

Template assisted polymerization of functional materials and their opto-electronic properties

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ABSTRACT

Highly ordered iron incorporated mesoporous silica (Fe-SBA15) was prepared and used as a template for catalytic polymerization of functional molecules. The mesoporous catalysts were used as an oxidative nano-reactor in heterogeneous catalytic reactions to afford highly fluorescent poly(methylene anthracene)s (PMA) when anthracene was used as a monomer. The structure of the mesoporous Fe-SBA15 was 2D channel with large surface area of 710 m²/g and pore size of 9.2 nm. The fluorescent polymer was synthesized with high yield of 90 % in short reaction time. The synthesized polymer PMA showed good emission properties with high excimer emission, which was highly affected by the pore size of the reactor. This indicated that the optical properties of fluorescent polymers synthesized from this method could be controlled by the pore size of the mesoporous templates.

Keywords: Fluorescent polymer, anthracene, mesoporous catalyst, Friedel-Crafts reaction, catalytic polymerization

1. INTRODUCTION

Metal incorporated mesoporous silica catalysts with highly ordered structure, large surface area, suitable pore size and large pore volume have been attracted in environment friendly green catalytic reactions due to their good selectivity, high yield, easy synthetic process, and high reactivity.[1-9] Recently, various mesoporous silica catalysts having different metal species are reported to tailoring the dimension and catalyst contents for effective catalytic reactions. Thus organic molecular reactions such as Friedel-Crafts acylation and alkylation, and benzylation are well known examples that have been successfully carried out with the highly effective mesoporous catalysts. [4-25] Contrary to these molecular reactions, polymerization reactions using metal incorporated silica catalysts have not been well known. Lin et

al. reported the oxidative polymerization of 1,4-diethynylbenzene using a Cu^{+2} incorporated MCM-41 to synthesize a conjugated polymer.[26] Although they could prepare polymeric materials, the average molecular weight of the resultant polymer was small and the mesoporous catalyst was damaged after polymerization, possibly due to the low reactivity and very weak mechanical stability of MCM-41 materials which have thin walls. Herein, we report the facile catalytic polymerization of anthracene from nano-sized reactor using mesoporous catalyst with good stability.

2. EXPERIMENTAL

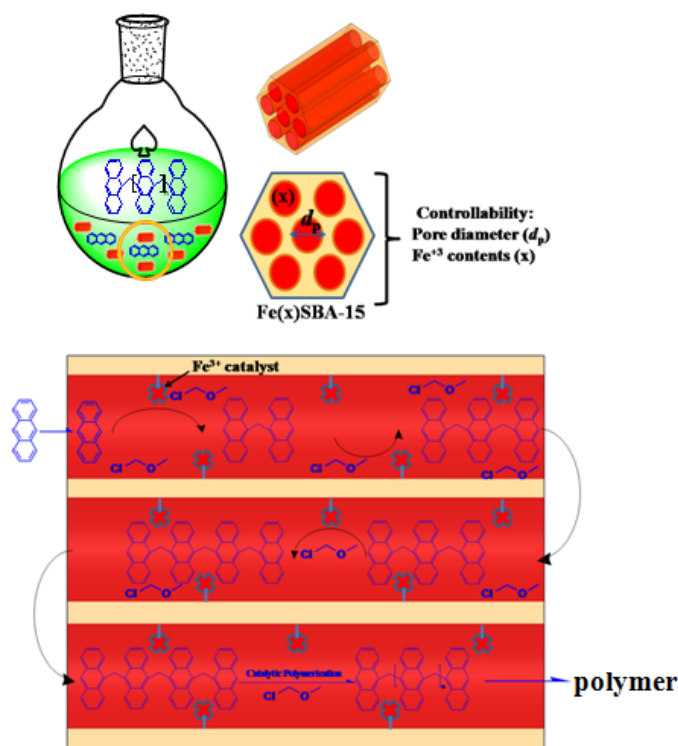


Figure 1. Schematic representation of catalytic polymerization of anthracene from Iron (III) incorporated mesoporous silica catalyst.

2.1. Materials

Ferric nitrate nonahydrate, tetraethyl orthosilicate (TEOS), anhydrous chloroform and triblock copolymer poly(ethylene glycol)-block-poly-(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, molecular weight) 5800, EO20PO70EO20) were purchased from Aldrich. Anthracene and chloromethyl methyl ether were purchased from TCI. Anthracene was used after washing with hot ethanol.

