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Preparation and characterization of three-dimensionally ordered macroporous syndiotactic poly(*p*-methylstyrene)

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Abstract

Three-dimensionally ordered macroporous(3DOM) syndiotactic poly(*p*-methylstyrene) (sPPMS) with pore size 170 nm was fabricated by means of silica templates using $(dbm)_2Ti(OPh)_2$/MAO catalytic system. The resulting polymers were characterized by SEM, ^{13}C NMR, DSC and GPC. The results indicated that the 3DOM sPPMS were highly syndiotactic. GPC curves showed that the 3DOM sPPMS possessed lower Mn and broader MWD compared with bulk one. Meanwhile, DSC results revealed that three 3DOM sPPMS exhibited crystalline form II, and bulk sPPMS form III.

Keywords: Dimensionally ordered macroporous polymer; Syndiotactic poly(*p*-methylstyrene); Coordination polymerization

1. Introduction

Recently, there has been extensive interest in the creation of three-dimensionally ordered macroporous (3DOM) materials due to potential applications in photonic crystals, sensors, hierarchic battery electrodes [1–4]. A variety of 3DOM materials of varied composition, ranging from metals, inorganic oxides, semiconductors to polymers [5–8] have been fabricated by replicating colloidal crystal templates. In this method, the corresponding precursor solution infiltrates the interstitial voids of a crystal template and solidifies without disrupting the parent framework. A new porous materials with long-ranged periodic structure is then created by subsequently removing the template. An important feature of this method is that the resulting spherical voids originally occupied by the templates are highly ordered and interconnected via small channels.

Up to now, As far as the preparation of 3DOM polymer is concerned, most previous studies have focused on the radical polymerization, crosslink by thermal treatment or exposure to UV light or X-radiation-initiated.[9–11] Instead of this, many 3DOM polymers have been fabricated by infiltrating colloidal crystals with solution of preformed polymers [12]. However, coordination polymerization which is sensitive to water and oxygen has been few reported.

As is well known, polymer with high syndiotacticity exhibits excellent physical properties, such as high melting temperature, fast crystallization rate and low dielectric constant, as well as permeability resistance to gas. We have reported the investigation of 3DOM syndiotactic polystyrene [13]. And, it is known that postmodification of the polymer is an important method for creating novel materials with some special function. Therefore, choosing the syndiotactic polymer with functional group as matrix of 3DOM polymer is significant for further functionalizating 3DOM polymer and broading the scope of application of the 3DOM sPPMS.

Therefore, in this communication, poly(*p*-methylstyrene) was used as candidate polymer by means of silica colloidal crystal template using β-diketonate titanium complex/methylaluminoxane (MAO) to fabricate the 3DOM polymer with high stereoregularity. Thus, the resulting 3DOM polymers can be functionalized in benzyl groups. And it is expected that some advanced materials used as photonic materials and sensors can be created.

2. Experimental

2.1. Materials

Ethanol, 25 wt% aqueous ammonia, 40 wt% hydrofluoric acid purchased from Tianjin Chemical Reagent Factory are of

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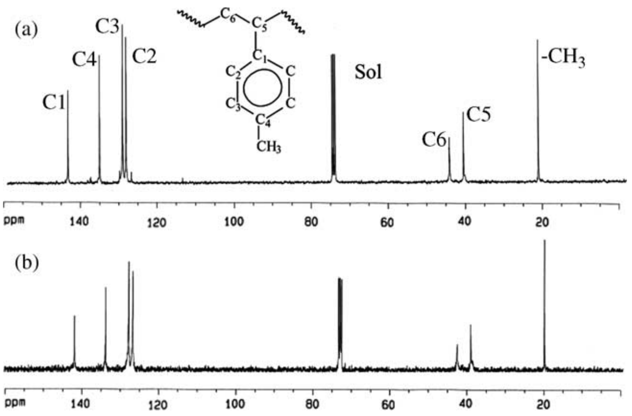

Fig. 1. ^{13}C NMR spectra of (a) bulk sPPMS and (b) 3DOM sPPMS.

reagent quality without further purification. Styrene from Beijing Chemical Reagent Factory and *p*-methylstyrene from Aldrich were dried over calcium hydride under reflux for 24 h, and distilled under reduced pressure before use. Tetraethoxysilane was commercially obtained from Beijing Chemical Limited Company. Methylaluminoxane (MAO, 10% solution in toluene) was purchased from Arbemarle Company. The synthesis of $(dbm)_2Ti(OPh)_2$, a β-diketonate titanium catalyst was reported [14].

