Polymer 54 (2013) 2498–2505

Contents lists available at SciVerse ScienceDirect

Polymer

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

A novel main chain benzoxazine polymer with the ability of UV-induced self-surface modification

Jing Bai, Zixing Shi*, Jie Yin

School of Chemistry & Chemical Engineering, State Key Laboratory of Metal Matrix Composite Materials, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

ARTICLE INFO

Article history:
Received 30 January 2013
Received in revised form
28 February 2013
Accepted 16 March 2013
Available online 23 March 2013

Keywords:
Polybenzoxazine
UV-induced surface modification
Benzophenone

ABSTRACT

In this paper, a series of benzophenone-based polybenzoxazine (PBD) was synthesized through the formation of oxazine rings, and the structures of the obtained polymers were confirmed by FTIR, ^{1}H NMR and UV–visible analysis. As the existence of benzophenone units in the main chain, PBD could initiate photopolymerization of various monomers. The photo-initiative behavior of PBD was tested by differential scanning photocalorimetry, which shows the high photopolymerization efficiency. Meanwhile, PBD could be used as film substrates for initiating photopolymerization of the monomers and change the surface performance without additional initiator. Through this method, the surface properties of PBD film could be tailored conveniently. The surface wettability modifications through the surface photopolymerization of styrene (St) and *N*-isopropyl acrylamide (NiPAM) were carried out for example, and the surface properties were investigated by water contact angle measurements (WCA), X-ray photoelectron spectroscopy (XPS) and Atom Force Microscopy (AFM) and the results showed that the surface properties PBD film could be well designed by selecting different kind of monomer through photopolymerization to realize an easy-tuned surface with desired wettability required.

1. Introduction

Modification of polymer surfaces is of great interest in recently materials research [1–5]. Activities involve the development of coatings with applications that range from enhancing wettability or adhesion to protect surfaces [6–8]. Several kinds of polymer materials possess desirable properties including good mechanical strength, chemical resistance, thermal stability, and low cost. These advantages make them promising candidates for various applications such as functional textiles, filtration devices and many others. However, the major drawback of them is the low surface energy, which results in inherent hydrophobicity. Polybenzoxazine is a recently discovered class of materials with low surface free energy [9]. In some situation, the surface performance cannot match the requirement of operating environment. Grafting polymer chains or monomers to surfaces is attractive for it can precisely control the chemical composition of the surface. Meanwhile, the lack of functional Groups on their surface makes grafting difficult. Recently, several methods including plasma treatment [10,11], electron beam [12], irradiation with UV light [13–15], and adsorption of surface active amphiphiles [16] are reported to modify surfaces. However, most of these methods need strict experiment conditions with complicated procedures.

Polybenzoxazines are a class of thermosetting phenolic resins with a wide range of interesting features which are synthesized with a primary amine, a phenolic derivative, and formaldehyde [9,17–19]. Recently, many useful materials of this kind of resins are being developed because they have lots of advantages such as good mechanical performance, high thermal stability, no strong acid catalysts or additives requirement for curing, high char yield of the cured products, low water adsorption, and near zero-volumetric change on curing [9]. Besides, they can be prepared from inexpensive, commercially available phenols, primary amines, and formaldehyde easily [17–22]. Meanwhile, molecular design flexibility can be achieved by varying the phenols and amines used, which could affect the properties of the obtained polybenzoxazines. According to our previous research of photo initiator, a kind of benzophenone derivatives 4,4-Dihydroxybenzophenone (DHBP) was chosen as difunctional phenols to synthesize the polybenzoxazine. Benzophenone [23–28] and its derivatives are well-known photo-initiators, and their photo-efficiency is high in the presence of hydrogen donors such as tertiary amines. Due to the existence of the structure of benzophenone and coinitiator amine contained in-chain; the polymers can initiate

---

* Corresponding author. Tel.: + 86 21 54743268; fax: +86 21 54747445.
E-mail address: zxshi@sjtu.edu.cn (Z. Shi).

0032-3861/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2013.03.031

efficient photopolymerization. Particularly, UV-assisted surface polymer grafting has been developing in recent years as a versatile means of changing the surface properties [29–31]. These methods of polymer grafting rely mainly on the attachment of initiators to surfaces via silane or thiol interface chemistry.

Our previous work has synthesized a kind of benzoxazine which can initiate the monomers to polymerize [32]. This research focuses on the synthesis of a novel series of polybenzoxazines (PBD), which possess benzophenone [33–37] and coinitiator amine in the main-chain. As a result, the PBD can initiate photo-polymerization of the monomers on its surface and change its surface performance. Therefore, it is unnecessary to attach the other initiators by physical and chemical methods with great convenience. In the meantime, this novel method can also overcome the drawbacks of traditional methods, including odor, toxicity, and migration in UV-curing caused by the low-molecular-weight initiator and the coinitiator amines added into the system. Moreover, considering its application of good adhesive agent toward many materials, this kind of PBZ could be used as photo active coating for modification of many different material surfaces to obtain the designed wettability surfaces with using different kinds of monomers.

