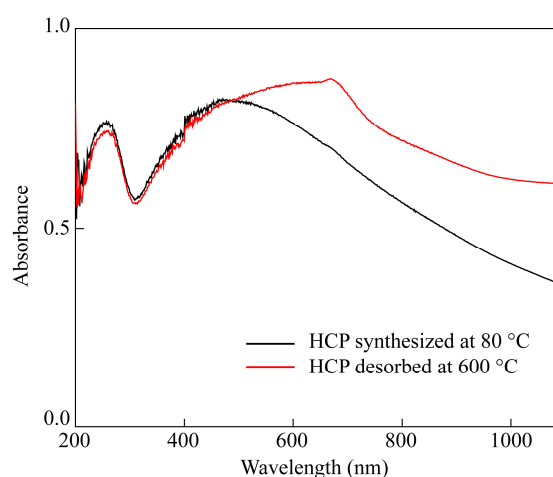


Fig. 7 DRS UV-Vis spectra of hypercross-linked anthracene synthesized at 80 °C and the corresponding heat treated (desorbed 600 °C) polymer

It also showed broad light absorption, but it was more intense than the spectrum of the corresponding as-synthesized polymer (Fig. 7). This observation suggests that in addition to desorption of solvents there might be

dehydrogenation of residual $-\text{CH}_2-$ bridges, which were not accessible to FeCl_3 , to form quinonoids. Since dehydrogenation is an endothermic process, the weight loss also increased with the increase in temperature. Since the absorbance increased with the increase in heat treatment, polymers prepared in this manner are better than the corresponding as-synthesized ones, if one plans for solar cell application of this polymer. Based on these results we suggest that the present heat treated polymer is better than any of the thiophene based or other materials so far reported for the fabrication of solar cell devices. Again we want to stress that all the as-synthesized hypercross-linked conjugated quinonoid polymers might be heat-treated further to enhance their light absorption characteristics, if they are mainly concerned for solar cell devices. Based on the results of TGA and DSC it is depicted that the polymers can be dried in the range of 500 to 600 °C in helium for testing their CO_2 sorption.

Diffuse Reflectance UV-Visible Spectroscopy

The DRS UV-Vis spectra of hypercross-linked anthracene are shown in Fig. 8. The spectrum of anthracene showed absorbance between 200 nm and 400 nm due to its π to π^* transition. In contrast, the spectra of the hypercross-linked polymers showed a broad absorption extending from 200 to 1100 nm. Absence of such a broad light absorption for anthracene and presence of the same for hypercross-linked polymers of anthracene confirm the conjugated anthracene. Conjugation requires dehydrogenation of $-\text{CH}_2-$ bridges resulting in the formation of hypercross-linked conjugated quinonoids. In the absence of dehydrogenation the anthracene nuclei of the polymers are isolated and the spectral property is the same as that of free anthracene. Though it is established in hypercross-linked anthracene, it is to be the case for all other hyper cross-linked aromatics synthesized with FeCl_3 catalyst. Hence the hypercross-linked polymers of Li *et al.*^[30], Zhang *et al.*^[36] and Davankov resins^[37] might be built with hypercross-linked conjugated quinonoids. We have synthesized all such polymers by repeating their procedures and confirmed quinonoid formation in support of our view. All these polymers are brown irrespective of the aromatic nuclei and all have broad light absorption characteristic thus confirming existence of hypercross-linked conjugated quinonoids. The quinonoids may be either *ortho* or *para* type and every quinonoid chromophore is a rigid, planar building block in the polymer matrix. Such blocks are unique in creating micropores in their materials^[34]. This study confirms that the polymerization of anthracene at 80 °C is better than at other temperatures to maximize cross-linking, dehydrogenation and micropore formation.

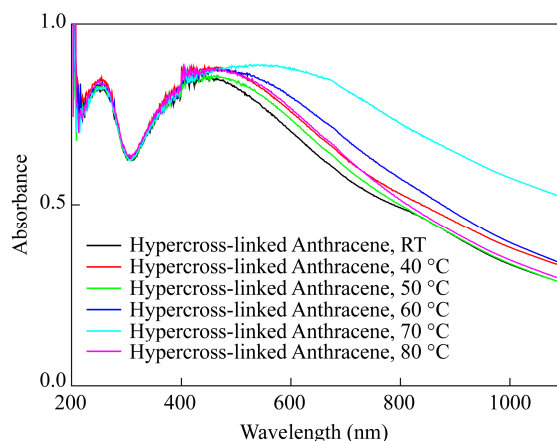


Fig. 8 DRS UV-Visible spectra of hypercross-linked anthracene synthesized at room temperature, 40, 50, 60, 70 and 80 °C

