

Note

PREPARATION OF P(MAH-co-VAc)-*b*-PSt COPOLYMER BY INITIATION OF PRECURSOR CONTAINING ISOPROPYLTHIOXANTHONE RESIDUES AND ITS APPLICATION IN FABRICATING HONEYCOMB STRUCTURED POROUS FILMS*

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Abstract A novel, facile method to prepare copolymers by virtue of the reinitiation of precursor containing isopropylthioxanthone (ITX) residues (ITXH) was reported. Using poly(maleic anhydride-co-vinyl acetate) (P(MAH-co-VAc)) with incorporated ITX residues as a macroinitiator, polymerization of styrene was performed, and poly(maleic anhydride-co-vinyl acetate)-*b*-polystyrene (P(MAH-co-VAc)-*b*-PSt) was produced. Applying the resultant copolymer in a breath figure procedure, honeycomb structure films having pore size around 250 nm were prepared under low temperature and relative humidity.

Keywords: Macroinitiator; ITXH; Block copolymer; Honeycomb film.

INTRODUCTION

Porous films are of great interest recently for a wide range of potential applications in diverse areas such as substrates for cell culture, antibody or enzyme immobilization^[1–3], membranes for selective transport and separation, high surface area supports for catalyst^[4], specific light-emitting devices^[5] and materials with super water- or oil-repellent surfaces^[6] *et al.*

It is well known that living free-radical polymerization techniques, such as the reversible addition fragmentation chain transfer (RAFT) process, atom-transfer radical polymerization (ATRP) and nitroxide-mediated polymerization (NMP), are of great efficiency in the fabrication of well-defined and complex architectures of copolymers. For example, amphiphilic block copolymers based on polystyrene, such as poly(styrene-co-acrylic acid)^[3], poly(ethylene glycol) monomethyl ether-*b*-poly(*N*-methacryloyl L-leucine methyl ester)s^[7] or poly((ethylene glycol)-co-styrene)^[5] were synthesized by RAFT or ATRP polymerization. Six- or five-arm star-shaped polystyrenes were generated either *via* coppermediated ATRP or by RAFT process using a multi-functionlized initiator^[5]. Novel amphiphilic diblock copolymers consisting of dendronized polymethacrylate-*b*-poly(ethylene oxide) were designed and synthesized *via* ATRP^[8].

Other favorable synthetic strategies for producing block copolymers under mild conditions include the employment of sequential free radical initiator such as di-*t*-butyl 4,4'-azobis (4-cyanoperoxyvalerate)^[9], macro-initiators such as PMMA precursors containing di-, tri-phenyl or phenoxy terminal groups, or macro-co-

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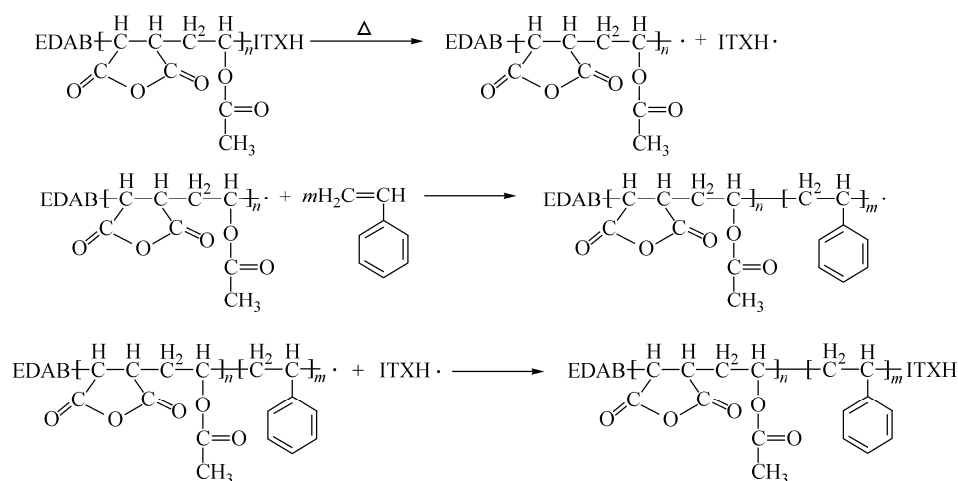
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initiators^[10] with active functional groups bound on their ends, such as prepolymers with amine end groups obtained by polymerization initiated with a binary system composed of aniline and benzophenone (BP).

In a bimolecular photoinitiating system comprising an electron donor come from macromolecular chains of polymeric film and an electron acceptor related to aromatic ketone such as BP and isopropylthioxanthone (ITX), the combination of propagating radicals with diaryl ketyl radicals and the reversible cleavage of the formed weak C—C bond under UV irradiation or thermal treatment suggest a possibility of performing living or controlled free radical polymerization, which was demonstrated by Yang, Bowman and Yamamoto in their researches of photograft polymerization occurred on the surface of polymeric materials^[11–13]. Moreover, in virtue of the reversible coupling and cleavage, composite core-shell particles were constructed with a commercially available vulcanized acrylonitrile butadiene rubber (NBR) emulsion as model latex^[14].

