

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

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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, ¹H 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.

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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

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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

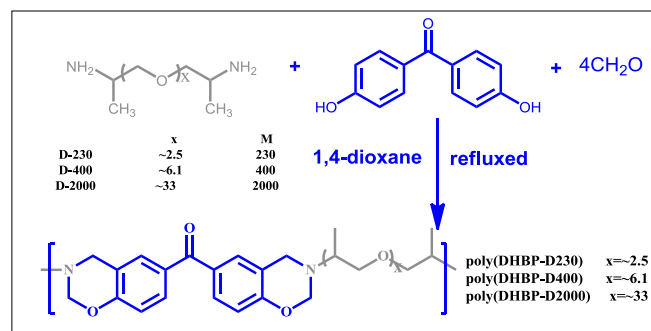
1,4-Dioxane (Sinopharm Chemical Reagent Co., Ltd), styrene (Sinopharm Chemical Reagent Co., Ltd), 4,4-Dihydroxybenzophenone (DHBP) (Sinopharm Chemical Reagent Co., Ltd), paraformaldehyde (Sinopharm Chemical Reagent Co., Ltd), benzophenone (Sinopharm Chemical Reagent Co., Ltd), poly(ether diamine) (Jeffamine)(The 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. ¹H NMR analysis

¹H 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 CHCl₃ 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/cm² 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,

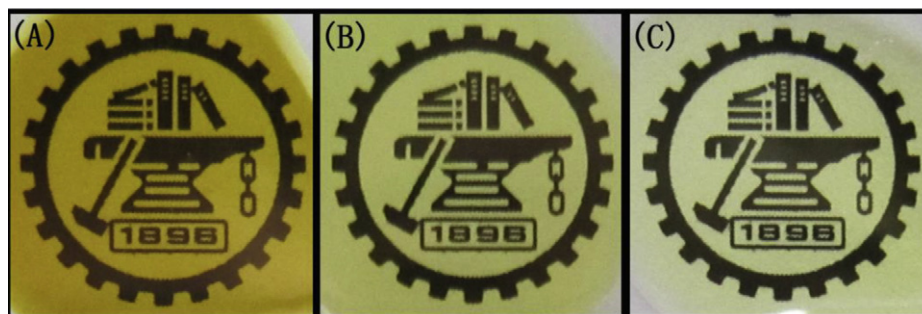


Fig. 1. Photo of the polymer films: (A) poly(DHBP-D230), (B) poly(DHBP-D400), (C) poly(DHBP-D2000).

when the reaction heat evolved at time t , t is the theoretical heat for complete conversion [38].

3.5. Water contact angle measurements

Water contact angle (WCA) measurements were measured with a contact angle meter (model CAM Micro) at room temperature. The precision of the angle measurement was $\pm 0.1^\circ$.

3.6. Atom force microscopy (AFM)

AFM images were taken by SII Nanonavi Esweep under ambient conditions. The AFM was operated in tapping mode.

3.7. X-ray photoelectron spectroscopy

XPS experiment was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) The base pressure of that analyzer chamber was about 5×10^{-8} Pa. Binding energies were calibrated by using the containment carbon ($C1s = 284.6$ eV).

4. Results and discussion

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

Typically, benzoxazine monomers are synthesized with phenol, formaldehyde, and amine (aliphatic or aromatic). In this article the

DHBP with hydroxyl group was acted as aromatic phenols molecules while poly(ether diamine) was used as amine monomer. Because there are two hydroxyl groups on DHBP and two amino groups on poly(ether diamine), two oxazine rings are formed in one repeating unit as shown in Scheme 1. The synthesized polymers are main-chain-type benzoxazine consisting of repeating units of bifunctional benzoxazine structure bonded to a relatively large polyetherdiamine structure to form the macromolecule chain. The polymers have good solubility with good filming ability; they are soluble in common solvents like acetone, ethanol, chloroform, and dioxane as well as dimethylacetamide, dimethylformamide, and dimethyl sulfoxide. The weight-average molecular weight (M.W.) of poly(DHBP-D230), poly(DHBP-D400), and poly(DHBP-D2000) were 6964, 7203 and 10,594 respectively, while poly dispersity index (PDI) were 1.74, 1.35 and 1.16.