2.2. Instruments

^1H NMR spectra were obtained using a Bruker 300 MHz spectrometer. FT-IR spectra were obtained using a TENSOR 37 (Bruker). Molecular weight was determined by gel permeation chromatography (YOUNGLIN, model: Acme 9000) and polystyrene (PS) and THF was used as calibration standard and solvent. UV spectra were obtained from a Guided Wave model 260 (Guided Wave, Inc., USA) and fluorescence was measured with a luminescence spectrometer (PerkinElmer, Model LS55). X-ray diffraction patterns were recorded on a Rigaku diffractometer with Cu K α radiation ($\lambda=0.154$ nm) and a step size of 0.01 at a scan speed of $0.1^\circ \text{ min}^{-1}$. Nitrogen adsorption and desorption isotherms were measured at -196°C on a Quantachrome Autosorb 1C analyzer after outgassing at 150°C for 24 h. The specific surface area was calculated by the BET method. The pore size distributions were obtained from the adsorption and desorption branch of the nitrogen isotherms by the Barrett–Joyner–Halenda method.

2.3. Preparation of Fe-SBA-15

Amphiphilic triblock copolymer Pluronic **P123** (2 g) was dispersed in 15 g of water and stirred for 4 h, and then 35 mL of 0.29 M HCl was added and the mixture was stirred for 1 h (pH = 2.2). Then 4.5 g of tetraethyl orthosilicate (**TEOS**) and the appropriate amount of ferric nitrate were added directly to the homogeneous solution with stirring. The resulting gel solution was aged at 40°C for 24 h and finally aged at 100°C for 48 h. The molar composition of the gel synthesis mixture was 1:0.143-0.5:0.016:0.46:127=TEOS:Fe $_2$ O $_3$:P123:HCl:H $_2$ O. After synthesis, the solids obtained were calcined in flowing air at 540°C to decompose the triblock copolymer. Finally red colored catalyst powder was obtained.

2.4. Synthesis of Poly(methylene anthracene)

Iron incorporated mesoporous silica catalysts were used right after synthesis for catalytic polymerization. The anthracene monomer (1 g, 5.61 mmol) was added to anhydrous chloroform 50 ml in two necked round bottom flask and then chloromethyl methyl ether (16.8 mmol) was added to above solution. After stirring for 10 min the catalyst (2.5 % of monomers) was added to reaction mixture under the N $_2$ atmosphere before heating. After mixing the temperature was slowly increased up to reflux condition temperature. As temperature increases the reaction solution becomes clear orange colored solution and then deep greenish final solution. The reaction mixture was cooled down to R.T. after 60 h then filtered with filter paper to remove catalyst. The final solution was concentrated by evaporator and then poured to 500 ml methanol with stirring magnetic bar. The yellowish precipitated solid was collected and dried. The yield was about 90 %. The filtered catalysts were collected and dried for XRD and BET measurements to confirm the stability of catalysts. There was not much change in weight of catalyst before and after polymerization. The polymerized PMA n showed molecular weight of 4300 g/mol with high yield of 90 %. ^1H NMR (CDCl $_3$, ppm) δ : 4.22 (s, -CH $_2$ -, between anthracene, 2H), 7.4 - 8.54 (m, anthracene, 8H).^{5a}

3. RESULTS AND DISCUSSION

3.1. Synthesis and properties of template catalyst

We prepared Fe^{+3} incorporated SBA-15 with high content of Fe^{+3} . Figure 2(a) shows powder X-ray diffraction (XRD) patterns for pristine **Fe-SBA15** before polymerization and XRD patterns show highly ordered hexagonal structure with (100), (110), and (200) peaks. As shown in Figure 2(b), after polymerization of anthracene, the catalyst showed clear

