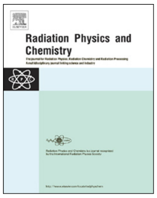
Radiation Physics and Chemistry 150 (2018) 157–162

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



New study on the rules of sub-nano level structures of ordered mesoporous polymers by using positron annihilation lifetime spectroscopy

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ARTICLE INFO

Keywords:
Ordered mesoporous polymers
Sub-nano level structures
Self-assembly
Positron annihilation
High temperature synthesis

ABSTRACT

We report here a high temperature directed, self-assembly to the synthesis of ordered mesoporous organic polymers (OMPs) with different nanopore sizes and BET surface areas. The synthesized OMPs have large BET surface areas (219–512 m^2/g), ordered mesopores, and adjustable pore volumes (0.20–0.48 cm^3/g). Their rules of sub-nano level structures such as free volumes, unopened nanopores and electronic environment in the synthesized OMP materials were systematically investigated by using positron annihilation lifetime spectroscopy, which acts as an important technique for investigating microstructures of ordered mesoporous organic polymers and optimization of synthetic conditions of porous organic polymers.

1. Introduction

Porous organic polymers (POPs) act as a class of *state-of-the-art* materials (Wu et al., 2012; Zeng et al., 2016; Lu et al., 2012a) that have received extensive research interests because of their wide applications in the areas of gas storage and separation, (Chen et al., 2012; Liu et al., 2017; Ji et al., 2016; Huang et al., 2016) catalysis, (Sun et al., 2015; Liu et al., 2012; Xie et al., 2013; Alkordi et al., 2016) energy harvesting, (Zhuang et al., 2015) chemical sensing, (Xie et al., 2010) and drug delivery (Fang et al., 2015). POPs show a variety of unique properties such as diversity in the building blocks, abundant nanoporosity, large BET surface areas, low skeleton density, flexible networks, facile functionality and excellent water-tolerance property. Up to now, various kinds of POPs such as covalent organic frameworks (COFs), (Zeng et al., 2016; Ding and Wang, 2013; Xiang and Cao, 2013) porous polymer networks (PPNs), (Yuan et al., 2011; Lu et al., 2012b, 2011) porous aromatic frameworks (PAFs), (Ben et al., 2009; Luo et al., 2012) polymers of intrinsic microporosity (PIMs), (Swaidan et al., 2015; Zhuang et al., 2014) nanoporous polydivinylbenzene (NPDVB), (Zhang et al., 2009a, 2009b) conjugated microporous polymers (CMPs) (Xie et al., 2013; Jiang et al., 2007) and ordered mesoporous polymers (OMPs) (Liang and Dai, 2006; Zhang et al., 2005; Meng et al., 2005) have been successfully prepared. OMPs is a kind of special and important member in the family of POPs because of their unique structural characteristics of large pore volumes, the combination of disordered micropores and ordered mesopores. The presence of interconnected micropores and ordered mesopores make the functional groups anchored onto the network of OMPs more accessible to the guest molecules with different sizes. Therefore, the functional OMPs have been widely used in the areas of catalytic conversion of bulky molecules and highly selective capture of polluted gases such as CO_2, H_2S from flue gas (Chen et al., 2012; Liu et al., 2017; Ji et al., 2016; Huang et al., 2016).