4.2. Characterization of benzophenone-based main-chain benzoxazine polymer

The structures of the linear polymers were confirmed by spectral analyses.

1H NMR spectra were recorded in DMSO- d_6 with $Si(CH_3)_4$ as internal standard. The 1H NMR spectrum of the polymers exhibited the specific signals of the benzoxazine ring. As can be seen from Fig. 2, two signals at 4.9 and 4.0 ppm correspond to $-CH_2$ protons of benzoxazine ring, the $N-CH_2-O$ protons at 4.9 ppm, and the $N-CH_2-ph$ protons at 4.0 ppm, respectively. These signals provide the evidence for the formation of benzoxazine ring. Peaks of the methyl group

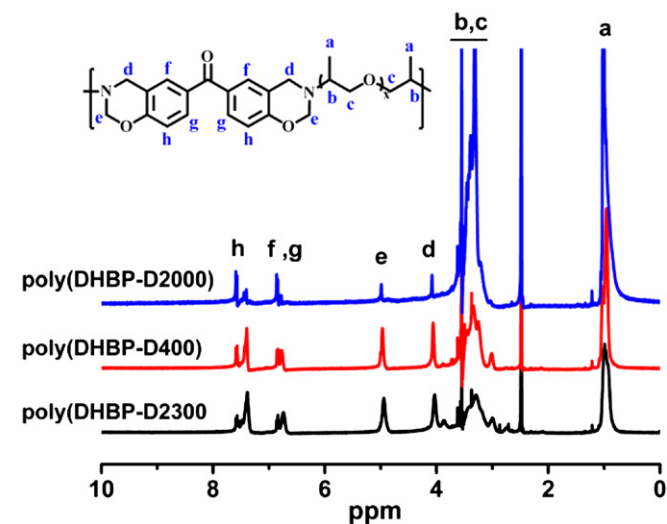


Fig. 2. 1H NMR of benzophenone-based main-chain benzoxazine.

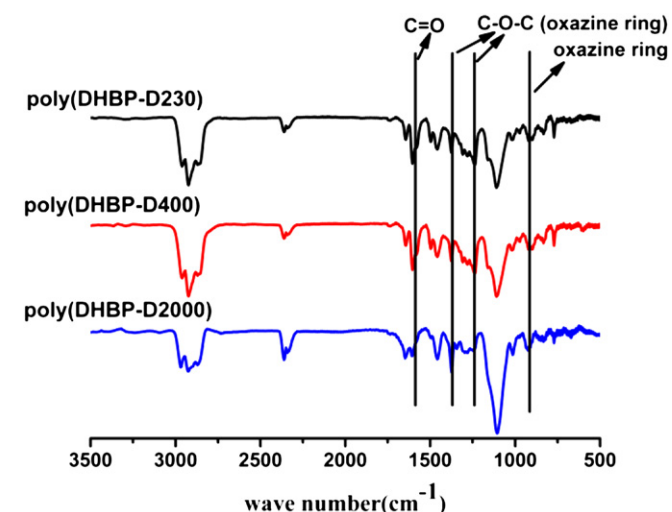


Fig. 3. FT-IR spectra of benzophenone-based main-chain benzoxazine.

