

Preparation and Characterization of Grafting Polyacrylamide from PET Films by SI-ATRP via Water-Borne System

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ABSTRACT: The grafted homopolymer and comb-shaped copolymer of polyacrylamide were prepared by combining the self-assembly of initiator and water-borne surface-initiated atom transfer radical polymerization (SI-ATRP). The structures, composition, properties, and surface morphology of the modified PET films were characterized by FTIR/ATR, X-ray photoelectron spectroscopy (XPS), contact angle measurement, and scanning electronic microscopy (SEM). The results show that the surface of PET films was covered by equable grafting polymer layer after grafted polyacrylamide (PAM). The amount of grafting polymer increased linearly with the polymerization

time added. The GPC data show that the polymerization in the water-borne medium at lower temperature (50°C) shows better "living" and control. After modified by comb-shaped copolymer brushes, the modified PET film was completely covered with the second polymer layer (PAM) and water contact angle decreased to 13.6°. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: poly(ethylene terephthalate) film; grafting polyacrylamide; surface-initiated atom transfer radical polymerization; hydrophilicity; surface tension

INTRODUCTION

The properties of materials in various applications does not only depend on their volume, but also on their surface performance and interface behavior.¹ The surface of main polymeric materials such as polyester, polyacrylate, and polyethylene is inert and hydrophobic when not chemically treated, which restrict its application. Several techniques, including chemical or physical processes,^{2–4} allow the modification of the surfaces. The choice of a specific technique or the combination of two or more techniques depends on the final polymer characteristics wanted. One of such techniques, tethering polymer brushes on a solid substrate is an effective method of modifying the surface properties of the substrate.^{5,6} In literature, different strategies for attaching polymer brushes are described, including

the "grafting to" and the "grafting from" technique.^{7–9} The latter results in a higher density of grafted polymer on the surface.¹⁰ Controlled/"living" radical polymerization techniques such as nitroxide-mediated radical polymerization (NMP),¹¹ atom transfer radical polymerization (ATRP),^{12,13} and reversible addition-fragmentation chain transfer polymerization (RAFT)¹⁴ have been particularly attractive for the preparation of polymer brushes following the "grafting from" strategy, as they allow accurate control over brush thickness, composition, and architecture.^{15–18}

Among the different controlled/"living" radical polymerization techniques available, atom transfer radical polymerization (ATRP) has been most extensively used to produce polymer brushes.¹⁹ This method can offer efficient ways to synthesize polymer chains with well-controlled molecular weight, low polydispersity, and novel architectures, while at the same time using easily accessible experimental conditions. Yet until now, the majority of work into surface-initiated ATRP (SI-ATRP) has made use of conventional inorganic substrates, including silica, metal oxide, clay mineral, gold, carbon, metal and semiconductor^{20,21} and nevertheless only a relatively small number of reports has been developed into the use of polymeric substrates, since organic materials usually show inert surface require an appropriate pretreatment or activation to introduce functional groups.^{22–24}

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Poly(ethylene terephthalate) (PET) is a semicrystalline and semiaromatic thermoplastic polyester of excellent basic properties such as mechanical strength, permeability to gases, transparency, chemical resistance, and insolubility in the majority of solvents.^{22,25} However, the strong hydrophobic character, low surface energy, and poor wettability of its surface due to the lack of polar groups limit its application as biocompatible materials for culture cell and healing wound.²⁶ The functional surface of PET film is very important in specific applications such as conductive film, biocompatible materials, and packing film.^{27,28} The surface-initiated atom transfer radical polymerization (SI-ATRP) has proven to be a useful tool to graft well-defined chains from the surface of polymer substrate. Up to now, few studies have been done on the modification of PET film using SI-ATRP because it is very difficult of introducing the ATRP initiator onto the PET surface. Recently, Mauricio et al. successfully grafted PNIPAM chains on the surface of PET film previously modified with poly(glycidyl methacrylate) (PGMA) and photo-oxidized.¹ Ulbricht and Friebe modified PET membranes via oxidative hydrolyses and grafted PNIPAM under ATRP conditions and varied the grafting density from "dilution" of immobilized initiator with a solution of ethanolamine and propylamine.²⁹ Roux and Demoustier-Champagne explored different methods of preparing PET surfaces with the aim of carrying out surface-initiated polymerizations of styrene.³⁰ Another example of PET and poly(ethylene naphthalate) (PEN) films as reported by Farhan and Huck is that poly(*N*-isopropyl acrylamide) brush on the surface of those polyester films has been synthesized by combining initiator and ATRP.²³

Acrylamide (AM) with biocompatible and water soluble property has been polymerized via ATRP and its polymerization possesses living behavior.^{31,32} Mandal et al. have polymerized acrylamide in glycerol-water mixture (*v/v* = 1 : 1) or pure water at 130°C using 2-chloropropionamide or 2-bromopropionamide and CuX (X = Cl, Br)/2,2'-bipyridine (bpy) complex as catalyst obtained PAM with MWD = 1.6–1.7.³² Furthermore, Cringus-Fundeanu et al. synthesized a dense and homogeneous PAM brushes in a controlled fashion within 48 h of polymerization time using a CuCl/bpy catalyst system in DMF and the grafting density of PAM achieved 0.6 chain nm⁻² on the silicon surface.³³ Huang and Wirth researched SI-ATRP of AM onto different surfaces such as silica and poly(dimethylsiloxane) (PDMS).^{34–38} Qiu et al. successfully prepared PAM brushes from chloromethylated polysulfone (CMPSF) membrane surface by SI-ATRP and linear control of PSF membrane's hydrophilic property was realized through adjusting polymerization time.³⁹ Luo et al. attached 2-bromoisobutryl bromide on the surface of ethylene-acrylic acid

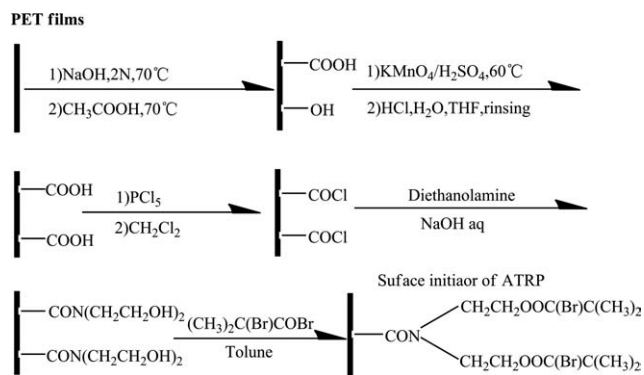
(EAA) copolymer film, and then grafted PAM from the surface by SI-ATRP. They found that the contact angle of grafted film, with high initiator density, decreased to 36° after 5 h of polymerization time.⁴⁰ Kong et al. grafted PAM brushes from the silicon surface by SI-ATRP and the advancing contact angle decreased to 12.2°.⁴¹ Fundeanu et al. reported that PAM grafted from the silicone rubber by SI-ATRP either in DMF at 130°C or in water at 90°C and PAM brush coatings were effective against microbial adhesion.⁴² All those previous works provide a meaningful reference for further research. However, until now more seldom are reports on the modification of PET film using acrylamide (AM) as monomer by SI-ATRP. Recently, our research groups have reported functionalized PET films with grafting several of homopolymer and copolymer including PAM via combining initiator and SI-ATRP.^{24,43} All those preceding modifications had been processed in high temperature, so degradation on the surface of PET films may be happened possibly in the experimental condition of high temperature and organic solvent.⁴⁴ Until now, there is no experimental study has been performed on modified PET film, AM as monomer, in aqueous media at lower temperature (50°C) by SI-ATRP, and researching the modified impact on the surface of PET films in different ratio of mixed-solvents.

In this article, the grafted homopolymer of poly(acrylamide) (PAM) from PET films have been successfully prepared by combining the self-assembled monolayer of initiator and water-borne SI-ATRP at lower temperature (50°C). The impact of modification on grafting PET films in different ratio of mixed-solvents also has been carefully studied. In addition, the comb-shaped polymer brushes on PET films have been constructed by combining SI-ATRP of poly(2-hydroxyethyl methacrylate) (PHEMA) and PAM orderly and esterification of 2-bromoisobutryl bromide to introduce ATRP initiator. The structures, composition, properties, and surface topography of modified PET films were characterized by FTIR/ATR, X-ray photoelectron spectroscopy (XPS), the simultaneous technique of GPC/MALLS, contact angle measurement, and scanning electronic microscopy (SEM).

EXPERIMENTAL

Reagents and materials

The PET film with a thickness of 75 μm was obtained from Yuxing Electrical Insulating, Changzhou, China. The films were cleaned by ultrasound in the mixed solvent of acetone/methanol (50/50 vol %), then dried under vacuum before use. Acrylamide (98.0%) supplied by Sinopharm Chemical Reagent, Shanghai, China was purified through recrystallization with acetone. CuCl (A.R.) also purchased from Sinopharm



Scheme 1 Synthetic procedures for preparing bromine-bounded PET film.

