

Preparation of hierarchical porous carbons from amphiphilic poly(vinylidene chloride-co-methyl acrylate)-*b*-poly(acrylic acid) copolymers by self-templating and one-step carbonization method



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ARTICLE INFO

Article history:

Received 29 December 2013
Received in revised form 4 May 2014
Accepted 10 May 2014
Available online 20 May 2014

Keywords:

Hierarchical porous carbon
Poly(vinylidene chloride)
Poly(acrylic acid)
Block copolymer
Self-templating

ABSTRACT

Based on our previous proposed method to fabricate the hierarchical porous carbons (HPCs), a series of amphiphilic poly(vinylidene chloride-co-methyl acrylate)-*b*-poly(acrylic acid) (PVDC-*b*-PAA) copolymers were prepared via RAFT polymerization and used to prepare the HPCs by self-templating and one-step carbonization method. The phase structure and thermal degradation behavior of PVDC-*b*-PAA copolymers, as well as the morphology and pore structure of corresponding carbons were investigated. It was found that all block copolymers exhibited micro-phase separation feature and showed the PAA-dispersed, bi-continuous, and PAA-dominated phase structures as the PVDC/PAA molar ratio varied from 3:1 to 0.77:1. Although the PVDC-*b*-PAA copolymers exhibited the individual glass transitions of each block, the thermal degradations of PVDC and PAA blocks were interacted and overlapped. The carbons prepared from PVDC-*b*-PAA contained the micro- and meso-pores, which were mainly originated from the thermal degradation of PVDC segment and the pyrolysis of PAA segment, respectively. The carbons prepared from PVDC₆₆-*b*-PAA₂₂ copolymer exhibited a maximum Brunauer–Emmett–Teller surface area of 1093 m² g⁻¹ and a maximum total pore volume of 0.51 cm³ g⁻¹. Due to the incomplete pyrolysis of PAA segment and the jamming effect to pores caused by the PAA-based carbon, the total pore volume of HPCs prepared from PVDC-*b*-PAA copolymers were lower than that of HPCs prepared from the PVDC-*b*-polystyrene copolymers (*J. Mater. Sci.* 49 (2014) 1090–1098).

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1. Introduction

Hierarchical porous carbons (HPCs) have attracted great research interests for their applications in the energy conversion and storage devices [1–5], catalyst supporting [6–10], due to their unique hierarchical porous structures and high porosity. Generally, three strategies have been employed for the preparation of carbon nanomaterials [11–16], i.e., the pyrolysis of organic precursors, physical/chemical vapor deposition, and template-based method. Many researches have aimed to prepare the nanoscale carbons with the well-defined structures by a cost-effective and facile strategy. The template-based strategy is a promising way to achieve this goal. However, the design of efficient templates remains challenging.

Currently, HPCs are mainly prepared by using the hard-/soft-templating [17–21] and templating/post-activation combined methods [22–25]. Zhang et al. [17] prepared the hierarchically

ordered porous carbons with interconnected macro-/meso-pores using sucrose as the carbon source, colloidal polymer as the soft template, and silica sphere as the hard template. Kim et al. [26] prepared a meso-/micro-porous carbon using ethanol as a carbon source within a β -zeolite template. The obtained hierarchical carbon exhibits a very high electrical double-layer capacitance. Zhang et al. [27] prepared the Sn-TiO₂/graphitic carbon by a simple colloidal crystal templating method. However, most of the used templates exhibit a special nanostructure or molecular structure and a complicate process is necessary to remove the templates from the carbon matrix by using the strong acids or bases. Therefore, it is urgently needed to develop a simple and cost-effective pathway for the fabrication of HPCs with tunable pore structure.

It is well known that the vinylidene chloride (VDC) polymers exhibit excellent barrier properties and good resistance to a wide variety of solvents. Besides, VDC polymer can be used as the source of carbon materials, because it can form a micro-porous structure by a high temperature carbonization without any additional activation process [24,28,29]. The use of VDC polymer to prepare molecular sieve was first reported in 1965 by Lamond et al. [30].

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However, efforts were mainly paid to prepare VDC polymer-based meso-/micro-porous HPCs by the catalyst activation [24] and hard templating methods [31]. The use of self-templating block copolymers as the carbon precursors has been proved to be a promising way to prepare HPCs [32,33]. In the previous work [34], we have proposed a novel method to prepare HPCs from the PVDC-based block copolymers, which consists of a pyrolyzable polystyrene (PS) block as the pore extender and a carbonizable PVDC block to generate the micro-pores in carbonization.

In this study, a new kind of PVDC-based block copolymers, consisting of VDC polymer and poly(acrylic acid) (PAA) blocks were used to prepare the micro-/meso-porous carbons by self-templating and one-step carbonization method. The block copolymers were synthesized by the reversible addition fragmentation-chain transfer (RAFT) polymerization. The thermal behavior of the block copolymers, the changes of phase-separated morphology upon heat treatment, and the microstructures of as-prepared carbons were studied. Despite of the incomplete pyrolysis of PAA sacrificed block, the PVDC block was converted to the microporous carbon and the PAA was degraded to form the mesoporous carbon in the carbonization process. The approach reported herein would have several unique characteristics. First, it develops a facile carbonization method to prepare PVDC-based HPCs. Second, it is easy to control pore size and structure via micro-phase separation. Third, micro-/meso-pore ratio can be achieved by varying composition of PVDC/PAA block.

2. Experimental

2.1. Materials

Vinylidene chloride (VDC) (industrial grade) was supplied by Juhua Group Co. (China) and distilled twice under N_2 atmosphere.