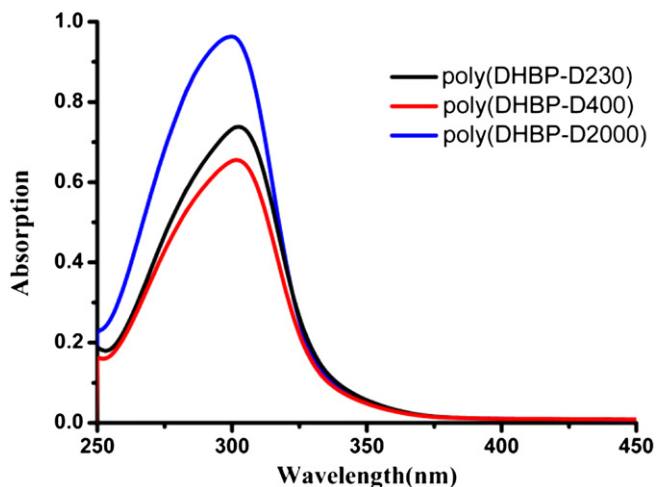
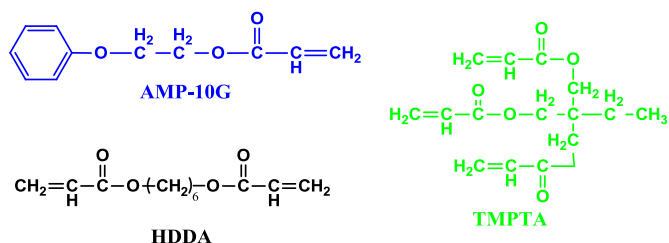


Fig. 4. UV-vis spectra of benzophenone-based main-chain benzoxazine.



Scheme 2. Properties and structures of acrylate monomers with different functionality.

appear at about 1.0 ppm, and methylene at about 3.2–3.7 ppm. The aromatic protons can be found in the region of 6.5–8 ppm.

FT-IR spectra of the polymers are shown in Fig. 3. The characteristic benzoxazine signal of the oxazine ring is at 1249 cm^{-1}

which corresponds to the asymmetric stretching vibration of C–O–C in the oxazine ring. In addition, the band corresponding to C–O–C oxazine ring mode at 1367 cm^{-1} and aromatic C–H stretching vibration at 2967 cm^{-1} , the band at 919 cm^{-1} for the benzene ring attached by oxazine ring and the signal of C=O at 1593 cm^{-1} are also observed.

In Fig. 4 is the UV-vis spectra of benzophenone-based main-chain benzoxazine polymer in chloroform, BP possessed strong absorption band at 255 nm due to the carbonyl group on BP and strong absorption band of the synthesized polymers at above 300 nm is due to the presence of oxazine rings in the products. It is well known that transitions in the region of 250–300 nm belong to the main benzenoid $\pi-\pi^*$ -type transitions of benzophenone [39]. Due to the appearance of the oxazine ring, the polymers exhibit significantly red-shifted maximal absorption. It indicates that oxazine rings have formed successfully, which is in good agreement with FT-IR and ^1H NMR results.

Based on the results of these spectral analyses, benzophenone-based main-chain benzoxazine linear polymers have been successfully synthesized with the predicted structure.

4.3. Photopolymerization of acrylate monomers

Photo-differential scanning calorimetry (Photo-DSC) was applied to investigate the Photo-polymerization behavior initiated by the synthesized benzophenone-based main-chain benzoxazine polymer. In the Photo-DSC measurements, the following three acrylate monomers having different functionalities (shown in Scheme 2) are usually used as standard monomers to test the efficiency of photo initiator. AMP-10G is a monofunctional monomer with low viscosity and can release high heat flow during polymerization. HDDA and TMPTA are the bifunctional and trifunctional monomers respectively. The double bond content of TMPTA is much higher than the bifunctional monomers which results in a high crosslinking density in polymerization.

The photo-DSC profiles of the photo-polymerization of AMP-10G, HDDA and TMPTA initiated by PBD are shown in Fig. 5.