Chemical Reagent was purified by stirring in glacial acetic acid, filtered, washed with absolute ethanol and ethyl ether, and dried under vacuum. D,L-ethylbromoisobutyryl (99.0%) and 2-bromoisobutyryl bromide (99.0%) was provided by Sigma-Aldrich, St. Louis, MO. Triethylamine (TEA) (A.R.) purchased from Sino-pharm Chemical Reagent was dried by calcium hydroxide (CaH₂) overnight, and then distilled under reduced pressure before use; 2,2'-bipyridine (bpy) (97.0%) supplied by Runjie Chemical Reagent, Shanghai, China was recrystallized twice with acetone. Toluene (A.R.) provided by Sinopharm Chemical Reagent was dried by CaH₂ for 24 h, and distilled. All the other reagents were used directly without purification.

Immobilization of the ATRP initiator on PET film

The immobilization process of surface initiators is shown in Scheme 1. First, the PET films (1.5 × 1.5 cm) were hydrolyzed and oxidated to produce carboxyl groups on the surface.³⁰ The carboxyl groups were then turned into acid chloride by reaction with PCl₅. To obtain high density initiator points on the film surface, bifurcated structures of diethanolamine were built up on the surface of PET film.⁴⁰ Then pre-treated PET films reacted with 2-bromoisobutyryl bromide in dried toluene with triethylamine and stirred for predetermined time. The films were cleaned with toluene, ethanol, deionized water, and acetone in turn and dried under vacuum.

SI-ATRP grafting of PAM from bromine-bounded PET film

A dry round bottom flask was charged with bromine-bounded PET films, 0.01 g of CuCl, 0.047 g of bpy, and 2.5 g of AM. The flask was sealed and cycled between vacuum and argon three times to remove oxygen. Then, 5 mL mixed solvent of acetone/deionized water was added by syringe. To characterize the molecule weight and its polydispersity, the 1 μL "sacrificial" initiator of D,L-ethylbro-

moisobutyryl was added to produce "free" polymer. The flask was then immersed in a 50°C oil bath for grafting polymerization. After a certain time, the polymerization was terminated by taking out the flask and exposing the system to air. The PET films were taken out, then immersed in deionized water for 12 h, and washed by ultrasound with deionized water at least five times to remove the adsorbed free PAM thoroughly and then dried under vacuum. The free polymer solution was diluted with deionized water, treated with cation-exchange resin Dowex 50W (Fluka), and precipitated in methanol. The experimental operation progress of grafting PAM from PET films by SI-ATRP at high temperature (130°C) was the same as described earlier except for the temperature and the solvent (DMF).

Construction of the comb-shaped polymer brushes from bromine-bounded PET film

SI-ATRP grafting of PHEMA from bromine-bounded PET film

A bottom flask in the presence of 0.01 g of CuCl, 0.047 g of bpy, and weighted bromine-bounded PET film was deoxygenated by several vacuum-nitrogen cycles. After argon bubbling 20 min, 5 mL of HEMA, 3 mL mixed solvent of acetone/deionized water (v/v = 50/50) was transferred with syringes to the flask. Then the flask was immersed in a 50°C oil bath for grafting polymerization. After 24 h, the modified films were washed by ultrasound with acetone for five times and dried under vacuum at 50°C to constant weight.

Modified hydroxyl-containing grafted polymer for preparing macroinitiator

The ATRP initiator on the surface of PHEMA-functionalized PET film was prepared by the esterification between 2-bromoisobutyryl bromide and the surface hydroxyl group (PET-g-PHEMA-OH). The PHEMA-functionalized PET films were immersed in a mixed solution of 15 mL anhydrous DMF, and 1.3 mL TEA. Then mixed solution of 1 mL (0.0095 mol) 2-bromopropionyl bromide and 15 mL anhydrous DMF was drop-wised under a nitrogen atmosphere. After 12 h, the PET films were thoroughly washed with ethanol-water-ethanol in sequence and dried under vacuum at 50 °C.

Synthesis of comb-shaped grafted polymer from PET film

The PET-g-PHEMA-Br substrate, CuCl (0.012 g), bpy (0.062 g), 3.0 g of AM, and the deactivator CuBr₂ (0.0027 g) were added to a 50 mL Schlenk flask. Then the flask was evacuated and back-filled with argon three times. After bubbled, the 6 mL mixed

solvent of acetone/water was transferred into the flask via syringe, and the reaction mixture was stirred at 50°C till predetermined time. The grafting polymerization was terminated by exposure to air, and then the modified PET film was removed from the reaction mixture and washed thoroughly with deionized water by ultrasound five times. Then, the modified membrane was dried under vacuum at 50°C to constant weight.

Characterization

To investigate the chemical changes between the pristine and modified PET films and confirm the immobilization of grafted polymer on the membrane surface, Fourier-transform infrared spectroscopy (Nicolet PROTÉGÉ 460) with an ATR unit (KRS-5 crystal, at an incident angle of 90°) was used. The chemical composition of the functionalized PET surfaces was determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed on an ESCA-LABMKLL spectrometer (VG Scientific Ltd. West Sussex, Britain) using a Monochromatic Al-K α X-ray source (1486.6 eV photons). Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors. Contact angles were measured on a digidrop apparatus (HARKE-SPCA, China). The surface free energy of substrate was calculated by Young equation with contact angle data of water and formamide. The Owens Wendt model was applied for determining the polar components.⁴⁵ A 25 μ L drop of liquid was projected on the samples. The contact angle (θ) was measured on the "image capture board" and captured electronically by an electron microscope. The molecular weight and polydispersity index (PDI) was determined by the simultaneous technique of GPC/MALLS at room temperature (ca. 30°C) using a Waters model 510 HPLC pump, a Waters series 2414 differential refractometer, and a multiangle laser light scattering (MALLS) detector (Wyatt Technology, DAWN EOS) with the light wavelength at 690 nm. An aqueous solution of 0.5M NaNO₃ was used as eluent at a flow rate of 0.5 mL min⁻¹. The same RI detector was used to determine the refractive index increment (dn/dc) of the PAM homopolymer in the aqueous solution of 0.5M NaNO₃ at 30°C. The morphologies of native and modified PET films were observed by using SEM (JEOL JSM-6360LA, Tokyo, Japan).

RESULTS AND DISCUSSION

Characterization of the ATRP initiator on the surface of PET film

A uniform and densely packed bromine-bounded substrate is indispensable for preparing the grafting

polymer brushes from the surface of PET film. After surface initiator-modification, XPS was used to confirm the formation of the initiator monolayer. Compared with the XPS spectra of pristine film [Fig. 1(a)], the Br3d peak at 71 eV and Br 3p peak at 182 eV are clearly visible in the spectra of bromine-bounded PET film [Fig. 1(b)], which are unambiguous proofs of the presence of a grafted initiator layer on the surface of PET films.⁴⁶ The peak of Br3d could be observed more clearly in the core-level spectrum of bromine-bounded PET film [Fig. 1(c)]. All these data suggest that the initiator of ATRP was immobilized successfully on the surface of PET film.

In our previous works, PAM grafting from PET films by via SI-ATRP always proceeded in high temperature (130°C). While under that condition, the degradation on the surface of PET films will be happened possibly. In addition, high temperature also may cause some uncontrollable reactions.^{24,43} In this work, water was introduced in reaction system to achieve high-density grafting polymer layer in lower temperature. Figure 2 shows the FTIR/ATR spectra of the (a) bromine-bounded PET film, (b) PET films grafted by PAM at high temperature (130°C), and (c) lower temperature (50°C), respectively. There are almost no differences between the IR spectra of PET film and bromine-bounded PET film, because of the relative low content of initiator. In the spectrum (a) of bromine-bounded PET film, the absorption peak at 3100–3000 cm⁻¹ was assigned to the stretching of C–H in benzene. The absorption peak at 2969 cm⁻¹ was attributed to the C–H stretching of –CH₂–. The four absorption peaks at 1600 cm⁻¹, 1578 cm⁻¹, 1505 cm⁻¹, and 1470 cm⁻¹ was attributed to the stretching of benzene skeleton. The absorption peak at 1343 cm⁻¹ was attributed to wagging vibration of –CH₂–. The absorption peak at 1248 cm⁻¹ was assigned to asymmetric and symmetric stretching of –C–O–C– group of aromatic ester. The absorption peaks at 1126 and 1022 cm⁻¹ were attributed to skeletal ring because of 1,4-substitution. The absorption peak at 875 cm⁻¹ was assigned to C–H deformation. After surface reaction, some absorption peaks changed. In the spectra of modified PET films by PAM at different reaction temperature (b and c), a wide and obvious absorption peak appeared at the range of 3500–3050 cm⁻¹ (assigned to asymmetric and symmetric N–H stretching of –NH₂) and beside the peak of 1730 cm⁻¹ (ester group), a new shoulder absorption peak was observed in 1670 cm⁻¹ because of –CONH₂. All those confirmed the formation of grafting PAM chains on the PET films successfully not only at high temperature (130°C) but also at lower temperature (50°C). From the IR spectra the fine grafting result can be obtained at lower temperature just as that got at high temperature, due to the acceleration of additive water. On

