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Effect of benzoylation on crystallinity and phase transition behavior of nanoporous crystalline form of syndiotactic polystyrene

Yi Wei, Yucai Ke, Xinyu Cao, Yongmei Ma*, Fosong Wang*

Laboratory of New Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

In order to improve the thermal stability of δ_e form of sPS that possesses nanoporous structure, benzoylation of the phenyl groups was adopted and performed by solution procedure or solid procedure. The solution procedure involves initial benzoylation of sPS in solution and then preparing δ_e form by solvent induction of benzoylated sPS; the solid procedure means benzoylation of δ_e form of sPS in solid state. Usual modifications of sPS by solution procedure greatly decrease the crystallinity of the nanoporous related δ_e form. In this work, sPS can well maintain its crystallinity of δ_e form after benzoylation by solution procedure, even when benzoylation degree reaches 20%. Thermally induced phase transition behaviors of corresponding δ_e form were investigated by Differential scanning calorimeter and temperature-dependent X-ray diffraction analysis. The results show that the δ_e–γ transition temperature increases after benzoylation by both two procedures, indicating improved thermal stability of δ_e form. The subsequent γ–α transition and the melting of α form both shift to lower transition temperature. Meanwhile, the transition of δ_e form to γ form was prohibited by solution procedure contrast to solid procedure.

1. Introduction

Nanoporous crystalline form (δ_e form) of syndiotactic polystyrene (sPS) has been identified by De Rosa et al. to present monoclinic unit cell with axes $a = 17.4$ Å, $b = 11.85$ Å, $c = 7.70$ Å, and $\gamma = 117°$ [1]. Chains in helical conformation $(T_2G_2)_2$ are packed and two pores in a molar ratio of 1/4 with respect to the styrene monomeric units are formed per unit cell. The pores formed are identical in volume and shape and can selectively provide residence for suitable size organic molecules. Such porous structure has prompted interests of its application as storage material and chemical separation as well as molecular filter material for the purification of air/water [2–5]. Actually, guest absorption studies have demonstrated that δ_e form of sPS is of high absorption rate and equilibrium absorption value and can absorb organic molecules even at very low activities [6]. In addition, the preparation of δ_e form samples is very simple, that is, by solvent induction of glassy sPS and then removing solvents by suitable extraction procedures [7–9]. At the same time, macroscopic materials based on δ_e form of sPS can be processed into various shapes and morphologies such as fiber and membrane etc. These all make it advantageous as functional material in many fields [10,11].

However, δ_e form of sPS is of low thermal stability due to weak interactions between molecular chains separated by empty spaces. Careful studies of thermally induced phase transition behaviors of δ_e form of sPS by Gowd, E.B et al. and Manfredi, C. et al. indicate that δ_e form transforms to γ form via an intermediate phase of disordered structure between 70 and 120 °C; the γ form then transforms to $\alpha(\beta)$ form between 180 and 200 °C [7,12]. It suggests that the δ_e form of sPS is unstable nearly the glass transition temperature (around 100 °C) at which the molecular segments are completely free to move. From the application point of view, it would be helpful to improve phase transition temperature of δ_e–γ transition and hence the thermal stability of δ_e form of sPS. A likely solution of this problem is to increase the glass transition temperature of the material. This can be achieved by chemical modification such as crosslinking or enlarging side phenyl groups of sPS by introducing functional groups.

An important premise for such modification is that the crystallinity of δ_e form of sPS has to be preserved since it is close related to the amount of nanoporous. Effect of molecular modification on the crystallization of sPS involving δ_e form has been reported in some literature. Manfredi, C. et al. studied the effect of introduction of *p*-methylstyrene comonomer with amount from 3 to 20 mol% on

* Corresponding authors. Tel.: +86 10 62659019; fax: +86 10 62532144.
E-mail addresses: maym@iccas.ac.cn (Y. Ma), wangfs@iccas.ac.cn (F. Wang).

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polymorphic behavior of sPS [13]. From their results it can be seen that the samples with comonomers below 7 mol% still can obtain the δ_e form after extraction by methyl ethyl ketone, while the extraction sample with 20 mol% tends to favor formation of γ form rather than the usual δ_e form. Napoli et al. reported the crosslinked δ_e form sample obtained from syndiotactic copolymer of styrene and divinylbenzene (DVB) [14]. The results show enhanced solvent resistant property but dramatically decrease of crystallinity. The sample is essentially amorphous when content of DVB reaches value of 8 mol%, therefore loose the porous structure.

Introduction of functional groups onto the phenyl groups of sPS may be a convenient way than by coordination copolymerization to get syndiotactic copolymer. The modification can be conducted either by solution procedure or solid procedure. The solution procedure involves initial modification of sPS in solution and then preparing δ_e form by solvent induction of modified sPS; the solid procedure means selective modification on amorphous phase of preformed δ_e form in solid state. The reports of sulfonation of sPS suggest that sulfonation by solution procedure lead to poor crystallinity and only sulfonation by solid procedure is suitable to preserve crystallinity of the nanoporous δ_e form [15,16]. Unfortunately, the modification by solid procedure can only proceed in limit depth below the surface. An effective way to carry out the modification by solution procedure which does not decrease the crystallinity of the product would be attractive and necessary. It should keep in mind that the δ_e form is prepared by induction of solvent. It is better that the functional groups introduced would not hinder the interaction between solvent and polymer. Considering that the usual solvents used to induce δ_e form are chloride and aromatic molecules, introduction of aromatic groups which has similar structure would be a sensible choice.