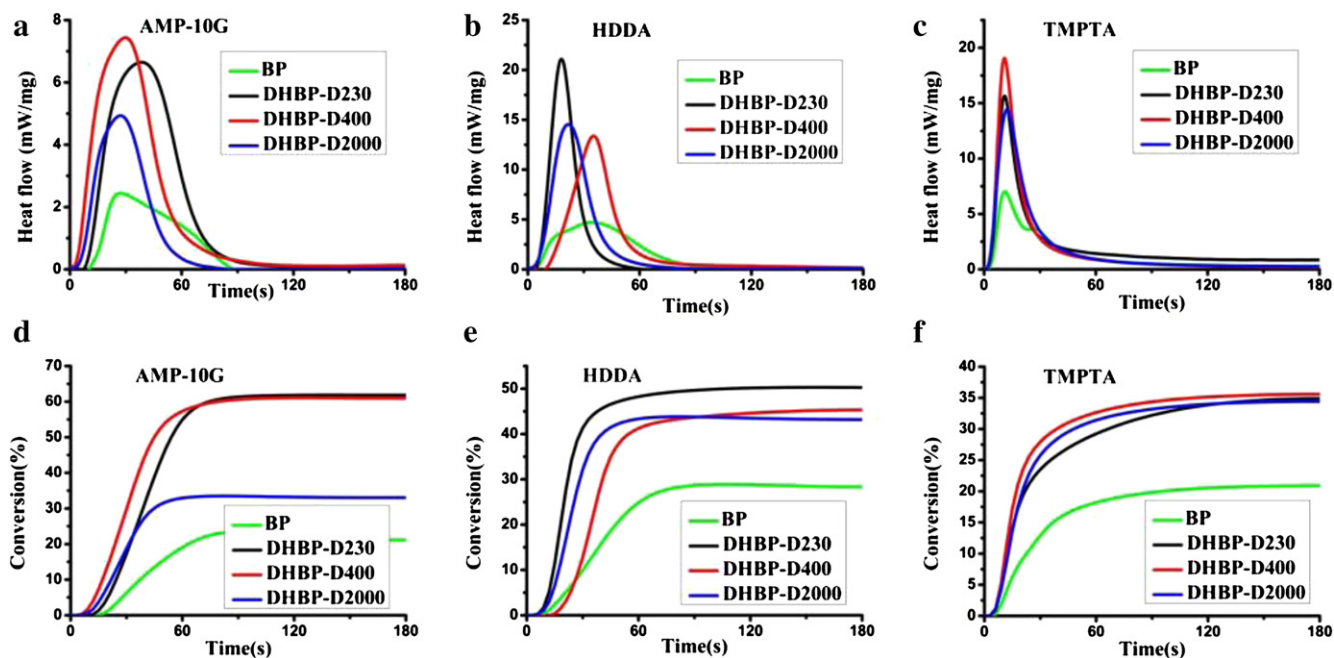
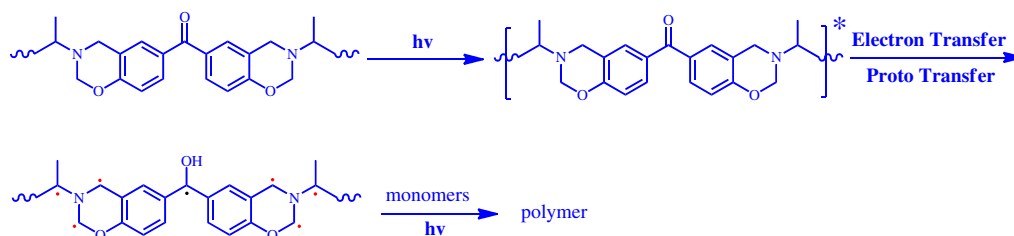


Fig. 5. Photo-DSC profile for polymerization of AMP-10G (a), HDDA (b) and TMPTA (c); conversion versus time curves for polymerization of AMP-10G (d), HDDA (e) and TMPTA (f) initiated by poly(ether diamine)-based main-chain benzoxazine polymers and BP cured at $25\text{ }^\circ\text{C}$ by UV light with intensity of 50 mW/cm^2 (The photo initiator concentration was 0.03 M in terms of BP moiety).