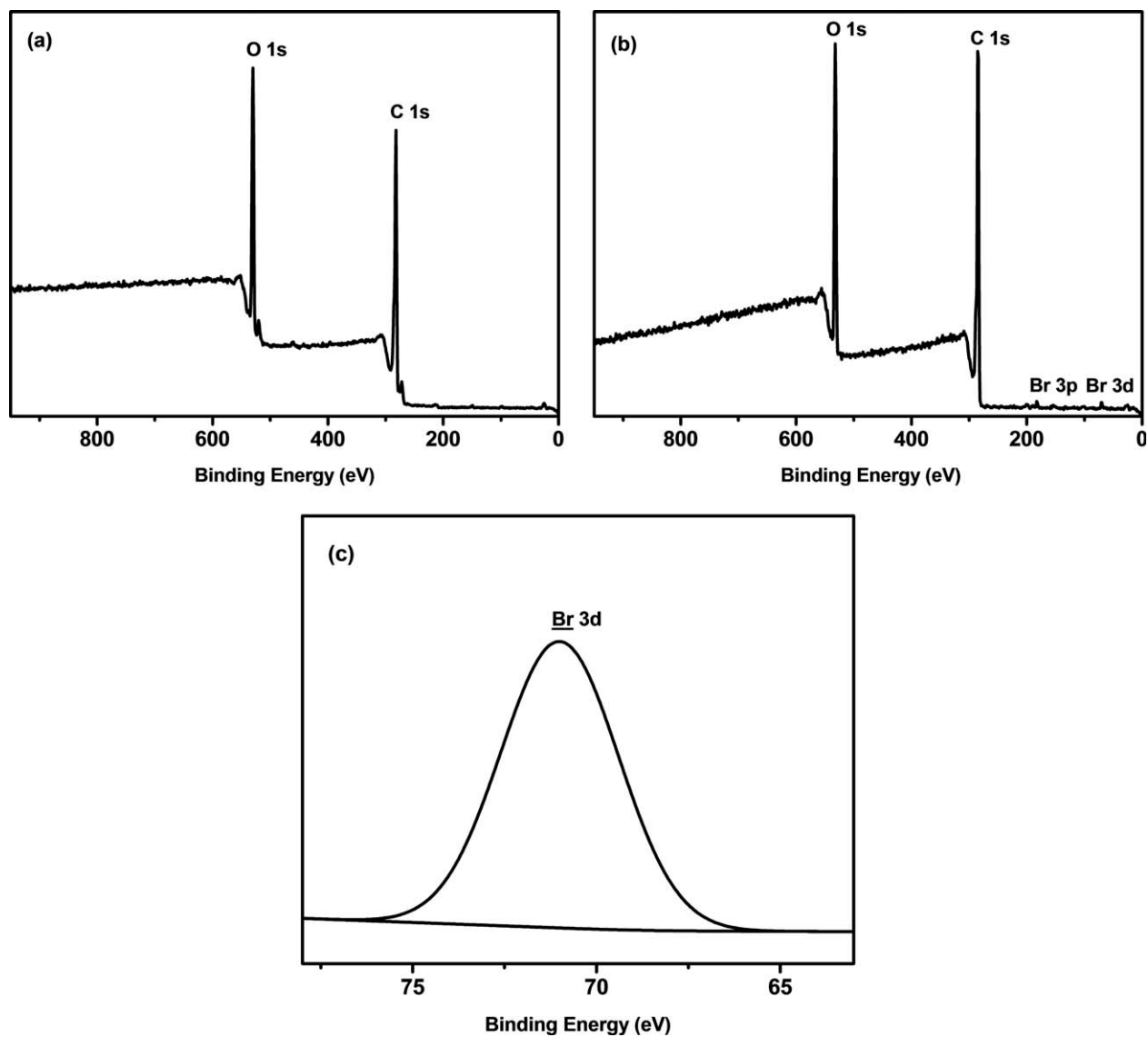


Figure 1 Typical wide-scan XPS spectra of (a) pristine PET film, (b) bromine-bounded PET film and (c) the Br3d core-level spectrum of bromine-bounded PET film.

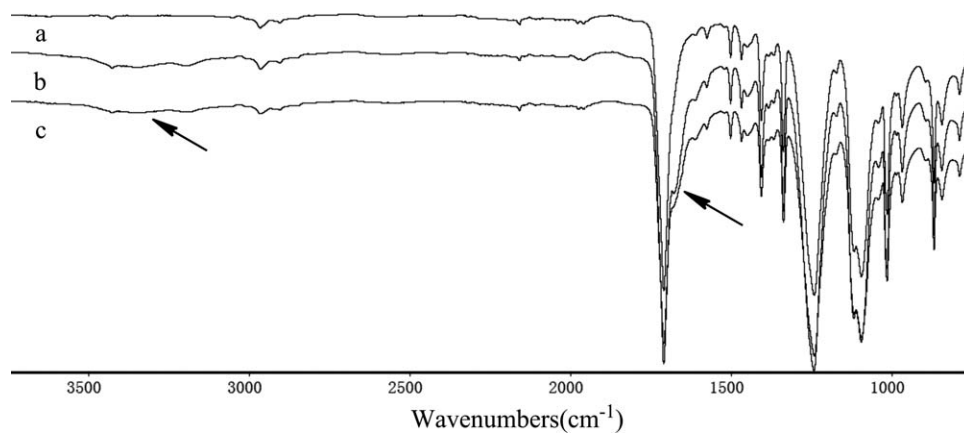


Figure 2 FTIR/ATR spectra of (a) bromine-bounded PET film, (b) PET-g-PAM in DMF (130°C, 4 h), and (c) PET-g-PAM in mixed-solvent of acetone/deionized water (v/v = 50/50) (50°C, 10 h).

TABLE I
Data of Free Polymer Synthesized at Different Solvent Ratio^a

No.	Solvent	Ratio (v/v %)	M_n^b	PDI ^b	PG% ^c
1	Water/acetone	0/100	–	–	0.40
2	Water/acetone	90/10	4.49×10^4	1.13	1.30
3	Water/acetone	70/30	3.68×10^4	1.16	1.70
4	Water/acetone	60/40	3.37×10^4	1.27	2.03
5	Water/acetone	50/50	3.13×10^4	1.36	2.65
6	Water/acetone	40/60	2.47×10^4	1.87	3.11
7	Water/acetone	30/70	1.50×10^4	2.36	4.24
8	Water/acetone	20/80	5.42×10^3	3.03	5.96
9	Water/acetone	0/100	–	–	0.43

^a Polymerization conditions for AM: $[M]_0 = 7.0M$, $[CuCl] = 1/3[bpy] = 20$ mM, $[EBiB] = 1$ μ L, at 50°C in different ratio of mixed solvent, polymerization time is 48 h. EBiB: ethyl 2-bromoisobutyrate.

^b Polymer formed in the solution, obtained by GPC/MALLS.

^c The data calculating for PG% all from the balance XS105 (accuracy: ± 10 μ g) (Mettler Toledo).

the other hand, absorptive polymer on the surface of modified PET films was unlikely because the modified PET films had been washed by ultrasonic cleaner in deionized water for several times.

The influence of solvent

In order to study the influence of solvent on grafting polymerization, a series of polymerizations with different ratio of mixed solvents had been operated. It is difficulty that obtaining the molecular weights of grafting polymer. Then the “free” polymer formed by “sacrificial” initiator in solution, which monitor the surface grafting polymerization. The free initiator not only functions as an indicator of polymerization, but also as a controller for ATRP on the PET film surface.^{47,48}

Table I shows the GPC data of “free” polymer generated under different ratio of mixed solvents at 50°C. The results show that with the content of water in mixed solvent increased, the polymerization was controlled well and high molecular weight and narrow polydispersity of “free” polymer was obtained, while the amount of grafted polymer was decreased. Because water is a kind of accelerator during the ATRP process,⁴⁹ the fast reaction rate and high molecular weight polymer obtained when the amount of water in polymerization system increased. While decreased the amount of grafted polymer on the surface of PET film appears to be not coincident with previous conclusion. The influence of solubility of initiator, generated polymers and the catalyst-ligand system in mixed solvent must be taken into account. The nonaqueous compatibility of the initiator and catalyst-ligand system result in low grafting density. Moreover, the acetone in polymerization system increased that resulted in low molecular weight and broad molecular weight

polydispersity (PDI) of polymer, which attributed to the poor solubility of the generated polymer in acetone. Additionally, when the ratio of acetone increased to 100%, the obviously reduced for grafted polymer also proves acceleration of water.