Scanning Electron Microscopy

The SEM images of anthracene (Fig. 9a) and hypercross-linked anthracene (Figs. 9b, 9c, 9d, 9e, 9f and 9g) showed distinguishing morphologies. The image of anthracene showed flakes, but that of polymers-microspheres. Similar morphology of the polymer synthesized at 30 °C as that of the other polymers illustrates occurrence of polymerization even at low temperatures. Since the catalyst was taken in large amount and the

entire monomer was added in the beginning in one lot, initiation of polymerization has to occur at numerous points. Hence polymerization resulted in the formation of numerous microspheres at every temperature. Each microsphere carries micropores through which CO₂ sorption occurred. The SEM images reveal that formation and size of microspheres are independent of polymerization temperature.

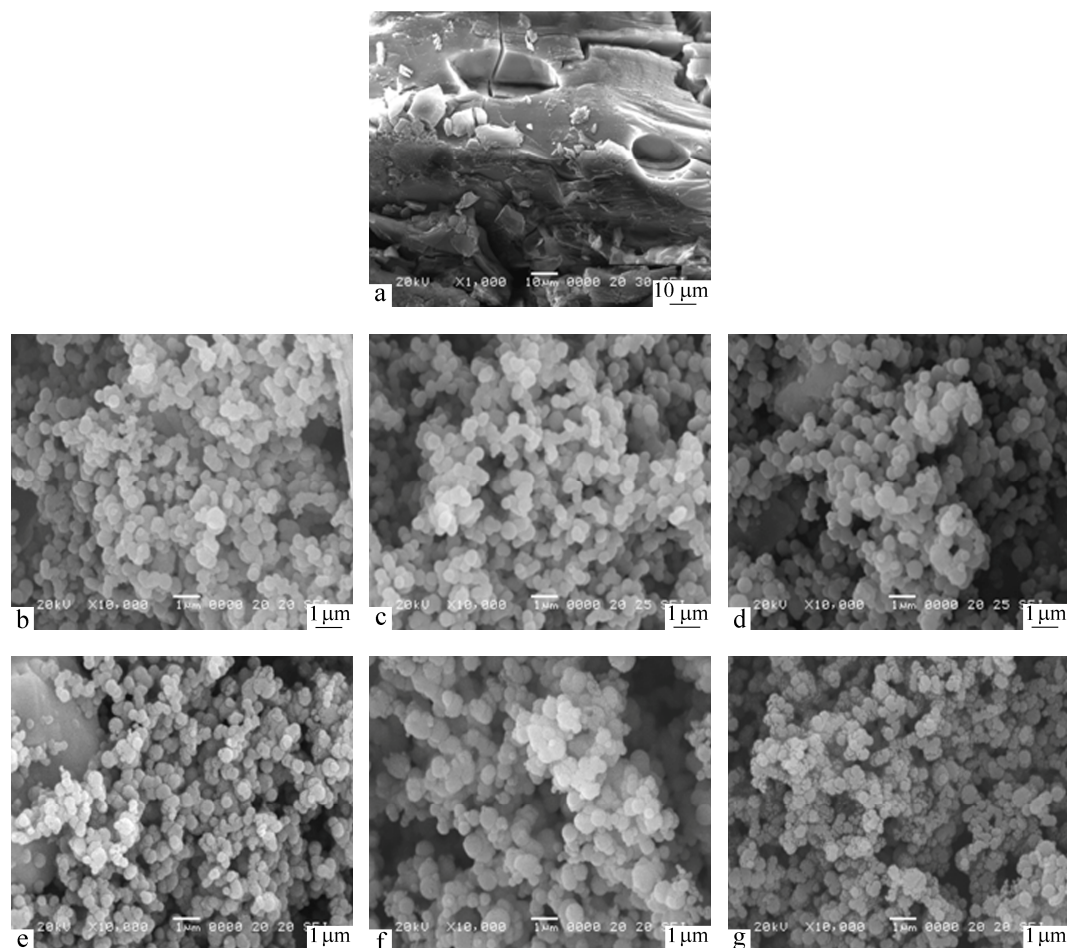


Fig. 9 Scanning electron micrographs of (a) anthracene and hypercross-linked anthracenes synthesized at (b) 30, (c) 40, (d) 50, (e) 60, (f) 70 and (g) 80 °C CO₂ adsorption