Table 1
Photopolymerization of AMP-10G, HDDA and TMPTA initiated by poly(ether diamine)-based main-chain benzoxazine polymers and BP cured at 25 °C by UV light with an intensity of 50 mW/cm². The photo initiator concentration was 0.03 M in terms of the benzophenone (BP) moieties.

	BP			Poly(DHBP-D230)			Poly(DHBP-D400)			Poly(DHBP-D2000)		
	AMP-10G	HDDA	TMPTA	AMP-10G	HDDA	TMPTA	AMP-10G	HDDA	TMPTA	AMP-10G	HDDA	TMPTA
T_{max} (s)	27.1	33.9	11.6	38.9	18.3	11.2	30.2	35.8	11	27.7	21.9	12.8
H_{max} (mW/mg)	2.44	4.70	6.97	6.65	21.06	15.63	7.43	13.35	19.04	4.93	14.53	14.38
Final conversion (%)	23.27	8.36	0.88	61.84	50.27	34.88	60.95	45.28	35.56	33.44	43.19	33.41



The black point means the radical site after electron+proton transfer and the red points is the probable sites where the radical can be situated.

Scheme 3. The photoinitiation mechanism of PBD.

As shown in Fig. 5, the photopolymerization related thermal releasing curves are observed after the exposure of the sample under the UV and this indicates that the synthesized benzoxazine polymer could show photo activity toward to initiate the polymerization of acrylate monomers and its polymerization behavior is largely influenced by diffusion, which is similar to other multifunctional and trifunctional monomers, viscosity be gradually formed which restricts the diffusion and mobility of macro-radicals toward pendant double bonds. This phenomenon would slow down the radical termination rate which results in promoting the rate of polymerization due to a buildup of radical species. However, as the reaction continued in further, the cross-linking degree increased

and eventually limited the monomer mobility which results in the decrease of overall polymerization rate. As the mobility of the reaction system is further reduced, the reactive species became trapped and the reaction was hindered [40].

Table 1 summarizes the H_{max} and Final conversion of the photopolymerization initiated by PBD obtained from Fig. 5. As shown in Table 1, it is found that final conversion of TMPTA was lower than the other two monomers with the same photo initiator. For example, the final conversion for TMPTA is only about 34.88% with the presence of poly(DHBP-D230). This low conversion is related with its high viscosity and crosslinking density which leads to the polymerization into the confusion controlled stage at relatively lower conversion. Based on the comparison of photo-initiation