Furthermore, a well correlation of normalized IR intensities of characteristic absorption peaks can be also monitored the grafted PAM on the surface of PET films. Figure 3 shows the FTIR/ATR spectra of the modified PET films by PAM under different ratio of mixed-solvents. The absorption peak at the range of 3050–3500 cm^{-1} and the shoulder absorption peak at 1670 cm^{-1} explicitly prove the desired polymer was clearly grafted. As the ratio of acetone in mixed solvent increased, the intensity of those peaks distinctly intensified, which indicates that the amount of grafted PAM on PET film increased. This result was consistent with the data of percentage of grafting (PG%). The GPC data and FTIR/ATR results show that the ratio of acetone/deionized water (v/v = 50/50) produce more grafted polymer, better control and faster reaction rate.

The “living” character of grafting polymerization

In order to prove the “living” character of grafting polymerization initiated from the surface of bromine-bounded PET films, the relationship of the polymerization time with the characteristic absorption peaks of carbonyl in amide ($-\text{CONH}_2$) were investigated. Figure 4 shows the FTIR/ATR spectra of PET films modified by PAM with different polymerization times in same mixed solution. As polymerization time increased, the intensity of absorption peaks at the range of 3500–3050 cm^{-1} and 1670 cm^{-1} significantly enhanced. This result suggests that more amide groups were introduced onto the surface of PET film. That is the grafting polymer chains of

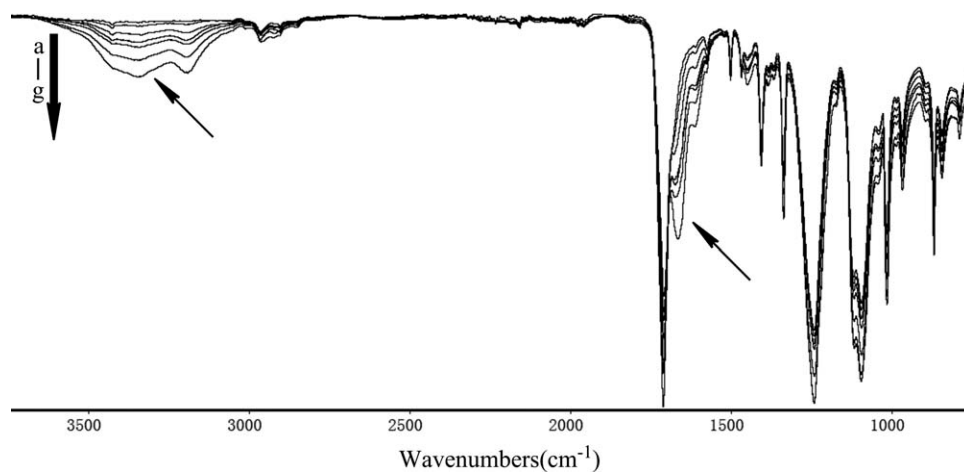


Figure 3 The FTIR/ATR spectra of the PET films modified by PAM in mixed-solvents (according to the arrow, from top to bottom) (a) water/acetone (v/v) = 100/0, (b) water/acetone (v/v) = 70/30, (c) water/acetone (v/v) = 60/40, (d) water/acetone (v/v) = 50/50, (e) water/acetone (v/v) = 40/60, (f) water/acetone (v/v) = 30/70, (g) water/acetone (v/v) = 20/80, all the polymerization had been progressed at 50°C for 48 h.

polyacrylamide grew longer as time increased, which indicates the “living” character of SI-ATRP.

XPS was also used to characterize the surface composition and structures of PET films before and after modified. Figure 5 shows the typical wide-scan spectra of the grafted PET films by PAM (the BE peaks at 284.6 eV for C 1s, 400.1 eV for N 1s, and 533 eV for O 1s). Compared with the XPS spectrum of the bromine-bounded PET film [Fig. 1(b)], the two peaks of bromide became hardly visible due to grafting PAM, and the emission peak at 400.1 eV ascribed to the binding energy of N 1s as the elemental marker obviously appeared in PET-g-PAM films, which indicate the formation of PAM layer on the surface of substrate. Furthermore, for the PET-g-

PAM, the N 1s peak significantly increased as reaction time added. The results agree with the conclusion of FTIR/ATR.

Table II shows the surface elemental composition data, in terms of [O]/[N]/[C], analyzed from the XPS scan of pristine PET film and modified PET films by PAM for different polymerization times. It can be clearly observed that the [O]/[N]/[C] ratio changed significantly from 1/0/3.8 for pristine PET film to 1/0.3/4.4, 1/0.7/4.5 as the grafting polymerization times increased. However, further increase the polymerization time to 16 h or 24 h, it did not show significant change in the [O]/[N]/[C] ratio. This is because the high grafting density and thick layer on the PET film surface reach a certain degree

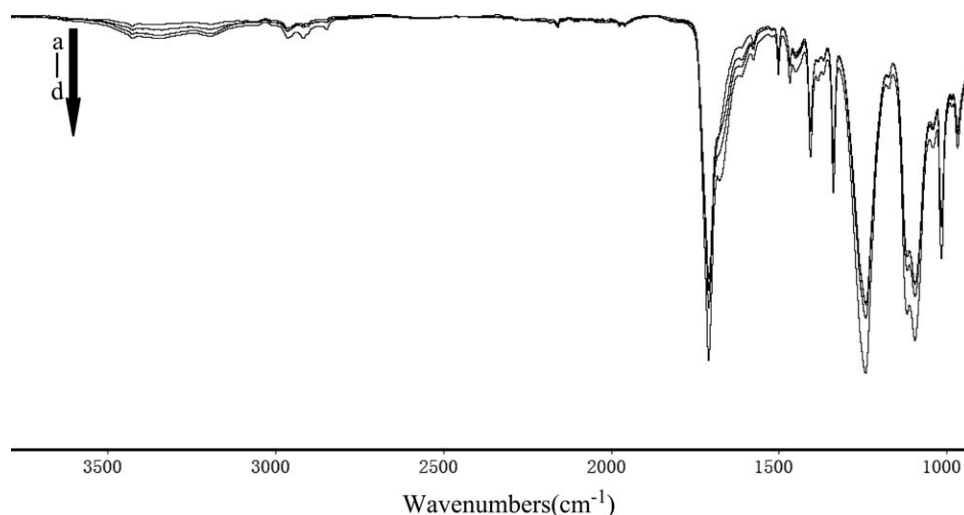


Figure 4 The FTIR/ATR spectra of the PET films modified by PAM for different polymerization time (according to the arrow, from top to bottom) (a) 4 h, (b) 10 h, (c) 16 h, and (d) 24 h, all the polymerization had been operated in mixed solvent acetone/deionized water (v/v = 50/50).