OMPs were firstly reported by Zhao's and Dai's group nearly the same time, which were innovativelly synthesized from self-assembly of block copolymer templates (F127, P123, F108 *etc*) with phenolic resol and curing at relatively low temperature (100 °C) (Liang and Dai, 2006; Zhang et al., 2005; Meng et al., 2005). The interconnected micropores was derived from hydrophilic chain of the templates, which insert into the network of OMPs during synthetic processes because of their strong H-bond interactions; While the ordered mesopores were derived from hydrophobic chains of the templates, which acts as an important role for formation of spherical or tube-like micelles (Wan and Zhao, 2007). The synthesized OMPs have been widely used in heterogeneous catalysis, selective adsorption and separation. However, the reported OMPs such as FDU-15, 16 were synthesized at relatively low temperature (≤100 °C) (Liang and Dai, 2006; Zhang et al., 2005; Meng et al., 2005, 2006; Wang et al., 2011, 2016; Wan et al., 2009), which usually exhibit low thermal and mechanical stabilities because of their low cross-linking degree (Knop and Pilato, 1985; Maciel et al., 1984; Liu et al., 2009). The industrial phenolic resin were usually cured at high temperature (up to 160 °C), which strongly improves their thermal and mechanical stabilities (Knop and Pilato, 1985; Maciel et al., 1984; Liu et al., 2009). In addition, the main characterization technique for the nanopores in OMPs were N_2 adsorption-desorption isotherms and

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https://doi.org/10.1016/j.radphyschem.2018.05.005
Received 26 December 2017; Received in revised form 2 May 2018; Accepted 4 May 2018

electron microscope, which could not give the detailed sub-nano level structures, free volumes and unopened nanopores of OMPs materials. In fact, the sub-nanoscopic pore architectures of OMPs play key factors for their properties in various research areas.

We reported here a high temperature directed, hydrothermal synthesis of OMP-Ts (where T stands for the synthetic temperature) materials with enhanced cross linking degree, adjustable and ordered mesopores, which could be used as stable and efficient supports for grafting with a variety of active species. In fact, the unopened porous structures, sub-nano level structures and free volumes strongly affect the incorporation of variously active species, further affecting the exposure degree of active sites and mass transfer in OMPs, which strongly affect their performances in the areas of catalysis and selective adsorption. The most reported technique such as gas adsorption-desorption isotherms and electron microscope usually give the information such as BET surface areas, pore sizes, and pore volumes. To reveal the detailed information of sub-nano level structures, free volumes, unopened nanopores and electronic environment in OMP materials. We innovatively investigate the structures of OMP-Ts by using positron annihilation lifetime spectroscopy (PALS) in this work, revealing a variety of effects such as skeleton defects, sub-nano level structures and free volumes on their nanopore sizes, BET surface areas and pore volumes. This study develops a novel and efficient technique to investigate the detailed sub-nano level structures of ordered mesoporous polymers, giving the optimal synthetic conditions of OMPs, which will be very important for rational design OMPs with enhanced properties in various research areas such as adsorption and heterogeneous catalysis.

2. Experimental section

2.1. Chemicals and reagents

All reagents were of analytical grade and used as purchased without further purification. Nonionic block copolymer template poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide) (Pluronic F127, molecular weight of about 12600) were purchased from Sigma-Aldrich Company, Ltd (USA). Phenol, formaldehyde solution (37 wt%), and NaOH were obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of samples

Ordered mesoporous organic polymers of OMP-*n* (where *n* stands for the synthetic temperatures) were hydrothermally synthesized at the temperatures of 100–180 °C. Ordered mesopore in OMP-*n* was constructed from the self-assembly of resol precursors and block copolymer template (F127) with a molar ratio of $C_6H_5OH/CH_2O/NaOH/F127/H_2O$ at 1/4.34/0.235/0.0093/90.6. As a typical run, 2.0 g of phenol and 7 mL of a formaldehyde solution (37%, w.t.) were dissolved in 10 mL of a 0.5 M NaOH solution, after stirring at 75 °C for 30–40 min. An aqueous solution containing 2.5 g of F127 ($EO_{106}PO_{70}EO_{106}$, M_W = 12,600) and 20 mL of deionized water was introduced, the reaction mixture was continuously stirred at 75 °C for another 3 h. Abundant brown precipitation was formed, which was then transferred into an autoclave for curing at a variety of temperatures (100, 120, 140, 160 and 180 °C) for 24 h. The pristine OMP-*n* with monolith morphology was collected by filtration, washed with abundant water, dried at 80 °C under vacuum condition for 24 h. The block copolymer could be removed by calcination at 370 °C for 5 h with flowing nitrogen gas containing a small amount (3.0%, v/v) of oxygen.