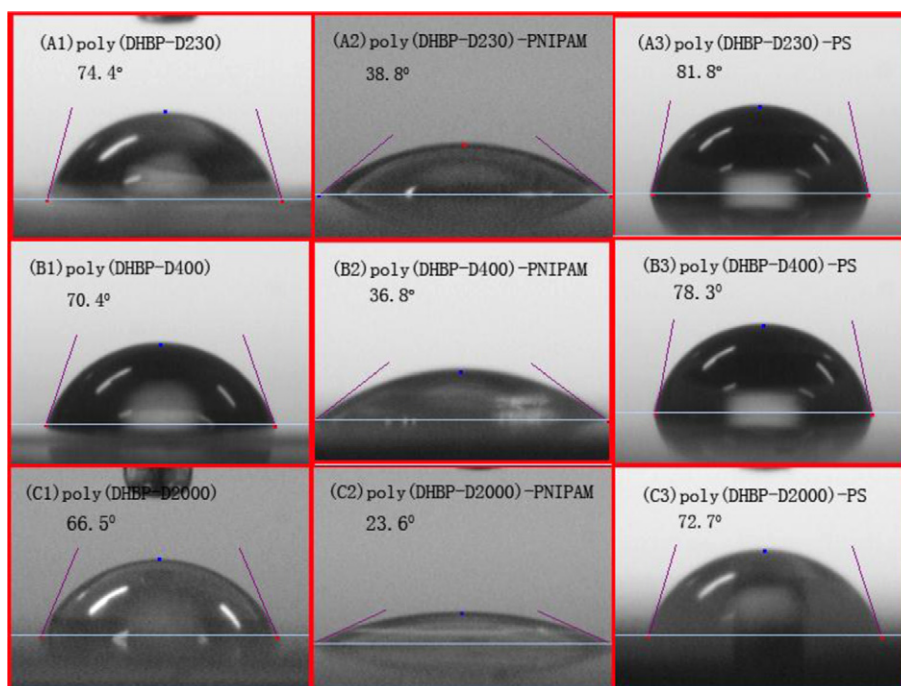


Fig. 6. Water contact angle on the different surfaces (A1) poly(DHBP-D230), (A2) poly(DHBP-D230)-PNIPAM, (A3) poly(DHBP-D230)-PS, (B1) poly(DHBP-D400), (B2) poly(DHBP-D400)-PNIPAM, (B3) poly(DHBP-D400)-PS, (C1) poly(DHBP-D2000), (C2) poly(DHBP-D2000)-PNIPAM, (C3) poly(DHBP-D2000)-PS.

efficiency for three synthesized benzoxazine polymers and BP, it is also observed that all the three synthesized polymers show higher photopolymerization efficiency than BP and poly(ether diamine)-based main-chain benzoxazine polymers synthesized with comparatively short-chain poly(ether diamine). It could be observed to initiate photopolymerization more effectively than that synthesized with comparatively long-chain poly(ether diamine) with poly(DHBP-D230) showing the highest photo efficiency. For example, the final conversion for AMP-10G is 61.84% initiated by poly(DHBP-D230), about 1% and 27.5% higher than that initiated by poly(DHBP-D400) and poly(DHBP-D2000) respectively. This result can be closely related with the fact that the steric hindrances of the long polymer chains not only prevent the recombination reaction between the radicals, but also prevent acrylate monomers from approaching initiator, so the poly(ether diamine)-based main-chain benzoxazine polymers synthesized with comparatively long-chain poly(ether diamine) have relatively lower photo-efficiency than its counterparts having short chain.

It is well known that the photolysis of BP, in the presence of hydrogen donors such as amines and thiols, leads to form two types of free radicals: a radical produced from carbonyl compound on

benzophenone moieties (ketyl-type radical) and the other radical derived from the hydrogen donor amine. The photopolymerization of vinyl monomers is usually initiated by the amine radicals; the ketyl radicals are usually not reactive enough toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron. In the structure of these synthesized PBD, both photo initiator-benzophenone and co-initiator amine are located in the same chain [41,42] and its mechanism of the photoinitiation is supposed in Scheme 3. Based on the results obtained from photo-DSC, it is concluded that the synthesized PBD could initiate photopolymerization effectively due to the following factors: First, tertiary amines from benzoxazine can act as co-initiator to facilitate energy transfer and hydrogen-abstraction reactions between the excited state of benzophenone moieties and amine moieties in the same polymer chain. Second, the steric hindrance of the macromolecular coil can prevent the recombination reaction between the radicals, which strongly limits the termination and prevent the reduction of the concentration of the radicals. Third, PBD can be dispersed well in these three kinds of acrylate monomers and radicals are easy to approach acrylate monomers and initiate polymerization. Therefore, they can be considered as efficient