2.2. Preparation of colloidal crystal templates

Monodispersed silica spheres with average diameter 214 nm was prepared according to Stöber–Fink–Bohn technique [15]. Three-dimensionally interconnected colloidal crystal pellets were obtained by gravitational sedimentation method. The resulting pellets were sintered at 400 °C for 2 h to enhance the connectivity between the spheres and then cool down to ambient temperature for further use as templates.

2.3. Preparation of 3DOM sPPMS

The silica template was treated under vacuum at 120 °C to remove the water and air in the templates completely. After the mixture of *p*-methylstyrene, MAO and the catalyst was fully filled into the template by means of ultrasonication, a coordination polymerization was carried out at 80 °C for 24 h under argon atmosphere, to prepared silica/sPPMS composites. The bulk polymer polymerized outside the template was peeled off. After silica template in the composites was removed with 40 wt% aqueous hydrofluoric acid under ultrosonication and then soaked in HF overnight, 3DOM sPPMS was obtained. The resulting 3DOM sPPMS was washed with distilled water several times and dried at 80 °C under vacuum.

2.4. Characterization

The vacuum-sputtered samples with Au were characterized using scanning electron microscopy (Hitachi S-530 SEM). In the SEM images, over 100 spheres or pore candidates were measured to determine their average diameter. ^{13}C NMR spectrum of the 3DOM sPPMS was run on a DMX-300 Bruker instrument at 50 °C in $CDCl_3$. Differential scanning calorimetric (DSC) analysis was performed on a Perkin–Elmer DSC-7 at a heating rate of 20 °C/min under nitrogen from ambient temperature to 280 °C. Gel permeation chromatography (GPC) measurements were carried out via PL-GPC-210 in trichlorobenzne (TCB).

3. Results and discussion

3.1. Structure of bulk and 3DOM sPPMS

Typical ^{13}C NMR spectra of the bulk and 3DOM sPPMS were shown in Fig. 1. According to the literature [16], the presence of single sharp resonance for the quaternary carbon C_1 at around 142.3 ppm in Fig. 1(a) showed that the bulk sPPMS was highly syndiotactic. The peaks at 126.8, 127.7 and 133.8 ppm can be assigned to the chemical shift of the three phenyl carbons [17]. The peaks appeared at 39.9, 43.2 and 20.2 ppm correspond to the CH, CH_2 and CH_3 carbons of sPPMS, respectively [17]. Compared with Fig. 2(a) and (b) displays the similar resonances, which revealed that 3DOM sPPMS sample was also highly syndiotactic, and the polymerization in the space between the microspheres of the silica template had little effect on the stereoregularity of sPPMS.

3.2. SEM of 3DOM sPPMS

Fig. 2(a) and (b) depict SEM images of silica colloidal crystal template with average diameter of silica microspheres

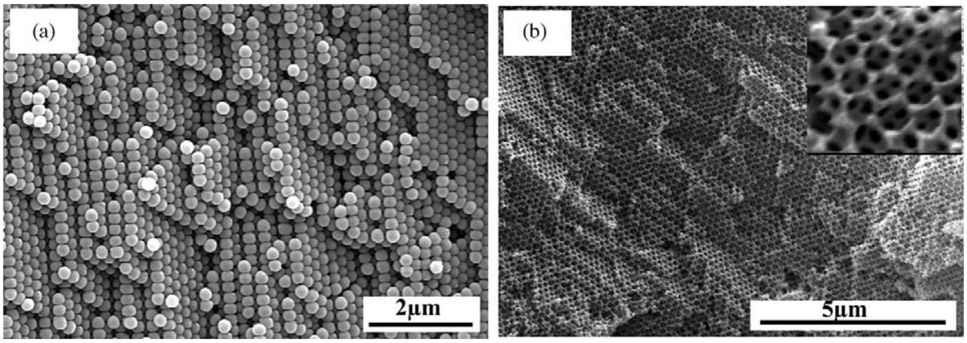

Fig. 2. SEM images of (a) silica colloidal crystal template and (b) the corresponding 3DOM sPPMS. The inset shows the higher magnification of the connecting windows formed between the pores.