In the present paper, we report a benzoylation method of sPS by solution procedure which not only enhances the thermal stability but also preserves the crystallinity of δ_e form of sPS. For comparison, benzoylation by solid procedure was also conducted. The crystallinity and phase transition behaviors of the resulted products were investigated by Fourier transform infrared spectroscopy (FTIR), Differential scanning calorimeter (DSC) and temperature-dependent X-ray diffraction (XRD) measurements. To our best knowledge, the study of benzoylation of sPS involving δ_e form has not been reported before.

2. Experimental

2.1. Materials

sPS pellets were purchased from Dow Chemical Co. The weight-average molecular weight (M_w) was of 2.1×10^5 g/mol with polydispersity index (M_w/M_n) of 2.8.

2.2. Sample preparation

2.2.1. δ_e form of sPS benzoylated by solution procedure

Amorphous films of sPS about 50 μm thick were obtained by hot press at 300 °C and then quenching the melt into ice water bath.

Benzoylation by solution procedure was conducted as follows. The amorphous films prepared of 0.5 g were first dissolved in chloroform at its boiling point (ca. 60 °C) for 1 h. Then 5 mL nitrobenzene was added to the solution and keeping at that temperature for 30 min. Aluminum chloride of 0.1 g and benzoyl chloride with various amount of 0.02 mL, 0.05 mL, 0.1 mL, 0.2 mL respectively were then added to the solution and reacted for 3 h. The solution was poured into large amount of HCl/methanol to precipitate the polymer. After filtration and washed thoroughly with methanol for three times, the benzoylated sPS (denoted as BzsPS) was obtained. The BzsPS powder was hot pressed at 300 °C and then quenching into ice water bath to prepare amorphous benzoylated sPS films.

δ_e form film samples of sPS and BzsPS were prepared by immersion the amorphous films into toluene for 24 h. The films were then taken out and extracted with acetone for 20 h and methanol for 10 h respectively to remove the solvent. The solvent was completely removed and confirmed by thermogravimetric analysis (TGA) measurements.

2.2.2. δ_e form of sPS benzoylated by solid procedure

Selective benzoylation by solid procedure on amorphous phase of δ_e form was performed as below. 0.5 g sPS δ_e form films originally obtained above, 0.2 g aluminum chloride and 1 mL benzoyl chloride were added to 50 mL nitrobenzene and reacting at 50 °C for 3 h. The films were then taken out and extracted with acetone and methanol respectively to remove the solvent.

2.3. Fourier transform infrared spectroscopy (FTIR) measurements

Fourier transform infrared spectroscopy (FTIR) measurements were conducted on instrument Tensor-27 (Brucker) with resolution of 2 cm^{-1}. Absorption band at 1660 cm^{-1} was adopted for characterization of benzoylphenyl group and bands between 400 and 800 cm^{-1} were used for analysis of chain conformation and crystal structure of solvent induced sPS and BzsPS.

2.4. ^1H nuclear magnetic resonance (NMR) measurements

^1H nuclear magnetic resonance measurements were conducted on instrument Brucker DMX 300 at 100 °C using tetrachlorodideuterioethane as solvent. Benzoylation degrees (molar fraction of benzoylated phenyl groups) were estimated from the ratio of areas of signals of corresponding phenyl groups (with shift of $\delta = 7.1$ and 6.6) and main chain methine and methylene groups (with shift of $\delta = 1.9$ and 1.4). A series of sample with benzoylation degree of 2%, 5%, 10%, 20% respectively by solution procedure and 25% by solid procedure were obtained.

2.5. X-ray diffraction (XRD) measurements

X-ray diffraction measurements either at room temperature (ca. 25 °C) or on heating for temperature dependence test were carried out on instrument X'Pert PRO MPD (PANalytical) with heating apparatus. Incident beam of Cu K_α ($\lambda = 0.15418$ nm) was used and scanning range was between 5 and 30° with scanning rate of 8°/min. For temperature-dependent measurements, specimens were heated successively at a step of 10 °C and hold at each step for 1 min to steady temperature before scanning.

2.6. Differential scanning calorimeter (DSC) measurements

Thermally induced phase transition behaviors were studied by Differential scanning calorimeter (DSC) using the TA Q2000 instrument at a heating rate of 10 °C/min. Prior to the DSC measurements, heat flow and temperature were calibrated with standard materials, indium and zinc.

3. Results and discussion

3.1. δ_e form of sPS benzoylated by solution procedure

3.1.1. Characterization of sPS benzoylated by solution procedure

Fig. 1 shows the FTIR spectra of solution benzoylated sPS with various benzoylation degrees. The appearance of band at