2.3. Characterizations

Small angle X-ray diffraction (XRD) patterns were recorded on Rigaku D/Max-2550 using Cu Ka radiation. Transmission electron microscopy (TEM) experiments were performed on a JEM-2100F electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. The nitrogen isotherms at the temperature of liquid nitrogen were measured by using a Micromeritics ASAP 3020 M system. The samples were outgassed for 10 h at 150 °C before the measurements. The pore-size distribution was calculated using the Barrett-Joyner-Halenda (BJH) model. Thermogravimetric analysis was performed on a PerkinElmer TGA7 in flowing nitrogen with a heating rate of 10 °C/min.

2.4. Positron annihilation experiments

Positron annihilation spectrometry measurement were carried out using a fast-slow coincidence ORTEC system, in which the time resolution were about 210 ps at full width at half-maximum (FWHM). A 13 μCi activity positron source (^{22}Na) was sandwiched between the two identical samples. A standard nickel sample was used to calibrate the contribution of positron source component (382 ps, 17.52%), and each spectrum was collected more than total counts of 3×10^6. All the lifetime spectra were analyzed by using the Maximum Entropy for Lifetime Analysis (MELT) routine under the same fitting condition parameters. The lifetime spectra of the samples were analyzed by using routine LT-9 method reported in the literature (Kansy, 1996). The assumed value of maximum entropy parameter was 8×10^{-7}. The as-obtained lifetime distribution was used to confirm the chosen number of components. The relation between cavity size and the lifetime of *o*-Ps in a hole was quantified in a model used by Tao-Eldrup, $\frac{1}{\tau_3} = 2\{1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin(\frac{2\pi R}{R+\Delta R})\}$, and $\Delta R = 0.1656$ nm in this model (Shukla et al., 1997; Tao, 1972).

3. Results and discussion

Fig. 1 shows small-angle XRD patterns the OMP-Ts synthesized at different temperatures. A well-resolved diffraction peak associated with (110) reflection could be clearly observed in these samples. Except for (110) reflection, another two broad peaks associated with (200) and (211) reflections could also be observed in OMP-120 and OMP-140, indicating typical body centered cubic space group (*Im-3m*) with highly ordered mesopores was formed in these samples (Meng et al., 2005). However, the signals associated with (200) and (211) reflections could not be clearly observed in OMP-100, OMP-160 and OMP-180, indicating their decreased orderings of mesopores in comparison with OMP-120 and OMP-140. The above results indicate the optimal synthetic temperatures for OMP-Ts should be ranged from 120 °C to 140 °C, which was favorable for formation of ordered mesopores in OMP-Ts. The high synthetic temperatures (> 150 °C) results in the decomposition of block copolymer templates (Wang et al., 2008); While the low synthetic temperatures (120 °C <) results in the looser (less cross-linked) structure of OMP-Ts that is easier modified during thermal

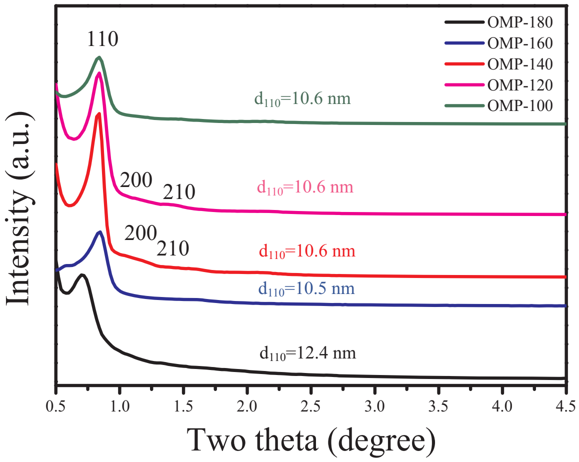

Fig. 1. Small angle XRD patterns of various OMP-Ts samples.