Herein, we report a facile, economic way to prepare block copolymers through the application of commercial available Norrish II photoinitiator ITX under mild conditions. At first, by using a binary photoinitiation system of ITX and ethyl 4-(dimethylamino) benzoate (EDAB), poly(maleic anhydride-co-vinyl acetate) (P(MAH-co-VAc)) with ITXH coupled on ends was prepared. Subsequently, in the presence of macroradicals derived from the cleavage of weak C—C bonds linked ITXH and P(MAH-co-VAc) chain, the polymerization of St was started in cyclohexanone and thus copolymer of P(MAH-co-VAc)-*b*-PSt was produced (Scheme 1). The construction of honeycomb-structured macroporous films *via* a simple breath figure procedure demonstrated the formation of the block copolymer.



Scheme 1 The mechanism for polymerization of styrene initiated by P(MAH-co-VAc)-ITXH precursor under thermal activation

EXPERIMENTAL

Materials

St and vinyl acetate (VAc) (Tianjin Chemical Reagent Co., Ltd) were purified by distillation under reduced pressure. Maleic anhydride (MAH) (Beijing Yili Fine Chemical Reagents Co., Ltd), ITX (2 & 4-isomer mixture) and EDAB (Th-unis Insight Co., Ltd) were used as received. All solvents were used without further purification.

Preparation of P(MAH-co-VAc)-*b*-PSt Copolymer

P(MAH-co-VAc) with ITX residues (P(MAH-co-VAc)-ITXH) was synthesized by a photo-induced polymerization using ITX/EDAB as an initiator system. Reaction conditions were as follows: monomer concentration (MAH/VAc mol ratio 1:1) was 23.8%, ITX/monomer concentration was 0.96%, and the weight ratio of ITX/EDAB was 100:1. The conversion of monomer (MAH/VAc) was 57.8%. With P(MAH-co-VAc)-

ITXH ($M_n = 13400$, PDI = 4.3, 2.95 wt%) as a macroinitiator, polymerization of St (49.85 wt%) dissolved in cyclohexanone was carried out at 95°C in a 250 mL, four-necked flask equipped with tetrafluoroethylene muddler, reflux condenser, nitrogen inlet and outlet, with argon purged. Samples were precipitated with an excess of hexane, filtered and dried in a vacuum oven at 50°C for 24 h.

Formation of Honeycomb Film

The films were prepared by casting the solution of polymer (P(MAH-co-VAc)-b-PSt, $w_{P(MAH-co-VAc)}/w_{PSt} = 1:7$) in a mixed solvent (THF/chloroform) onto a glass slide and drying with a moist gas flow at RT. A carrier gas (nitrogen) was bubbled through a water reservoir, and then sent from a nozzle vertically onto the surface of polymer solution in a certain flow speed. The obtained films were dried at room temperature.

Characterization

The number- and weight-average molecular weights (M_n and M_w), molecular weight distribution (PDI) of the obtained polymers were evaluated by gel permeation chromatography (GPC 515-2410, Waters) with tetrahydrofuran (THF) as an eluent. FT-IR spectra were collected on a NEXUS 670 (Nicolet). The membrane morphology was observed by a scanning electron microscope (SEM, S4700 Hitachi). Pore diameters were directly measured from SEM images.

RESULTS AND DISCUSSION

In the presence of P(MAH-co-VAc) copolymer with ITXH bonded at ends, polymerization of St in solution was initiated by virtue of the disconnection of ITXH from P(MAH-co-VAc) chains and thus the generation of macroradicals at a temperature of 95°C. The produced radicals ITXH· could only serve as a terminating species (Scheme 1). It was seen that the conversion of styrene increased progressively with a prolonged reaction time, and the molecular weight of produced polymers improved accordingly, while accompanying a narrower distribution (Fig. 1). This polymerization behavior exhibited the formation of P(MAH-co-VAc)-b-PSt copolymer. GPC measurements clearly showed that the peak arising from P(MAH-co-VAc)-ITXH at relatively low conversion disappeared gradually, indicating that P(MAH-co-VAc)-ITXH could completely get involved in polymerization and thus act as an efficient macroinitiator under thermal activation. The normalized GPC curves showed that the half-peak width of each curve became narrow, indicating the decrease of PDI. This was because the polymerization was initiated by the reversible coupling-fragmentation of ITXH dormant group which was different from the normal macroinitiator containing azo group. FT-IR spectra analysis further confirmed the achievement of P(MAH-co-VAc)-b-PSt copolymer (Fig. 2). The absorption bands at 1744, 1785, 1859 cm^{-1} were attributed to the —C=O stretching of P(MAH-co-VAc) segments. The absorptions at 700, 757 cm^{-1} were associated with the C—H stretching and mono-substituted C—H bending vibration of the PSt fraction, respectively.