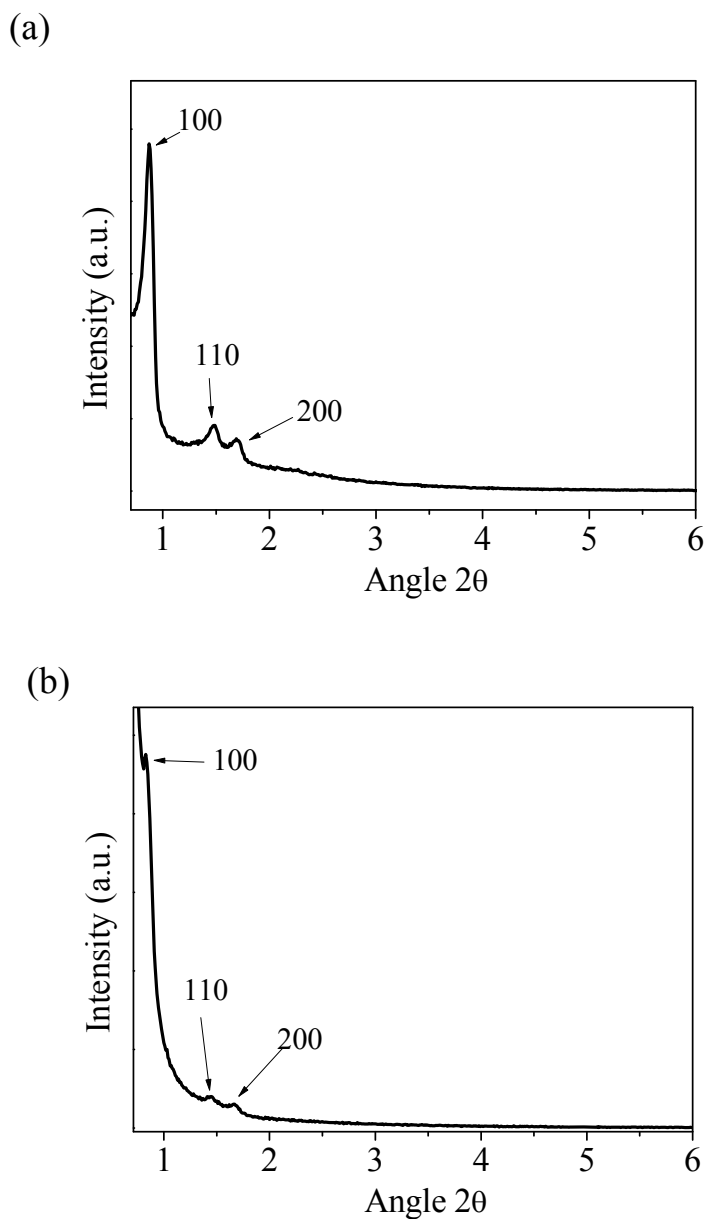


Figure 2. Powder X-ray diffraction patterns of (a) pristine Fe-SBA15 and (b) after catalytic polymerization of anthracene.

peaks at same position, which mean that the catalyst had good stability in reaction. It has been known that some mesoporous silica catalysts showed poor stability of break of catalyst structure after reaction due to the poor mechanical property of silica catalyst. The broken small particle of catalyst could be impurity and affect to purity of final product. Therefore, the stability of mesoporous silica based catalyst is very important in catalytic reactions. The synthesized mesoporous silica catalyst exhibited large surface area of 710 m²/g, pore size of 9.2 nm, and pore volume of 0.9 cm³/g from BET N₂ adsorption-desorption isotherms and BJH pore-size distribution measurements exhibited that all the FeSBA-15 have narrow pore size distribution. Interestingly, the BET N₂ adsorption-desorption isotherms showed similar results before and after polymerization of anthracene in reflux condition. From XRD and BET measurements, mesoporous catalyst showed good stability and reactivity in catalytic polymerization. The monomers could enter the ~ 10 nm pores and the pore could play a role of very small size reactor with high reactivity.

3.2. Optical properties of synthesized PMA_n

As shown in Figure 3 the synthesized polymer PMA_n from the template (PMA_n-Temp) showed absorbance peak maximized at 390 and 409 nm in chloroform solution (10⁻⁵ M), which are different from that of monomer, anthracene.

The emission peak of the PMA_n-Temp was appeared at 430 and 515 nm and the fluorescence quantum yield (Φ_E) was determined as 52 %. The emission peak at 515 nm is ascribed to the anthracene excimer emission, which is generally observed in the highly concentrated anthracene solution and film [27]. The excimer emission of the PMA_n-Temp was stronger than that of PMA_n synthesized from FeCl₃ without template (PMA_n-FeCl₃) [28]. This indicates that excimer formation is be more favorable and anthracene molecules are bound closely in PMA_n-Temp, to enhance anthracene-anthracene (A-A) interactions.