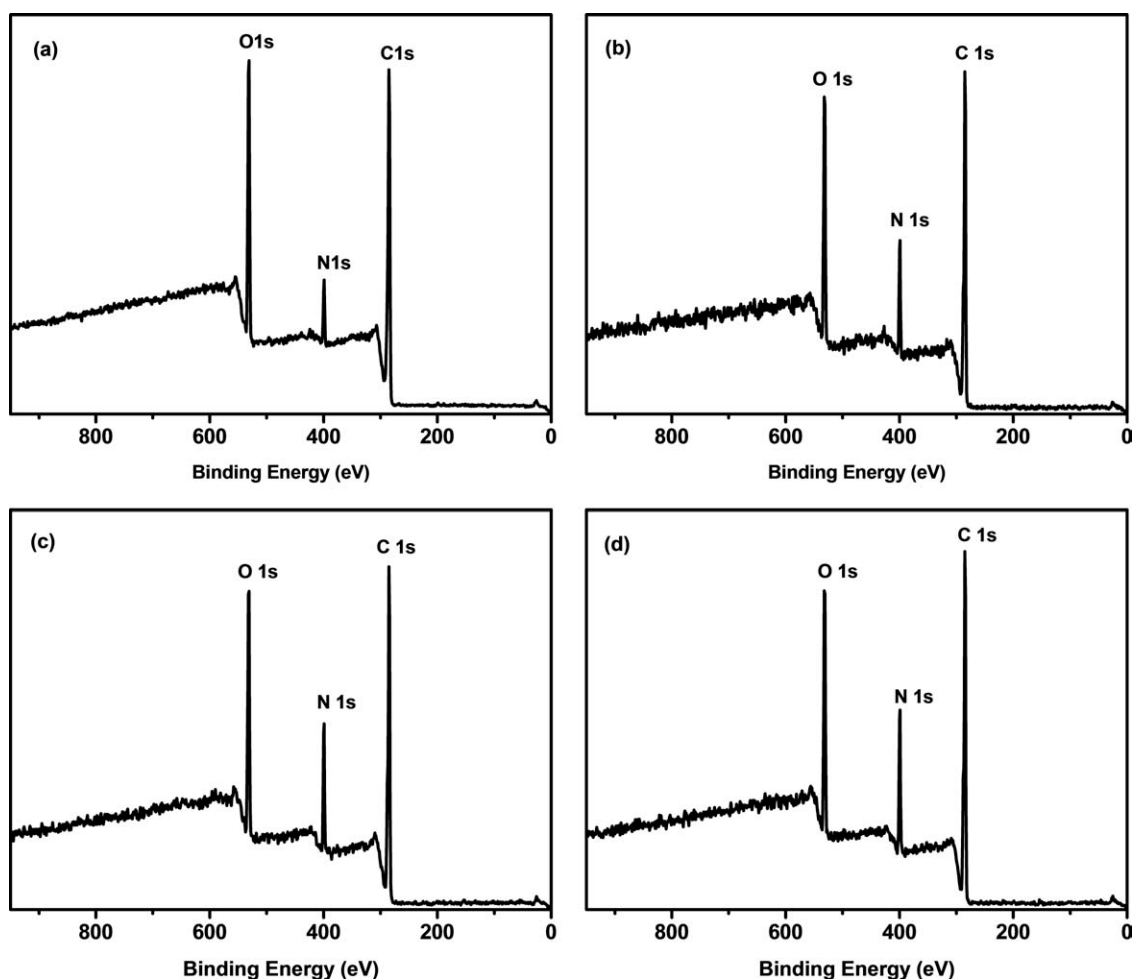


Figure 5 Typical wide-scan XPS spectra of the modified PET films by PAM for different time (a) 4 h, (b) 10 h, (c) 16 h, (d) 24 h, all the polymerization had been progressed in mixed solvent acetone/deionized water ($v/v = 50/50$).

after grafting polymerization time more than 10h. The theoretical nitrogen content of pure PAM and the experimental values under the grafting polymerization time of 24 h from XPS summarized in Table II matches quite well. Those results indicate that the surface of modified PET film almost covered by a thick PAM layer completely after grafting 24 h. The absence of the copper in the XPS spectra indicates that the ligand-catalyst system was effectively removed during the washing procedure.

Moreover, Figure 6(a) shows the C1s core-level spectrum of the bromine-bounded PET film that can be curve-fitted with three peak components representing different carbons in PET film: (A) aliphatic and aromatic hydrocarbon ($C-C/C-H$, at a binding energy of 284.5eV), (B) the methylside ester ($C-O$ at 286.2 eV), and (C) the carboxyl carbon ($O=C-O$ at 288.6 eV), respectively. But the grafted PET films by PAM for different times showed four kinds of carbon, as shown in Figure 6(b-d): (A) aliphatic and aromatic hydrocarbon ($C-C/C-H$, at 284.5 eV), (B) the methylside ester ($C-O$ at 286.1 eV), (C) the am-

ide carbon ($O=C-NH_2$ at 287.8 eV), and (D) the carboxyl carbon ($O=C-O$ at 288.6 eV) were found, respectively. The relative contents of the four carbon components were showed in Table III. The

TABLE II
Surface Elemental Composition of the Pristine PET Film and PET-g-PAM Films for Different Grafting Polymerization Time from XPS Analyses^a

Type of films	Reaction time (h)	Atom concentration ratio ([O]/[N]/[C])
PET theoretical	–	1/0/2.5
Pristine PET	–	1/0/3.8
PET-g-PAM	4	1/0.3/4.4
PET-g-PAM	10	1/0.7/4.5
PET-g-PAM	16	1/0.8/4.7
PET-g-PAM	24	1/0.9/4.5
PAM theoretical	–	1/1/3

^a Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors.

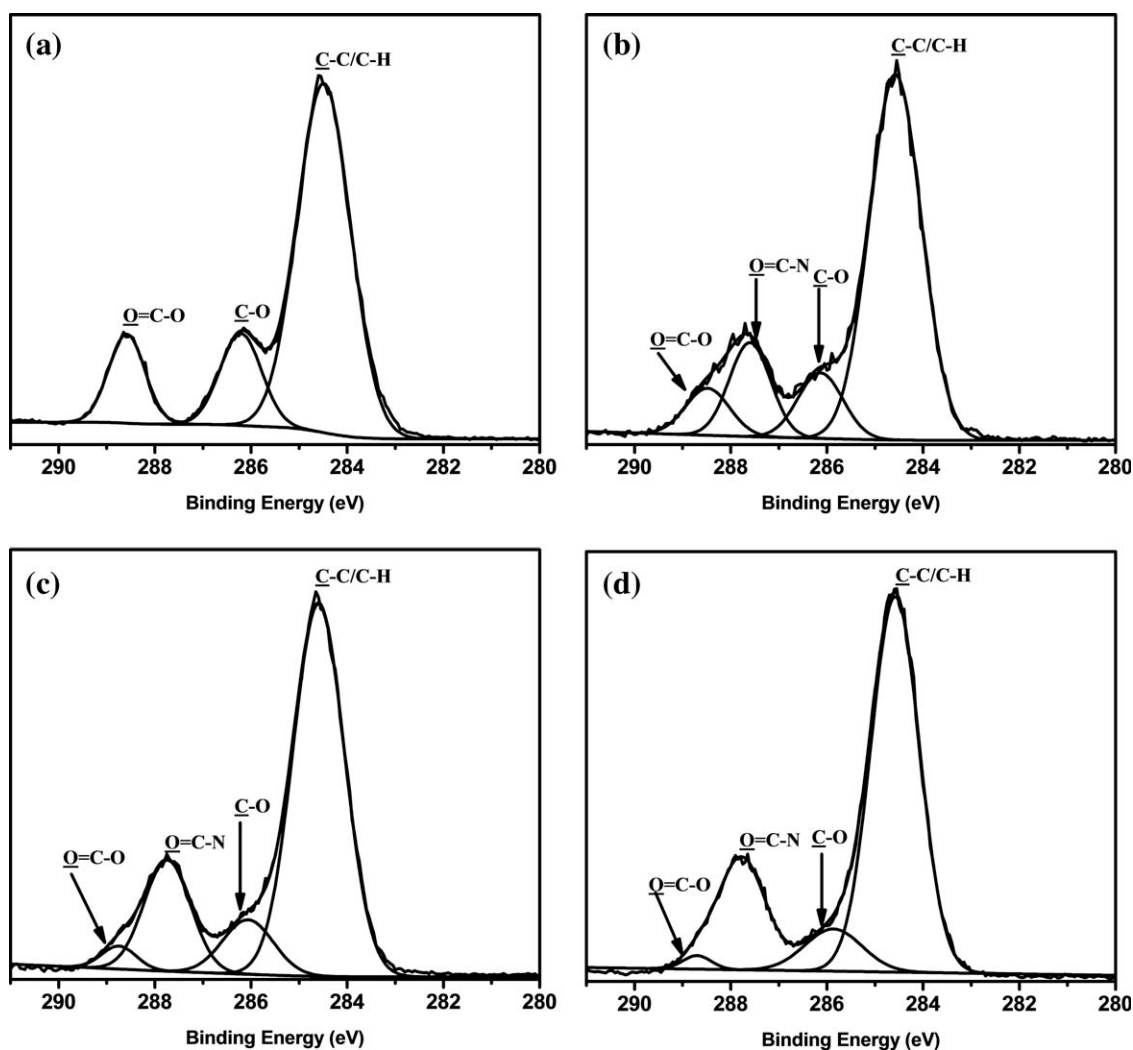


Figure 6 XPS C1s core-level spectra of (a) bromine-bounded PET film, (b) PET-g-PAM for 10 h, (c) PET-g-PAM for 16 h, (d) PET-g-PAM for 24 h, all the polymerization had been progressed in mixed solvent acetone/deionized water ($v/v = 50/50$) under 50°C .

appearance of the XPS carbon peak of $\text{O}=\text{C}-\text{NH}_2$ also demonstrated that PET films had been successfully grafted by PAM chains. The content of the binding energy peak of the amide carbon ($\text{O}=\text{C}-\text{NH}_2$ at 287.8 eV) significantly enhanced and the peak of carboxyl carbon ($\text{O}=\text{C}-\text{O}$ at 288.6 eV) and methylester ($\text{C}-\text{O}$ at 286.2 eV) weakened

as polymerization time increased. After grafting 24 h, the peak of carboxyl carbon almost disappeared. This result was consistent with the conclusion of Table II and the testing of infrared spectroscopy and PG%, which is a proof for the living/controlled nature of grafting polymerization from the surface of bromine-bounded PET films.