In addition, by following a breath figure procedure, the solution of produced copolymers in a mixed solvent (THF/chloroform, V/V 1:4) was cast onto a glass slide under humid conditions, and regular honeycomb structured porous films were generated (Fig. 3). This phenomenon further ascertained the generation of P(MAH-co-VAc)-b-PSt copolymer by the initiation of P(MAH-co-VAc)-ITXH. Under a humid atmosphere, anhydride groups of the produced copolymer of P(MAH-co-VAc)-b-PSt were converted into carboxylic groups by hydrolysis. This change enhanced the hydrophilicity of the copolymer and promoted the formation of polymer envelope around water droplets, thus providing a possibility of generating honeycomb porous films.

The average pore diameter of the porous film was estimated at around 250 nm (Fig. 3), probably close to the lowest value^[6] of pore sizes that can be generated using breath figure approach, and comparable to that obtained with a complex 18-arm star polymer (molecular weight 10000, PDI 1.2) synthesized by RAFT process^[15].

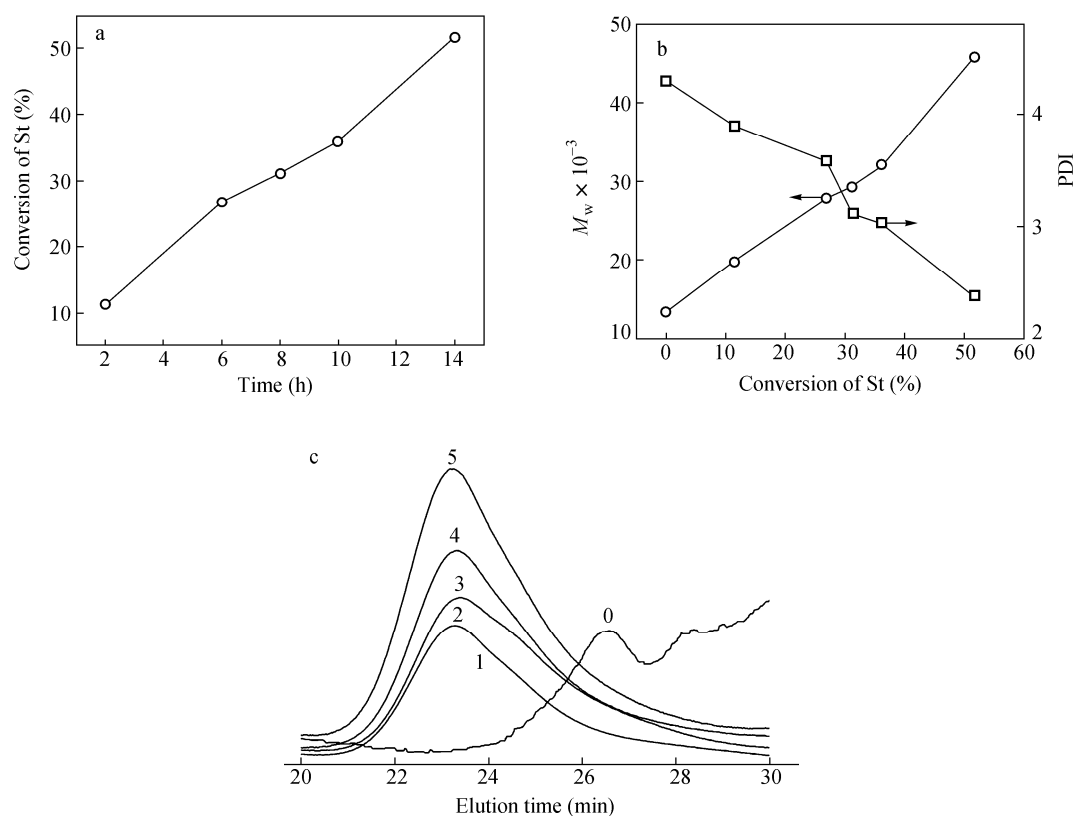


Fig. 1 Plots of conversion versus time (a), M_w versus conversion (b) and GPC traces (c) (Conversion of St: 1) 11.4%, 2) 26.8%, 3) 31.2%, 4) 36.1%, 5) 51.7%; 0) P(MAH-co-VAc)-ITXH) for the polymerization of styrene in cyclohexanone at 95°C: St 49.85 wt%, P(MAH-co-VAc)-ITXH 2.95 wt% ($M_n = 13400$, PDI = 4.3)