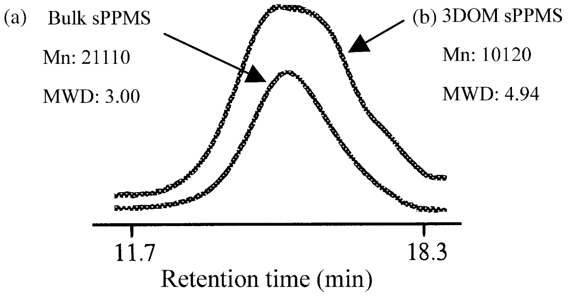

Fig. 3. GPC curves of (a) bulk sPPMS and (b) 3DOM sPPMS.

214 nm and the corresponding 3DOM sPPMS, respectively. The spherical voids in the samples were all matched with the size of starting silica template and maintained their three-dimensionally closed-packed structures. At high magnifications shown in inset of Fig. 2(b), it was observed that each pore was connected to its twelve neighbors by small channels with 72 nm. The center-to-center distances between air microspheres in the resulting 3DOM sPPMS was about 176 nm, which were smaller than that of the pristine silica template. This indicated that the 3DOM sPPMS will shrink after the removal of rigid silica template, and the shrinkage was approximately 17.8%. The phenomenon can be explained in terms of confinement effect of the polymer chains in the confined space [18].

3.3. GPC analysis

As is shown in Fig. 3, the number average molecular weight (M_n) and molecular weight distribution (MWD) of the bulk sPPMS were 21100 and 3.00, and 3DOM sPPMS were 10120 and 4.94. It was revealed that 3DOM sPPMS possessed the lower M_n and the broader MWD than the bulk one. Obviously, the coordination polymerization within the template affected the Mn and MWD of the resulting 3DOM sPPMS.

3.4. DSC analysis

Some information relative to the polymorphic behavior of the two resulting polymers can also be obtained by an analysis of the DSC scans (Fig. 4). The DSC scans of bulk and 3DOM sPPMS were reported in Fig. 4. In Fig. 4(a), the bulk sPPMS showed an endothermic peak, centered at 203.6 °C, corresponding to melting point of form III [19]. A second endothermic peak shown in Fig. 4(b), appeared at 183.5 °C, was due to melting of form II [20].

sPPMS is crystalline as polymerized, does not crystallize by cooling from the melt or by annealing the amorphous phase. The different crystalline forms and the clathrate structures of sPPMS are formed depending on the solvent, the crystallization technique or other parameters. As describe in Ref. [21], form II can be obtained by annealing the THF clathrate in the temperature range 90–150 °C and form III by annealing form I or form IV at high temperature (e.g. 210 °C) [22]. However, the results which form II and III obtained in our experiment have been few reported.

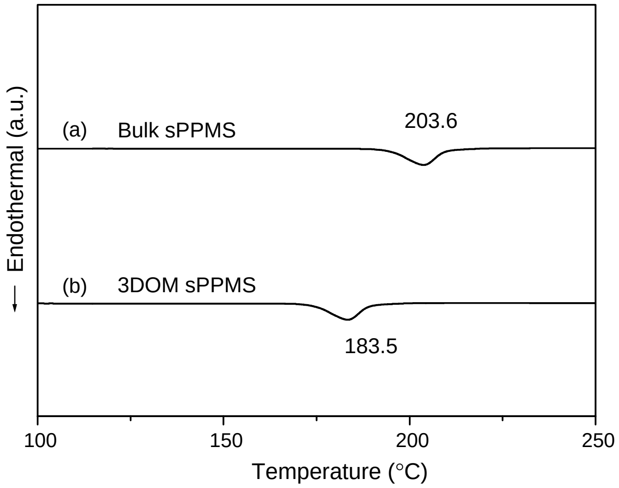

Fig. 4. DSC charts for the bulk and 3DOM sPPMS during the first heating scan.

4. Conclusion

In summary, 3DOM sPPMS with pore size 170 nm was prepared by means of silica templates using $(dbm)_2$-$Ti(OPh)_2$/MAO catalytic system. The resulting polymers were characterized. ^{13}C NMR spectra illustrated that the bulk and 3DOM sPPMS were highly syndiotactic. From the SEM images, It was observed that both silica spheres within the template and pores in the 3DOM sPPMS were arranged in highly ordered fashion, and the shrinkage of the pores in the macroporous sPPMS was 17.8%. GPC curves showed that the 3DOM sPPMS possessed lower M_n and broader MWD compared with bulk one. Meanwhile, DSC results revealed that three 3DOM sPPMS exhibited crystalline form II, and bulk sPPMS form III.

Acknowledgements

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