TABLE III
Data of the XPS Carbon Peaks

Samples	Reaction time (h)	Relative content of different carbons (peak area, %)			
		C-C/C-H	C-O	O=C-NH ₂	O=C-O
Bromine-bounded PAM	–	72.8	14.8	–	12.4
PET-g-PAM	10	68.4	10.6	13.9	7.4
PET-g-PAM	16	68.7	9.9	18.6	2.8
PET-g-PAM	24	68.9	9.2	20.5	1.5

TABLE IV
Polymerization Data of Free Polymer^a

No.	Solvent	Time (h)	\bar{M}_n^b	PDI ^b
1	Water/acetone	4	7.33×10^3	1.38
2	Water/acetone	10	1.25×10^4	1.37
3	Water/acetone	16	1.70×10^4	1.38
4	Water/acetone	24	2.22×10^4	1.31
5	Water/acetone	48	2.72×10^4	1.36
6	DMF	4	1.72×10^4	1.16
7	DMF	6	3.25×10^4	1.70
8	DMF	8	3.82×10^4	2.09

^a Polymerization conditions for AM: $[M]_0 = 7.0M$, $[CuCl] = 1/3[bpy] = 20 \text{ mM}$, $[EBiB] = 1\mu\text{L}$, at 50°C in water-borne medium, water/acetone = 50/50 (v/v %) or at 130°C in DMF; EBiB: ethyl 2-bromoisobutyrate.

^b Polymer formed in the solution, obtained by GPC/MALLS.

Table IV shows the GPC data of “free” polymers prepared under lower and high temperature, respectively. The results of GPC indicate that all of grafting polymerization in water-borne medium at 50°C shows better “living” and control, however that at high temperature (130°C) in DMF originally had good controllability, but then lost control after 4 h due to some side reaction caused by high temperature.

The evolution of GPC traces shown in Figure 7 is consistent with the increase in molecular weight as the polymerization time added. These results indicate that the progress of the grafting of PAM from PET film surface by aqueous SI-ATRP technique was living and controlled.

To further prove the “living”/controlled nature of polymerization initiated from bromine-bounded PET film, the effect of the polymerization time on the percentage of grafting (PG%) was investigated by gravimetric analysis, which was calculated according to the following expression:

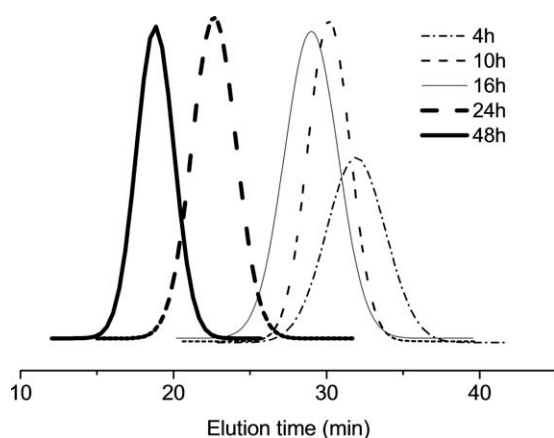


Figure 7 GPC traces of free PAM for different polymerization.

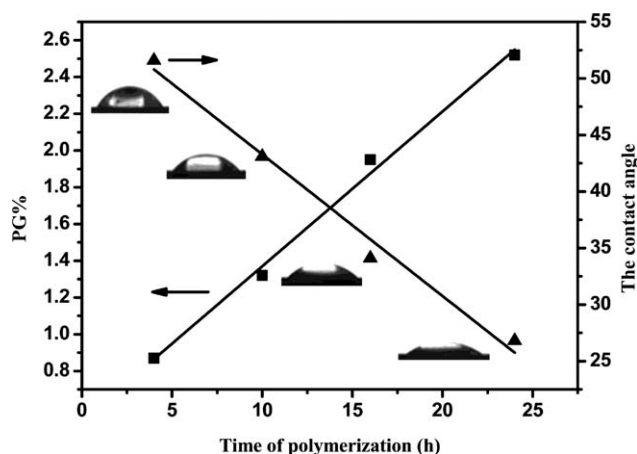


Figure 8 Effect of the grafting polymerization time on PG% and the contact angle.

$$\text{PG}\% = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 is the weight of film before grafting and m_1 is the weight of film after grafting. Figure 8 shows PG% increased linearly with polymerization time added, and reached 2.52% after 24 h, which suggests that SI-ATRP of AM from the surface of PET films in aqueous-based medium at lower temperature has the characteristics of “living”/controlled. The inference is to be identical with GPC dates.

Calculation of the graft density of polymer

The number-average molecular weight of the final polymer from solution using the “free initiator” was determined by GPC as $\bar{M}_n = 22190 \text{ g mol}^{-1}$, after 24 h. Knowing: the number-average molecular weight of the polymer (\bar{M}_n), the mass of grafted PAM (M_{PAM}), the area of membrane surface (S), the grafting density (σ) can be calculated by using eq. (2),³⁹ yielding a grafting density equal to 36.18 nm^{-2} , which points to the presence of a dense polymer brush.

$$\sigma = \frac{N_A M_{\text{PAM}}}{2SM_n} \quad (2)$$

According to the research of Cringus-Fundeanu et al.,³³ the separation between the mushroom and brush regimes in water as solvent for the molecular weight ($M_n = 22,190 \text{ g}\cdot\text{mol}^{-1}$, $N = 312$) can be calculated using eq. (3) to occur at $\sigma_{\text{calc}}^* = 0.046 \text{ nm}^{-2}$, where N is the number of monomer units.

$$\sigma_{\text{calc}}^* = C \times N^{-6/5} \quad (3)$$

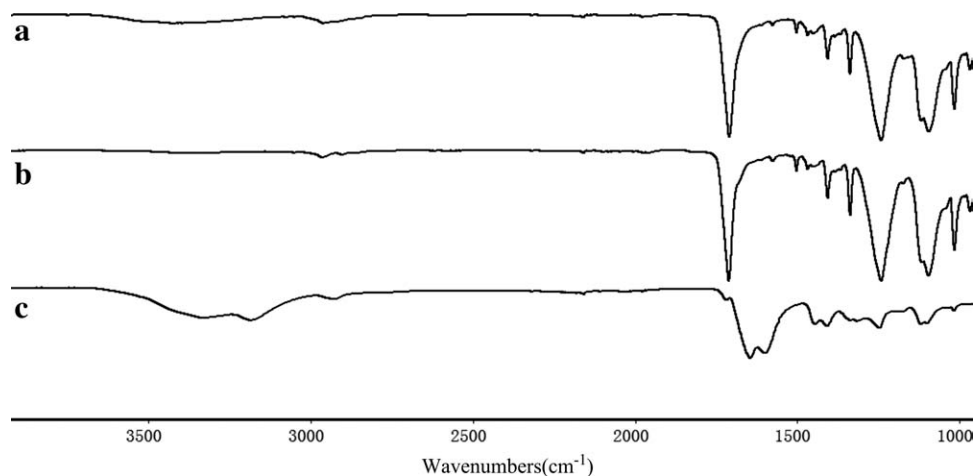


Figure 9 ATR/FTIR spectra of (a) grafted PET film by PHEMA for 24 h, (b) PET-g-PHEMA-Br, (c) PET-g-PHEMA-g-PAM for 6 h.

The calculated grafting density in dry state ($\sigma = 36.18 \text{ nm}^{-2}$) of PAM chains having $\overline{M}_n = 22,190 \text{ g}\cdot\text{mol}^{-1}$ is well above the threshold for the brush regime in water (0.046 nm^{-2}) for the same \overline{M}_n .

Characterization of comb-shaped grafting copolymer from PET film

In order to further study the surface structures, composition, and properties, the comb-shaped grafting copolymer had been constructed. The PET film firstly had been grafted by PHEMA. Then hydroxyl groups changed into initiator of ATRP which were used to initiate the AM forming complex structure grafting PAM on the surface of PET film.

Figure 9 shows the FTIR/ATR spectra of modified PET films. Comparing with the spectrum of bromine-bounded PET film, the spectrum of grafted PET film by PHEMA shows a wide and obvious absorption peak at the range of $3450\text{--}3200 \text{ cm}^{-1}$ (assigned to stretching of —OH and the formation of hydrogen bonding). In addition the peak at 2966 cm^{-1} was intensified (due to stretching of $\text{—CH}_2\text{—}$) because of grafting PHEMA. All those data confirmed the formation of the grafting PHEMA layer on the surface of PET film successfully.