The PMA_n-Temp film showed similar absorbance as those in solution. However fluorescence of the PMA_n-Temp was greatly changed in the film as shown in Figure 4. The fluorescence band of the PMA_n-Temp film was red-shifted than the film of PMA_n- FeCl₃. Taking advantage of the enhanced fluorescence of the PMA_n-Temp, we examined electrofluorescence switching properties of the of the PMA_n-Temp film. The fluorescence of the PMA_n-Temp film was electrochemically controlled under redox condition. The fluorescence on/off ratio was 2, which is higher than the PMA_n-FeCl₃ (1.3).[29] The electrofluorescence switching of a two-electrode device using PMA_n-Temp was reversible and operated under low potential of -2 V and +2 V, as shown in Figure 5.

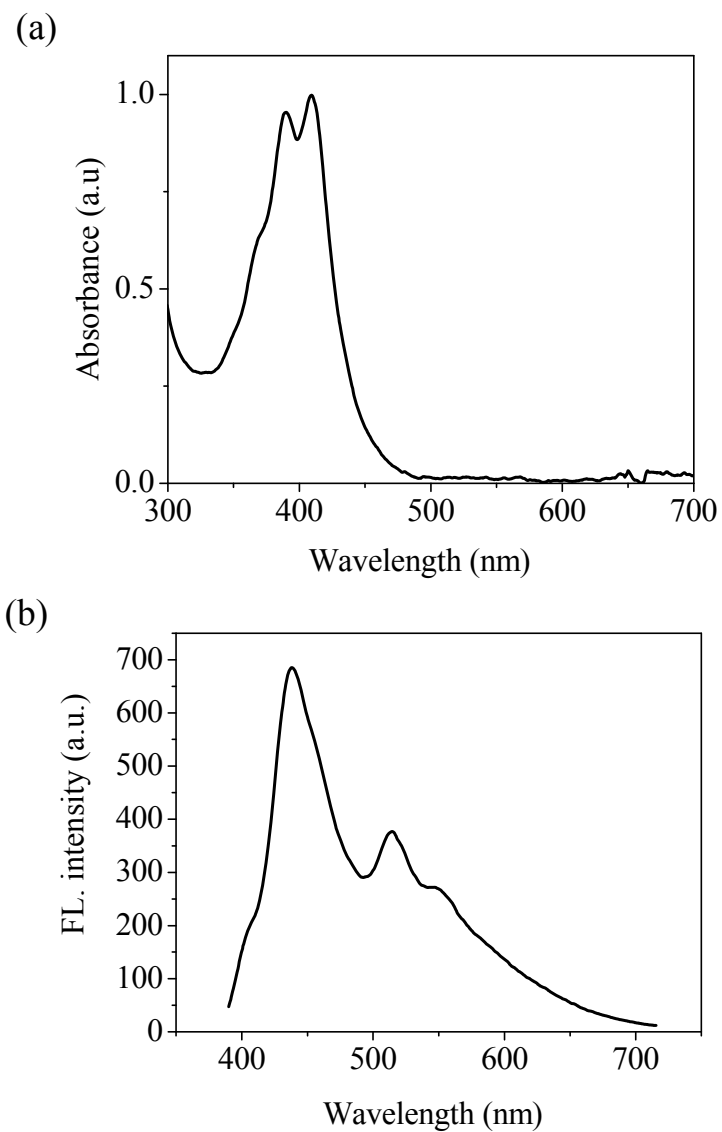


Figure 3. Normalized UV-Vis (a) and fluorescence emission (excited at 370 nm) (b) spectra of synthesized PMAn in chloroform solution (10^{-5} M).