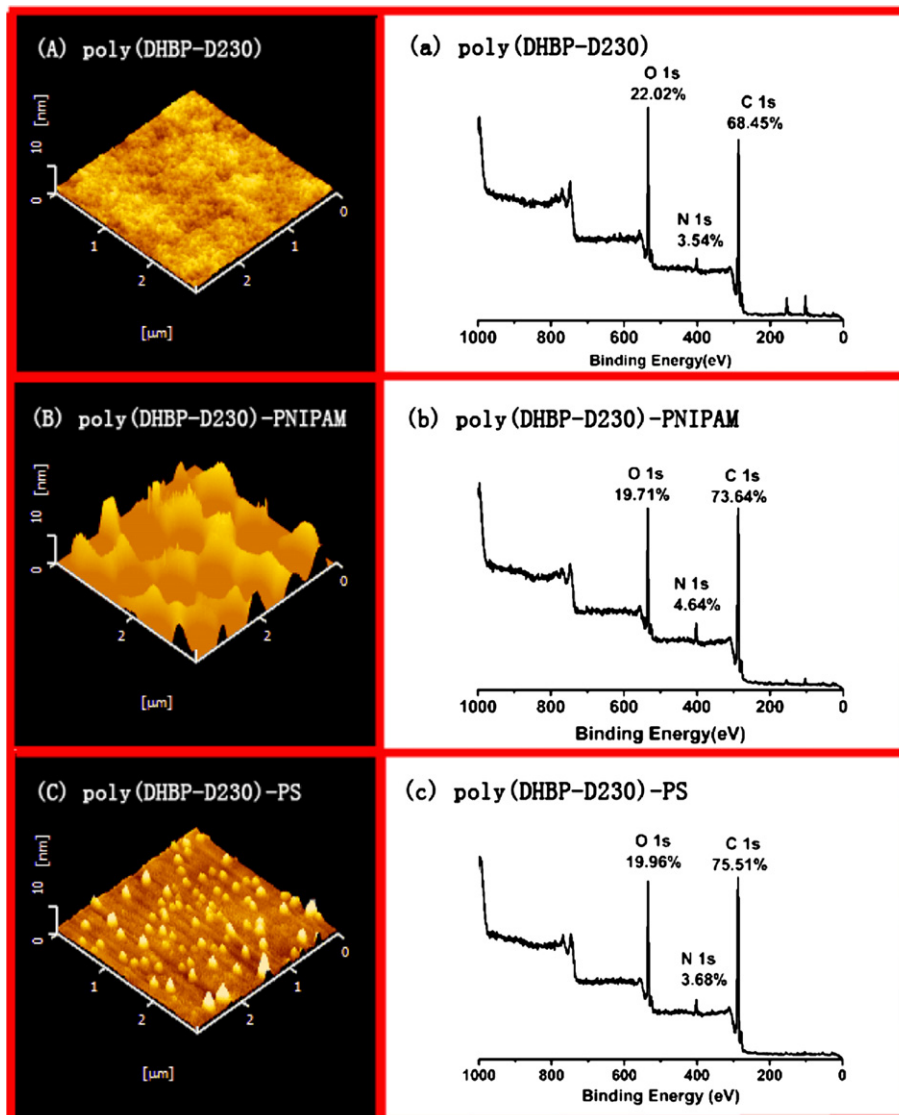


Fig. 7. AFM pictures of (A) poly(DHBP-D230) (B) poly(DHBP-D230)-PNiPAM (C) poly(DHBP-D230)-PS; XPS spectra of (a) poly(DHBP-D230) (b) poly(DHBP-D230)-PNiPAM (c) poly(DHBP-D230)-PS.

photoinitiators for photopolymerization without the addition of any other chemicals, which avoids the migration of small molecules, a shortcoming in the conventional photoinitiation blending system.

4.4. Surface modification performance measurements

Since it is found that the synthesized PBD with BP group have high effective photo-initiative functionality toward the acrylic monomer, it is highly desirable and convenient to use this functionality to tailor the surface properties by photopolymerization of olefin monomers on its surface. Two different polymer coatings with different hydrophobic and hydrophilic properties were selected to be grafted from the PBD substrate under UV-light irradiation to illustrate the change on their surface performance. These selected polymers include poly(*N*-isopropyl acrylamide) (PNiPAM) which is hydrophilic at room temperature and polystyrene (PS) which are universal plastics with hydrophobic surface.