The process which we defined as UV-induced self-surface-modification is also very convenient. When irradiated with UV light, monomers covered on the substrate were initiated followed by polymerization. Through photopolymerization of on the PBD film, the PBD with designed surface properties could be obtained.

2. Experimental part

2.1. Materials

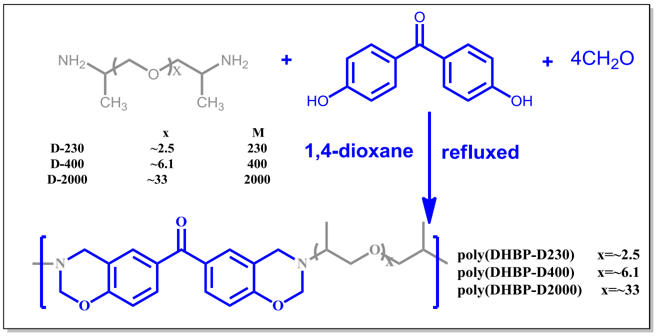
1,4-Dioxane (Sinopharm Chemical Reagent Co., Ltd), styrene (Sinopharm Chemical Reagent Co., Ltd), 4,4-Dihydroxybenzophenone (DHBP) (Sinopharm Chemical Reagent Co., Ltd), paraformaldehyde (Sinopharm Chemical Reagent Co., Ltd), benzophenone (Sinopharm Chemical Reagent Co., Ltd), poly(ether diamine) (Jeffamine)(The structure of them was shown in Scheme 1) *N*-isopropyl acrylamide (NiPAM) came from TCI Chemical CO., Ltd.

2.2. Synthesis of benzophenone-based main-chain benzoxazine polymer

The series of polymers bearing benzoxazine moieties were prepared from 4,4-dihydroxybenzophenone (DHBP), poly(ether diamine) and paraformaldehyde as shown in Scheme 1. 4,4-dihydroxybenzophenone (DHBP) (10 mmol), poly(ether diamine) (10 mmol), and paraformaldehyde (40 mmol) were added into a three-necked flask with magnetic stirring in the presence of 100 ml 1,4-dioxane, refluxed for 6 h. The resulting viscous, transparent yellow compound was washed in ether for several times and placed at least 48 h at room temperature. The series of benzophenone-based main-chain benzoxazine polymers were named as PBD.

2.3. The preparation of polymer films

All films were prepared by a solution-casting method. The PBD was dissolved in toluene for 20 wt%, and magnetically stirred until complete dissolution was achieved. Then these solutions were cast onto glass plates and dried in oven at a heating rate of 10 °C/h from 50 °C to 180 °C. Ring-opening polymerization of the oxazine ring in the main chain thermally activated, and then this polymer can be crosslinked and form 3D-net structure. The photos of these films were shown in Fig. 1.



Scheme 1. Synthesis of benzophenone-based main-chain benzoxazine polymer.

2.4. Surface modification of the PBD resins

The PBD substrates were spin-coated with monomer chloroform solution (10 wt%). Two kinds of monomers were chosen including styrene and *N*-isopropyl acrylamide. After dried at room temperature, these films were irradiated with 365 nm UV light for 15 min. The films were then dipped in chloroform for 5 min to remove the unreacted monomers.

3. Measurements

3.1. ^{1}H NMR analysis

^{1}H NMR spectra were taken on a Mercury Plus 400 MHz spectrometer, all samples were dissolved in DMSO-d6 and tetramethylsilane was used as an internal standard.

3.2. FT-IR analysis

FT-IR spectra were recorded on a FT-TR spectra were recorded on Perkin–Elmer Paragon 1000 spectrophotometer. The samples were prepared as KBr disks.

3.3. UV–visible analysis

UV–visible spectra of the prepared polymers were carried out by Shimadzu UV-2550 spectrophotometer in $CHCl_3$ solution. The concentration of the sample is 5.0×10^{-5} mol/L in terms of BP moiety.

3.4. Photodifferential scanning calorimetry (Photo-DSC)

The photopolymerization of AMP-10G, HDDA and TMPTA was monitoring surveyed by photo-DSC (DSC 6200, Seiko Instrument Inc.) with incident light 365 nm and intensity was 50 mW/cm^2 under the nitrogen flow of 50 ml/min. The PBD was dissolved in the liquid monomers at room temperature for 24 h under vigorous stirring, so the samples for photo-DSC were composed of both monomers and PBD. The PBD was used as initiator and co-initiator at the same time. The concentration of PBD was 0.03 M in terms of benzophenone (BP) moiety. During the measurement the temperature was kept at 25 °C, about 2.0 mg sample mixture was placed into an aluminum DSC pan.

During the measurement the temperature was kept at 25 °C. The reaction heat liberated in the polymerization was directly proportional to the number of vinyl groups related to the system. The conversion of the vinyl groups and the extent of reaction can be determined by integrating the area under the exothermic peak,