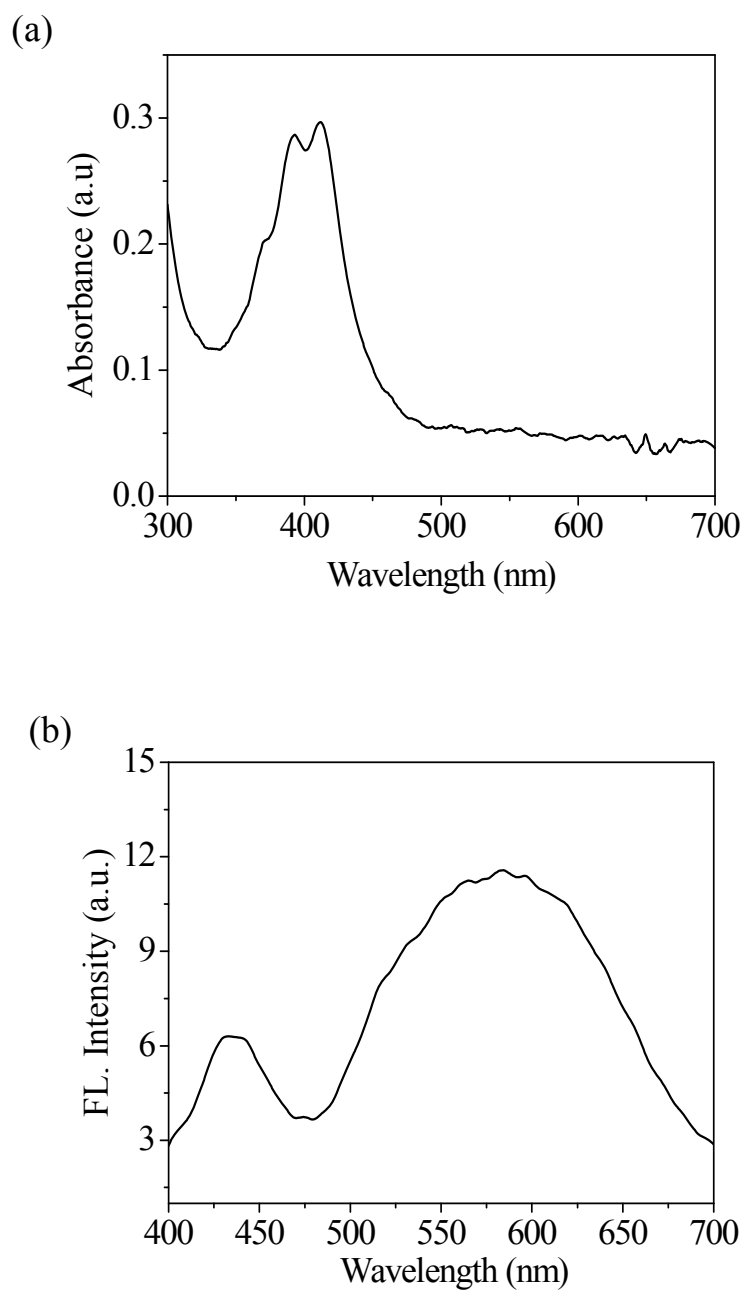


Figure 4. Normalized (a) UV-Vis and (b) fluorescence emission (excited at 370 nm) spectra of PMAAn-Temp film.

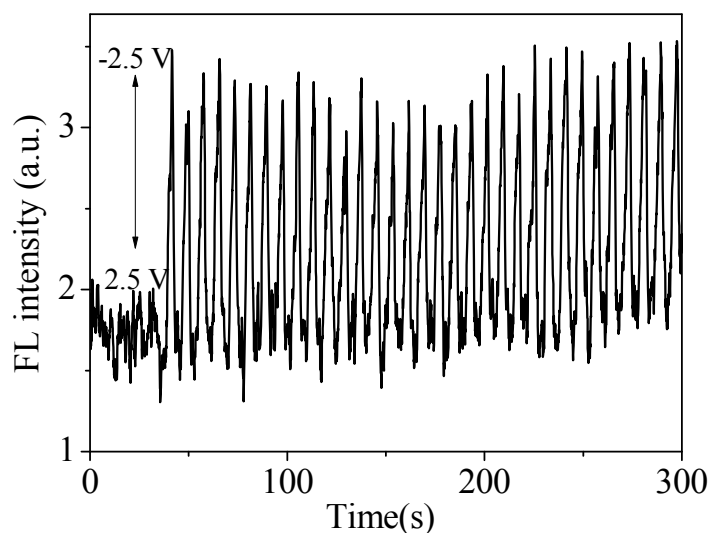


Figure 5. Electrofluorescence switching of a two-electrode device containing PMAAn-Temp from -2 V and +2 V with 8 sec for each step. ($\lambda_{\text{exc}} = 390$ nm, monitored at 520 nm).

4. CONCLUSIONS

In conclusion, we demonstrated that the Fe^{+3} incorporated highly ordered mesoporous silica template with large surface area, 10 nm pore and large pore volume could be successfully used for catalytic polymerization of anthracene in good reactivity and yield. The catalytically polymerized fluorescent polymer, PMAAn-Temp, showed high quantum yield of 52 % and strong excimer emission due to the enhanced anthracene-anthracene (A-A) interactions. In film state, the PMAAn-Temp showed red-shifted fluorescence compared to homogeneously polymerized PMAAn, and fast switching with higher fluorescence on/off ratio. This catalytic polymerization of functional molecule using Friedel-Crafts type reaction can open the new method to various optically active monomers, having good yield, well-structured polymer, highly enhanced optical properties.

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