CO₂ Adsorption

The CO₂ sorption and desorption profiles of the polymers are shown in Fig. 10. For all the polymers the adsorption was conducted at 25, 50 and 75 °C. Prior to CO₂ adsorption the polymers were degassed at 150 °C for about 5000 min. A common trend is decrease of adsorption with the increase in temperature, hence CO₂ is only physisorbed. The polymer synthesized at 80 °C showed higher amount of adsorption than the others, as shown in Table 3. It is due to large size of the anthracene building block in the quinonoid form compared to that of benzene. For the formation of micropores, it is essential to have large rigid building blocks. Here large anthracene in the quinonoid form can form higher level of micropores than benzene. It is also in line with the requirement of such building blocks for the microporous polymers. As the polymers do not interact covalently with CO₂ like amines, a large decrease in adsorption with the increase in temperature was observed. The increase in adsorption with the increase in the synthesis temperature of the polymers is due to increase in quinonoid content which facilitates formation of higher level of micropores and surface area. An important observation in this study is the recross-linking of the polymer synthesized at 80 °C showed an increase in CO₂ adsorption

capacity to 8 wt%. Re-cross-linking enhanced CO₂ sorption, as this process can reduce surface area, pore diameter and pore volume of the parent polymer. In order to verify this, the re-cross-linked polymer was characterized by BET adsorption isotherm. The results are presented in Table 2. In correspondence to our view, the surface area, pore volume and pore diameter of re-cross-linked polymer attained lower values than the parent polymer. Re-cross-linking in beads of hypercross-linked polymers generally occur on the external surface, as FeCl₃ cannot diffuse into the pores. Therefore, the surface pores may be partly blocked and pore size may be reduced. In addition the beads may be cross-linked, so the surface area may be reduced. Hence, re-cross-linking is essential for all the hypercross-linked polymers synthesized with aromatic monomers and FeCl₃ catalyst.

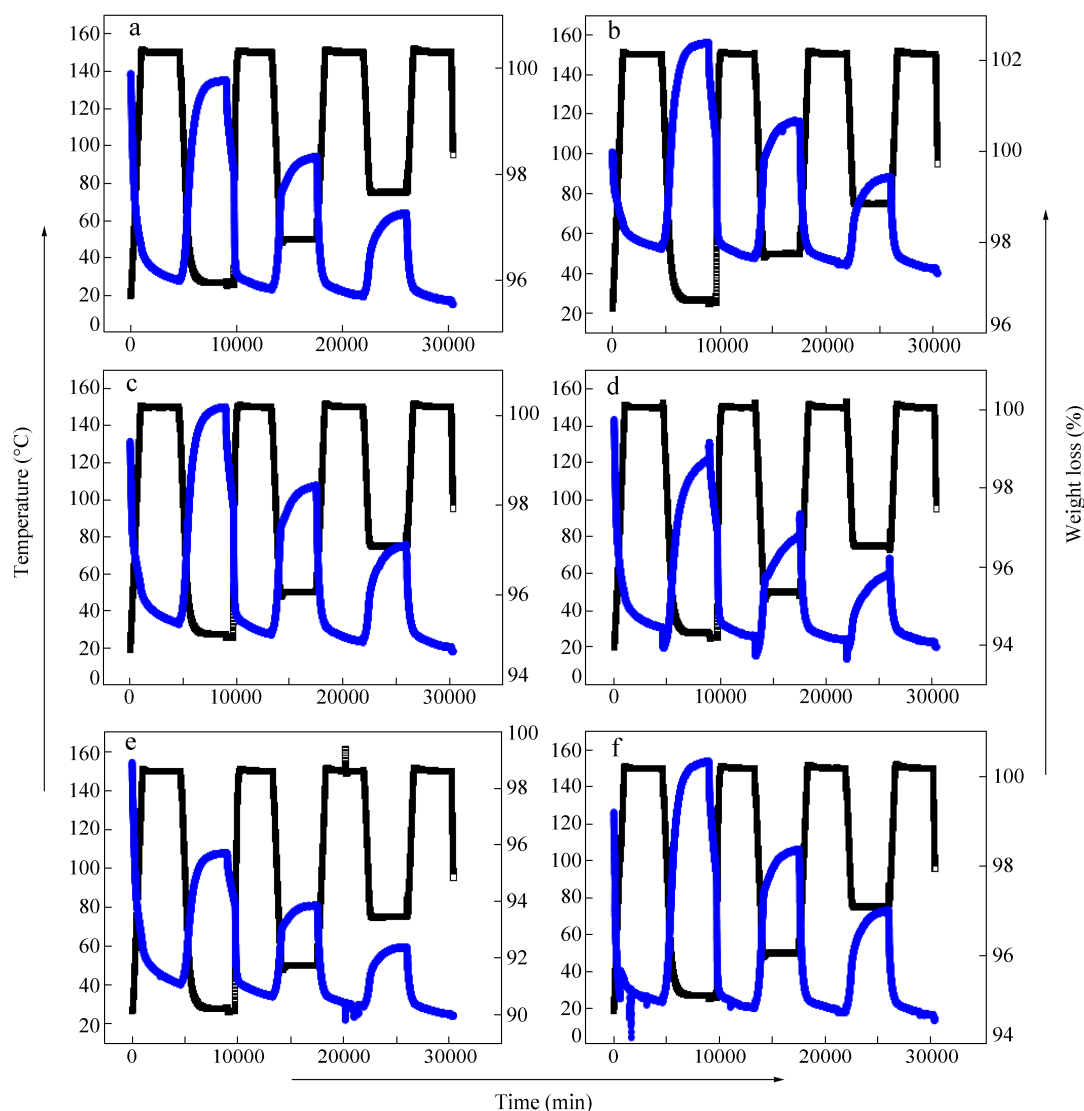
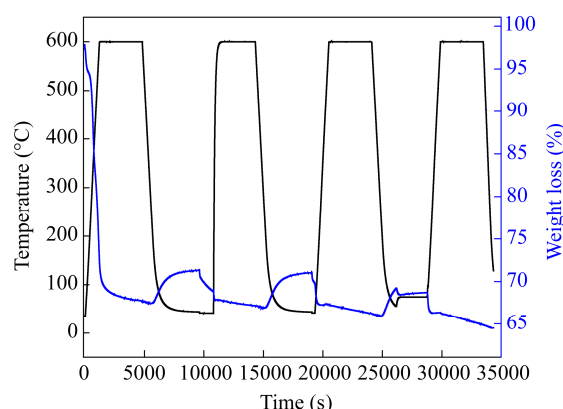