The homogenous solutions of both two respective monomers in chloroform were spread out on the PBD substrate, respectively and bubbling with nitrogen to avoid oxygen inhibition. Then these substrates were exposed to UV light at 365 nm at room temperature for photopolymerization, the unreacted monomers were removed through washing with chloroform. The surface wettability characteristics of the PBD films with and without the three polymer coatings are investigated by Water contact angle (WCA) measurement and the results are shown in Fig. 6. Before surface photopolymerization, the WCA of the synthesized polymers is increased from poly(DHBP-D230) to poly(DHBP-D2000) (Fig. 6) and this phenomenon is attributed to the monomers' hydrophilicity increasing from D230 to D2000. After surface photopolymerization with *N*-isopropyl acrylamide, it is found that the poly(DHBP-D230) coated with PNiPAM are more hydrophilic (WCA = 38.8°) than the pure poly(DHBP-D230) film (WCA = 74.4°) and the same trends are also observed for the other two synthesized polymers. By contrast, after photopolymerization of styrene on its surface, the WCA of poly(DHBP-D230) is increased from 74.4 to 81.8° with increasing hydrophobic properties and the surface of the other two polymers also show increased hydrophobic properties after photopolymerization of styrene. These comparisons in the change of WCA exhibit the successful coating of PNiPAM and PS on the PBD surface. Therefore, the wettability of the surfaces can be tailored by attaching different kind of polymer coating through surface photopolymerization.

Meanwhile, the surface morphology of PBD films and the films with the polymer coatings were revealed by AFM images (Fig. 7), and the polymer coatings on the substrates can be observed in the images. As shown in Fig. 7, the surface of the PBD films is relatively smooth, while honeycomb-like polymer clusters appear on the surface of PBD films after coating of PNiPAM. However, there are many "bamboo shoot-like" polymer clusters with about 5 nm high on the surface after PS was attached on its surface. These phenomena exhibit the successful coating of the corresponding polymers on the PBD surface and different surface morphology after different polymer attaching on its surface can also account for the change of wettability on its surface, as reflected on the results of WCA. These results can be further proved by XPS measurements. The mole ratio of carbon and oxygen elements of all the two polymer coating is less than the PBD substrate. As shown in Fig. 7, the carbon atomic content increases while the oxygen atomic content decreases after coating of the two kinds of polymers, which also indicates the successful coating on the PBD films and part of the surface was covered with the corresponding polymer coatings.

The results of WCA, AFM and XPS demonstrate that polymers can be coated on the surface of the PBD films through surface-initiated polymerization successfully. Therefore, this would

change the surface properties of the PBD films at the same time. This UV-induced self-surface-modification system with PBD films can tune the wettability through both changing the PEG chain length of poly(ether diamine) in the backbone of PBD and the kinds of photo-initiated polymer coatings. This method is very convenient and avoids the use of complicated instrumentation and expensive materials. Moreover, the PBD films can adhere to many kinds of common materials such as glass slide and silicon wafer, as a result, it's a more universal method for surface modification of various materials, which has potential application for the development of multifunctional devices, such as biological molecules/cells attachment and growth.

5. Conclusions

We have synthesized a novel kind of benzophenone-containing polybenzoxazine (PBD) through the oxazine-rings-formation reaction with benzophenone-containing biphenol and poly(ether diamine), which can form film at the surface of silica wafer and etc. It was found that the PBD possessed the ability of initiating the photopolymerization of olefin monomers due to the existence of benzophenone and hydrogen donors. This functionality can be applied to change the surface performance such as hydrophobicity. The characteristic of the PBD surface after photopolymerization modification was investigated by XPS, AFM and WCA measurements and the results illustrate that the surface wettability could be easily-tuned by attaching different kind of polymers through the surface photopolymerization. In this system, PBD is utilized as both substrates and initiator without the demand for the addition of other initiator. This UV-induced-self-modification would provide a very easy and convenient method for surface-modification.

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