After most of hydroxyl groups changed into ATRP initiator, the peak at the range of $3450\text{--}3200 \text{ cm}^{-1}$ almost vanished. The spectrum of PET-g-PHEMA-g-PAM presents a completely different peak shape from those spectra. The two absorption peaks around $3500\text{--}3050 \text{ cm}^{-1}$ were assigned to asymmetric and symmetric stretching of —NH_2 . The absorption peak at 1647 cm^{-1} attributed to the hydrogen bond between —CONH_2 groups. The absorption peak at 1604 cm^{-1} was assigned to wagging vibration of —NH_2 . The almost disappeared absorption peak at 1730 cm^{-1} was attributed to ester

group. The four absorption peaks at 1600 cm^{-1} , 1578 cm^{-1} , 1505 cm^{-1} , and 1470 cm^{-1} attributing to the stretching of benzene skeleton also disappeared. The absorption peaks at 1450 cm^{-1} and 1410 cm^{-1} was attributed to vibration of $\text{—CH}_2\text{—}$. All these data suggested that the surface of PET film had been covered completely by a thick and high density grafting polymer layer.

Comparing with the typical wide-scan XPS spectrum of bromine-bounded PET film [Fig. 2(a)], two major binding energy peaks at 284.6 eV for C1s and 533 eV for O1s of modified PET film by PHEMA [Fig. 10(a)] was almost no change except that the binding energy peak of O1s became more intense because the oxygen content of PHEMA is higher than that in the PET film. In addition, the C1s core-level spectrum of the PET-g-PHEMA surface [Fig. 10(d)] also could be resolved into three peaks: the binding energy peak at 284.5 eV was assigned to the aliphatic and aromatic hydrocarbon (C—H/C—C) and the binding energy peaks at 286.2 and 288.6 eV were ascribed to the methylside ester (C—O), and ester group (O=C—O). The area ratios of C1s peaks of the ester (C—O) between the methylside in the bromine-bounded PET film and PET film grafted PHEMA were found to be 14.8 and 18.9, respectively. These data proved that the surface of PET film had been modified by PHEMA layer. The initiator immobilization was confirmed by the appearance of Br 3d (71 eV) and Br 3p (182 eV) peaks in the XPS spectrum [Fig. 10(b)]. After surface-initiated ATRP of AM, a new binding energy peak of N1s appeared at 400.1 eV [Fig. 10(c)] because of grafted PAM chains on the surface of PET-g-PHEMA film. The C1s peak of the PET-g-PHEMA-g-PAM surface can only be fitted by two unique carbon moieties [Fig. 10(e)]: (A) C—C/C—H (284.5 eV), (B) O=C—NH_2 (287.8 eV). The peaks of C—O (286.1 eV) and

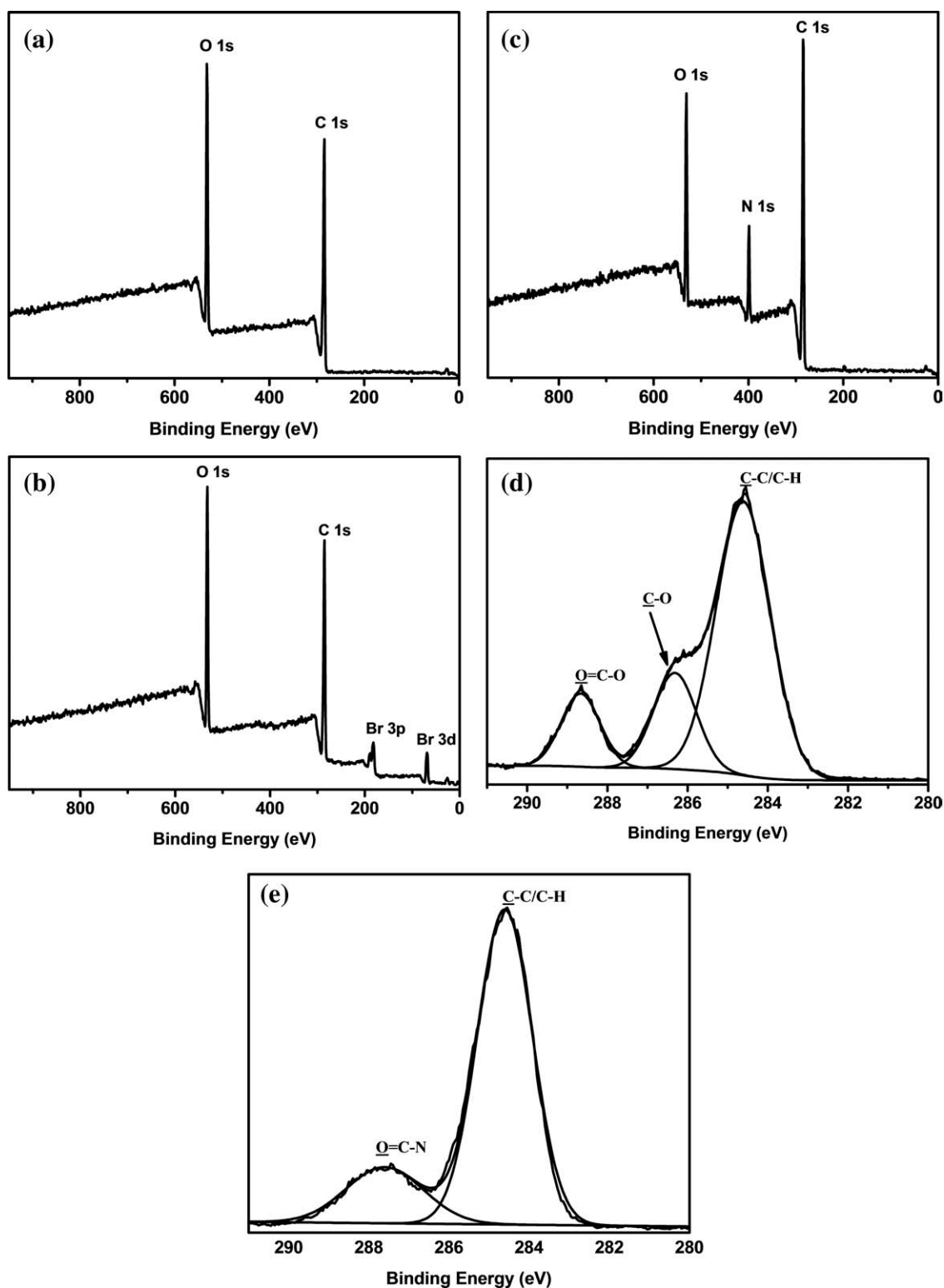


Figure 10 Typical wide-scan XPS spectra of (a) PET film grafted PHEMA for 24 h, (b) PET-g-PHEMA-Br, (c) PET-g-PHEMA-g-PAM for 6 h and XPS C1s core-level spectra of (d) PET film grafted PHEMA, (e) PET-g-PHEMA-g-PAM for 6 h.

O=C—O (288.6 eV) of PET film disappeared because the PET film was covered completely by grafting PAM. From these data, the surface of comb-shaped copolymer modified PET film was completely covered by the second grafting polymer layer (PAM).

The conversion of initiator ($C_{\text{initiator}}$) and the degree of polymerization (DP) were calculated from mass weighting data obtained by the gravimetric analysis as follows: the amount (mol) of grafted HEMA (N_{HEMA}) was calculated by eq. (4).

$$N_{\text{HEMA}} = \frac{W_1 - W_0}{130} \quad (4)$$

And the amount (mol) of immobilized ATRP initiator (N_{Br}) from the film grafted PHEMA chains was calculated by eq. (5)

$$N_{\text{Br}} = \frac{W_2 - W_1}{149} \quad (5)$$

Therefrom, the conversion of initiator could be obtained as

$$C_{\text{initiator}} = \frac{N_{\text{BR}}}{N_{\text{HEMA}}} \quad (6)$$

The amount of PAM (N_{PAM}) grafted by surface-initiated ATRP was calculated by eq. (7)

$$N_{\text{PAM}} = \frac{W_3 - W_2}{71} \quad (7)$$

Thus, the polymerization degree of PAM could be defined as

$$\text{DP} = \frac{N_{\text{PAM}}}{N_{\text{Br}}} \quad (8)$$

where W_0 is the weight of bromine-bounded PET film, W_1 is the membrane weight after grafted by PHEMA and W_2 is the membrane weight after initiator immobilization from the surface of grafted membrane by PHEMA, W_3 is the weight of modified PET film by comb-shaped copolymer. Where 130 is the repeat unit mass of the grafted PHEMA chain, and 149 is the molecular weight increase gained by the immobilization of the ATRP initiator from the PHEMA grafted membrane. The repeat unit mass of grafted PAM chains is 71. The conversion of initiator could be calculated by eq. (6) which is 0.78, and the polymerization degree of PAM calculated by eq. (8) which is about 42.