Fig. 10 CO₂ sorption profiles (weight %) of hypercross-linked polymers of anthracene synthesized at (a) 30, (b) 40, (c) 50, (d) 60, (e) 70 and (f) 80 °C

The hypercross-linked polymer synthesized at 80 °C was subjected to desorption at 600 °C in nitrogen, and subsequently CO₂ sorption was carried out (Fig. 11). We observed 4.1% of CO₂ sorption at 50 °C, which is a high value compared to the previous value (3.5% at 50 °C). So, as discussed above, when the temperature is raised to 600 °C, the —CH₂— bridges are completely dehydrogenated with the formation of large rigid building blocks that form micropores.

Table 3. The effect of adsorption and desorption temperature for CO₂ adsorption in hypercross-linked conjugated quinonoid chromophores (All the experiments were carried out at 0.1 MPa.)

Hypercross-linked conjugated quinonoid chromophores	CO ₂ adsorption temperature (°C)	Desorption temperature (°C)	Adsorption capacity (wt%)	Adsorption capacity after re-cross-linking (wt%)
Synthesized at 30 °C	25	150	3.3	
	50	150	2.7	
	75	150	1.5	
Synthesized at 40 °C	25	150	4.3	
	50	150	3.0	
	75	150	1.6	
Synthesized at 50 °C	25	150	4.8	
	50	150	3.7	
	75	150	3.1	
Synthesized at 60 °C	25	150	4.4	
	50	150	3.4	
	75	150	2.0	
Synthesized at 70 °C	25	150	4.7	
	50	150	3.3	
	75	150	2.0	
Synthesized at 80 °C	25	150	5.1	8.0
	50	150	3.5	5.8
	75	150	2.1	4.4

**Fig. 11** CO₂ sorption profiles of hypercross-linked anthracene synthesized at 80 °C (desorbed temperature 600 °C)

CONCLUSIONS

This study establishes that the skeleton of the polymers of hypercross-linked anthracene mainly contains hypercross-linked conjugated quinonoids. They offer high microporosity and surface area because the quinonoids are large size rigid building blocks as they are derived from anthracene. So, hypercross-linked polymers of polynuclear aromatics could be better than those derived from mononuclear aromatics such as benzene to have high degree of micropores to adsorb CO₂. They are thermally stable up to 600 °C. They do not associate with water and possess negligible nitrogen adsorption. The polymers can be synthesized by a simple Friedel Crafts alkylation route. They are all strong solar light absorbers, and hence they can be used very well as strong electron donors in solar cell devices. Additionally heat-treated polymers are verified to have enhanced light absorption characteristic, and so it is good to heat-treat the as-synthesized polymers, if they are suggested for fabrication of solar cell devices. Heat treated polymers as well as re-crosslinked polymers are better than as-synthesized ones for CO₂ adsorption.

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