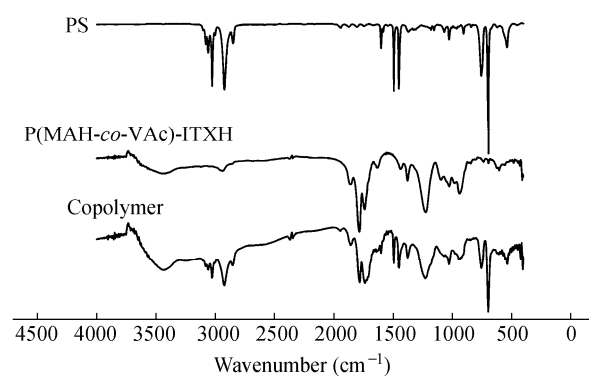


Fig. 2 IR spectra of P(MAH-co-VAc)-ITXH, block copolymer P(MAH-co-VAc)-b-PS and PS (standard sample)

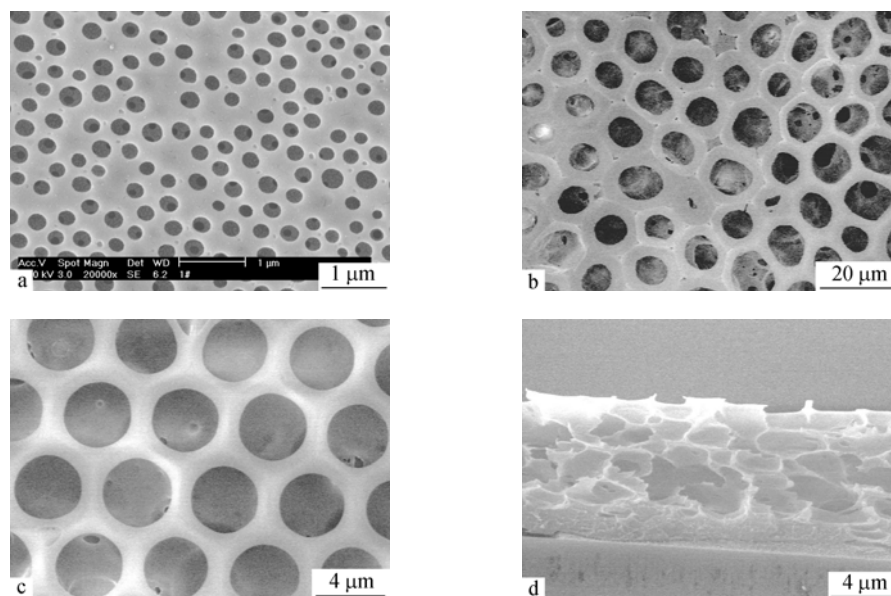


Fig. 3 SEM images of honeycomb structure films

Casting conditions: weight ratio of P(MAH-co-VAc)/PSt in copolymer = 1:7, mixed solvent of THF/chloroform (V/V, 1:4); a) Copolymer concentration: 1 mg/mL, temperature: 12°C, relative humidity (RH): 60%; b) Copolymer concentration: 1 mg/mL, temperature: 12°C, RH: 80%; c) Copolymer concentration: 10 mg/mL, temperature: 22°C, RH: 45%; d) Cross-section view of (c)

Moreover, it could be observed that several layers of pores were formed, and hexagonal arrays of pores were presented by applying the P(MAH-co-VAc)-b-PSt copolymer in casting (Fig. 3d). Also, clear open surface structure of the porous film was displayed from the cross-sectional view. These not only evidenced the formation of P(MAH-co-VAc)-b-PSt copolymer, but also revealed that P(MAH-co-VAc)-b-PSt copolymer could stabilize the water droplets packed closely sheet by sheet and prevent their fusion. The hydrolyzed P(MAH-co-VAc)-b-PSt copolymer might occur self-assemble due to the induction of water droplets and endow good envelope and stabilization to the close-packed water droplets, which was favorable to the formation of the multi-layered breath figure patterns.

According to the mechanism of breath figure method, the hydrophilic parts of the copolymer were located in the surface of the pores. The concentration of anhydride or carboxylic acid (if anhydride hydrolyzed) was very high in the pores. It has been reported the application of maleic anhydride copolymers in protein synthesis *in vitro*^[16], versatile platform for molecular biosurface engineering^[17] and protein immobilization^[18]. Herein the films produced by P(MAH-co-VAc)-b-PSt would have potential application in biochemistry.

CONCLUSIONS

We have shown that P(MAH-co-VAc) precursor with coupled ITX residues was capable of initiating the polymerization of St in solution by thermal activation. The formation of P(MAH-co-VAc)-b-PSt block copolymer and its application in producing honeycomb porous films confirmed the initiation ability of P(MAH-co-VAc) contained ITXH. This technique based on macroinitiator-contained ITXH is expected to be easily applied to the preparation of block copolymers and fabrication of highly ordered porous materials with a uniform pore size, honeycomb morphology.

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