Surface behavior of modified PET films

The contact angle of native PET film was 70.3° , corresponding to its hydrophobic surface. This value was close to that reported by Shadpour et al. for the high-degree crystallized PET ($75 \pm 4^\circ$).⁵⁰ After fixed with initiator, the contact angle appeared slight decreasing to 68.7° . After modified by PAM, the contact angle presents significantly decreasing compared with pristine and bromine-bounded PET films, because a great quantity of hydrophilic groups were introduced onto the surface of the modified PET films which improve the surface hydrophilic property.⁵¹ Figure 8 shows that the contact angles of

the PET films modified by PAM for different time present significantly decreasing as the polymerization time increased. Moreover, the surface hydrophilicity of the modified PET films increased with the polymerization time added. After 24 h, the contact angle of modified PET film reaches 26.8° . The contact angle of the PET film grafted comb-shaped copolymer PHEMA-*g*-PAM is even to 13.6° , because of much more hydrophilic groups on the surface.

From contact angles the surface tension and two kinds of contributions (dispersion and polarity) were obtained by expanded Fowkes eqs. (9)–(11).⁵²

$$\gamma_L(1 + \cos\theta) = 2(\gamma_s^d \times \gamma_L^d)1/2 + 2(\gamma_s^p \times \gamma_L^p)^{1/2} \quad (9)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (10)$$

$$\gamma_L = \gamma_L^d + \gamma_L^p \quad (11)$$

γ is the surface tension of liquid (γ_L) or sample (γ_s); γ^d and γ^p are the dispersive, polar contributions to surface tension, respectively.

The boundary layers formed on the surface of PET films by grafting PAM could contribute some new and valuable properties to the substrate. Determination of contact angle of the modified films could provide information regarding surface tension and polarity. Table V gives the surface tensions of modified PET films by SI-ATRP. Compared with pristine PET film, the surface tensions of the modified PET films by PAM significantly increased. After modified for 24 h, the surface tension of PET-*g*-PAM films increased to $69.9 \text{ mN}\cdot\text{m}^{-1}$. Because the surface of native PET film was composed of benzene ring and hydrocarbon from ethylene glycol, so the value of γ^p of PET film was very small and γ^d was quite large, suggesting that the surface of native PET film was hydrophobic. But the modified PET films by SI-ATRP all provided high values of γ^p , demonstrating a hydrophilic surface. Apparently, grafting modification with PAM by SI-ATRP could effectively turn the PET surface from hydrophobicity into hydrophilicity.

Figure 11 shows the morphology of PET film and modified PET films. From Figure 11(a), we can see that the surface of pristine PET film is very smooth. Because of hydrolysis and oxidation, the surface of bromine-bounded PET film changed pattern. After grafting polymer, the formation of the grafted polymer layer provided a much more rough surface morphology of the modified PET films than that of pristine PET film and bromine-bounded PET film. This result indicates that the grafting density of modified PET film by polymer is very high. Furthermore, the surface of modified PET film was covered equably by grafted polymer, which offered some new properties to the surface of PET films.

TABLE V
Contact Angle and Surface Tension of Samples

Samples	Contact angle (°)		Surface tension (mN·m ⁻¹)		
	H ₂ O	HCONH ₂	γ	γ^d	γ^p
Water	–	–	72.8	29.1	43.7
Formamide	–	–	58.2	35.1	23.1
Pristine PET film	70.3	54.7	37.2	27.7	9.5
Bromine-bounded PET	68.7	52.3	37.2	27.7	9.5
PET-g-PAM (4 h)	51.6	38.5	47.9	20.3	27.6
PET-g-PAM (10 h)	43.8	29.4	54.1	19.9	34.2
PET-g-PAM (16 h)	34.1	20.2	62.3	16.1	46.2
PET-g-PAM (24 h)	26.8	16.1	69.9	12.2	57.5
PET-g-PHEMA	40.9	27.3	56.6	18.1	38.5
PET-g-PHEMA-Br	57.1	36.1	48.3	34.7	13.6
PET-g-PHEMA-PAM	13.6	7.8	80.6	8.4	72.2

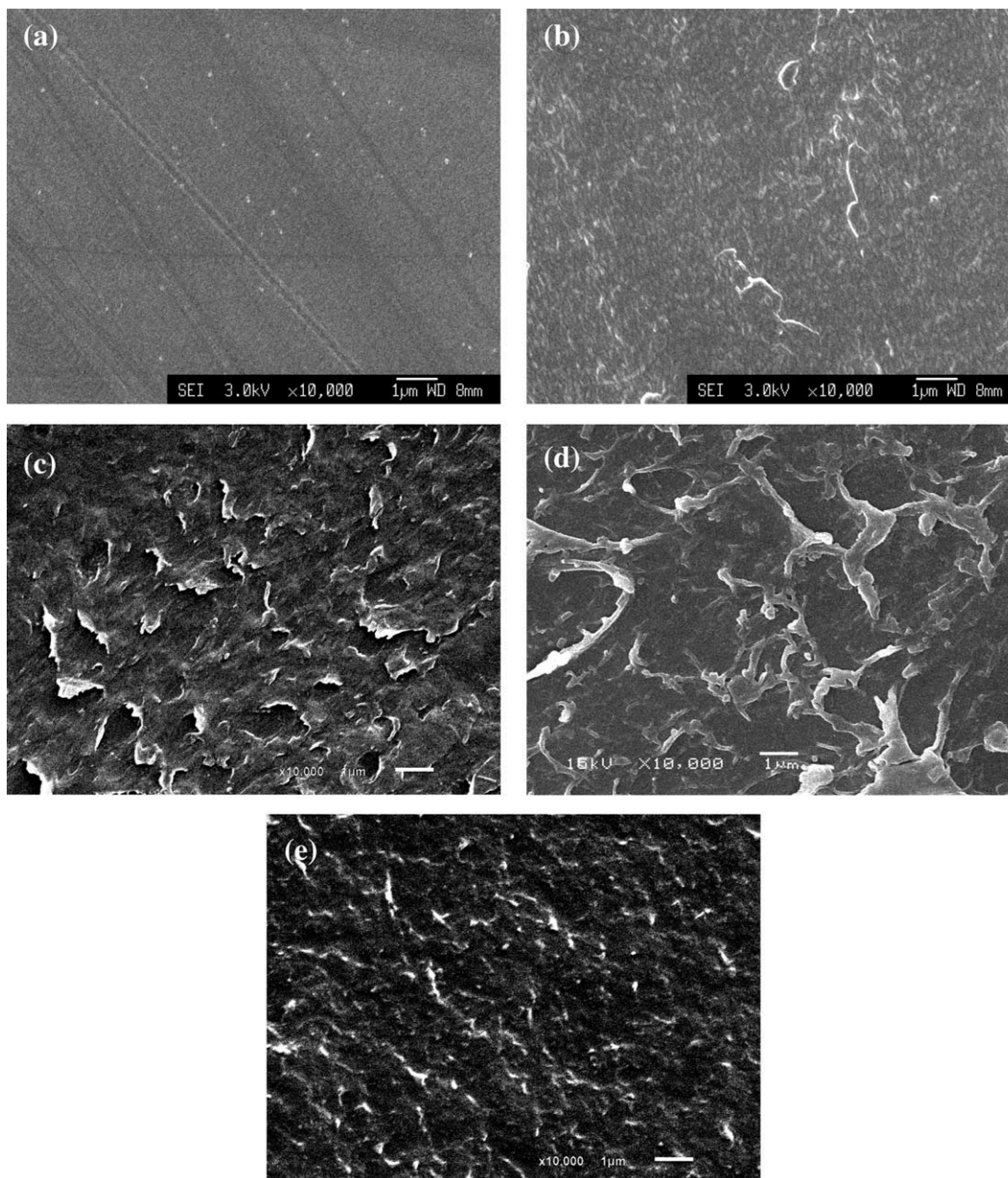


Figure 11 SEM images of (a) pristine PET film, (b) bromine-bounded PET film, (c) PET-g-PAM, (d) PET-g-PHEMA, and (e) PET-g-PHEMA-PAM.

CONCLUSIONS

The grafted homopolymer and comb-shaped structure PAM had been successfully prepared from the surface of PET films by SI-ATRP. The grafting polymerizations progressing with different ratio of mixed solvents showed the character of "living"/controlled. The dense brush regime has been obtained as determined by the grafting density equal to 36.18 nm^{-2} which is well above the threshold for the brush regime in water (0.046 nm^{-2}) for the same \overline{M}_n . The structures and properties of the modified PET films were characterized by FTIR/ATR, X-ray photoelectron spectroscopy (XPS), measurements of contact angles, and scanning electronic microscopy (SEM). The results show that the surface of PET film was grafted by polyacrylamide, which own different surface morphology from that of pristine PET. The GPC dates show that compared with the polymerization at high temperature (130°C) in DMF, the reaction in water-borne medium shows better living and control. The static water contact angle (θ) of the grafted membrane by PAM decreased as polymerization time added. This indicated that the hydrophilic property of the films was obviously correlated with the chain length of graft polymer. After covered with the second polymer layer (PAM) completely, the modified PET film by comb-shaped copolymer brushes shows a hydrophilic surface.

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