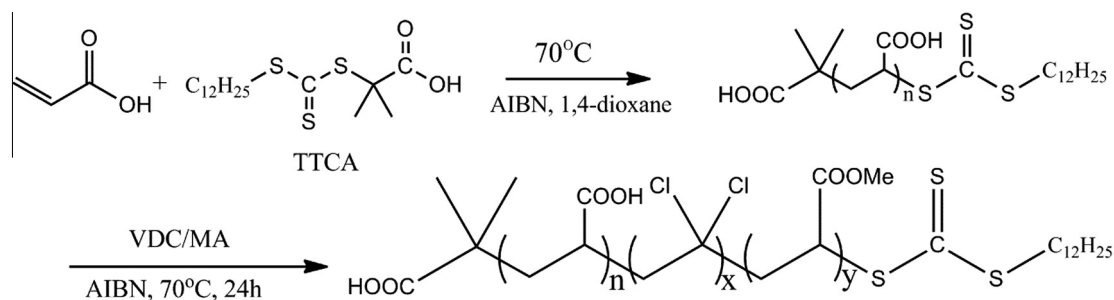
Methyl acrylate (MA) and acrylic acid (AA) purchased from J&K Chemical Reagent Co. Ltd., were purified by vacuum distillation. 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (TTCA) was synthesized using Lai's method [35] and recrystallized from hexane. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%) was recrystallized from ethanol before use. 1,4-Dioxane (99%) and tetrahydrofuran (THF, 99%) were dried with CaH_2 and then distilled. THF- d_8 and DMSO- d_6 (Cambridge Isotope Laboratories, Inc.) used in NMR analysis were purchased from J&K Chemical Reagent Co. Ltd. The other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd., with analytical grade and used as received.

2.2. Synthesis of PVDC-*b*-PAA copolymers

PVDC-*b*-PAA copolymers were prepared by a two-step polymerization sequence, as shown in Scheme 1.

The RAFT polymerization conditions for synthesis of PAA macro-chain transfer agents (CTAs) are shown in Table 1. 2.906 g (8.0×10^{-3} mol) of TTCA and 0.087 g (5.3×10^{-3} mol) of AIBN were dissolved in 25 ml of 1,4-dioxane in a 100 ml jacket flask. Then, 7.963 g (1.1×10^{-1} mol) of AA was added into the flask with another 25 mL of 1,4-dioxane. After bubbling with N_2 for 30 min, the mixture was heated to 70 °C to start the polymerization. After 140 min, the reaction was terminated by exposing the mixture to air. The product was dissolved in THF and purified by precipitation twice in diethyl ether. The product was isolated by filtration and dried to a constant weight at 60 °C under vacuum.

The typical process for preparation of PVDC-*b*-PAA is shown in Table 2. 1.263 g (6.4×10^{-4} mol) PAA macro-CTA prepared in Entry 1 and 0.02 g (1.2×10^{-4} mol) AIBN were dissolved in 50 ml 1,4-dioxane and added into a 200 ml stainless tube. 9.0 g (9.3×10^{-2} mol) VDC and 1.0 g (1.2×10^{-2} mol) MA mixed with another 50 ml 1,4-dioxane in ice-water bath and added into the



Scheme 1. Synthetic route of PVDC-*b*-PAA block copolymers.

Table 1
Synthesis conditions, molecular weight and polydispersity of PAA macro-CTAs.

Entry	AA (mol·L ⁻¹)	TTCA (mol·L ⁻¹)	AIBN (mol·L ⁻¹)	Temp. (°C)	Time (min)	M _n ^{NMR} (g·mol ⁻¹)	M _n ^{GPC} (g·mol ⁻¹)	PDI
1	2.21	1.6×10^{-1}	1.1×10^{-2}	70	140	1309	1970	1.06
2	1.52	3.8×10^{-2}	3.8×10^{-3}	70	80	1921	2340	1.13
3	1.61	1.8×10^{-2}	1.8×10^{-3}	70	120	2682	3050	1.24
4	1.67	2.0×10^{-2}	2.0×10^{-3}	70	720	3445	3500	1.21

Table 2
Molecular weight, polydispersity data for PVDC-*b*-PAA copolymers synthesized in the presence of PAA macro-CTAs.

Samples	PAA-CTAs (mol·L ⁻¹) ^a	AIBN (mol·L ⁻¹)	VDC (mol·L ⁻¹)	MA (mol·L ⁻¹)	Temp. (°C)	Time (h)	M _n ^{GPC} (g·mol ⁻¹)	PDI
PVDC ₆₆ - <i>b</i> -PAA ₂₂	6.4×10^{-3} [1]	1.2×10^{-3}	9.3×10^{-1}	1.1×10^{-1}	70	24	8385	1.37
PVDC ₄₉ - <i>b</i> -PAA ₂₇	6.4×10^{-3} [2]	1.2×10^{-3}	9.3×10^{-1}	1.1×10^{-1}	70	24	7130	1.55
PVDC ₃₅ - <i>b</i> -PAA ₃₇	6.3×10^{-3} [3]	1.2×10^{-3}	9.3×10^{-1}	1.1×10^{-1}	70	24	6435	1.64
PVDC ₃₄ - <i>b</i> -PAA ₄₄	6.4×10^{-3} [4]	1.2×10^{-3}	9.3×10^{-1}	1.1×10^{-1}	70	24	6823	1.48

^a [1], [2], [3] and [4] correspond to PAA-CTAs prepared in entry 1, 2, 3 and 4 in Table 1.

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