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Study on reconstruction mechanism at the surface of a glassy polymer

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Abstract

The introduction of hydrophilic functional groups at various depths in the functionalized interfacial region of poly(4-methylstyrene) (P4MS) provided a system for studying the surface reconstruction mechanism of this glassy polymer. The degree of surface reconstruction (RD) and the rate of surface reconstruction ($1/t_{1/2}$) were employed to compare the surface reconstruction behavior for various samples. The results showed that $1/t_{1/2}$ decreased with increase of the depth in the functionalized interface region at a temperature below T_g of poly(4-methylstyrene). By studying the relation of water contact angles and the surface free energy of the samples with temperature, it was found that surface reconstruction of surface-oxidized P4MS samples took place in two steps when the samples were heated in air. The first step took place below 80 °C, in which polar side groups turned into the bulk, leaving a relatively nonpolar backbone projecting out of the surface to form a "hydrophobic conformation". The second step occurred above the P4MS T_g (110 °C), in which P4MS molecular chains migrated to the surface in order to minimize the interfacial free energy between surface-oxidized P4MS film and air, since oxidized P4MS molecules containing carbonyl groups have higher surface free energy than the unmodified P4MS molecules. As the depth of the functionalized interfacial region increases, a longer time is needed for the polar side groups to reorient (the first step) and for unoxidized P4MS molecules to migrate to the surface (the second step), which resulted in the sample with deeper functionalized region having lower reconstruction rate and RD using the same treatment condition.

Keywords: Surface reconstruction; Polymer surface; Poly(4-methylstyrene)

1. Introduction

The ultimate application of materials depends not only on their bulk properties, but also heavily on their surface and interfacial behavior, including friction, lubrication, abrasion, wetting, adhesion and adsorption [1–4]. Therefore, surface-modifications, such as grafting and plasma treatment, were usually employed to obtain appropriate surface properties of materials while keeping the bulk properties unchanged. However, the surface wettability of the hydrophilic treated polymer generally decreases and that of hydrophobic treated one increases with time; sometimes, reverting to that of the untreated polymer [5,6]. This behavior was attributed to surface reconstruction, since the polymeric surface is capable of modifying its structure in contact with the surrounding medium and an equilibrium state will be attained corresponding to a minimal interfacial free energy between the two media [7]. Recently, in many studies, special attention has been devoted to the interface for specific applications, and to the careful design of the topmost surface layer controlling a predictable surface response, or a variable surface response under different conditions [8–12]. Meanwhile, study on kinetics of reconstruction is necessary since it will help us fabricate this kind of material and understand well the phenomenon of environmental response on polymer surfaces. What parameters should be used to describe surface reconstruction behavior of polymer? By what mechanism does reconstruction occur? The majority of researchers think that surfaces typically reconstruct, via conformational changes of segments and/or diffusion of chains, to produce configurations having lower interfacial free energy

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[13–15]. The kinetics of reconstruction depend on the temperature, and presumably, the glass-transition temperature of the polymer as well. But there were few studies to pay attention to the kinetics and mechanisms of polymer surface reconstruction, which were significant in controlling the surface environmental responses.

We chose poly(4-methylstyrene) as a model glassy polymer because oxidation of the *p*-methyl group near the surface to carboxylic acid and other hydrophilic groups provided a surface whose reconstruction was easily monitored by contact angle measurement. In addition, the T_g of P4MS is 110 °C, which allowed the convenient measurement of the kinetics of reconstruction. In this paper, the variations in surface composition were evaluated by studying surface wetting behavior of surface-oxidized poly(4-methylstyrene) with various depths of the functionalized interfacial region. The aim was to gain a better understanding of the mechanism of the surface reconstruction. At the same time, the degree of surface reconstruction and the rate of surface reconstruction were employed to compare the surface reconstruction behavior for various samples.

2. Experimental section

2.1. Materials and general methods

Poly(4-methylstyrene) (P4MS) ($M_w = 76\,000$, $T_g = 110\ °C$) was purchased from Aldrich Co. *tert*-Butyl hydroperoxide (*t*-BuOOH, reagent grade) was purchased from Shanghai Linfeng Chemicals Ltd. Other chemicals were all of reagent grade and used without further purification.

Contact angles (θ) of water were measured by the sessile drop method at room temperature and ambient humidity with a Krüss (Hamburg, Germany) DSA-10 contact angle goniometer. Samples which had been heated in air were cooled to room temperature before θ measurement. The reported θ values are the averages of at least eight different measurements taken within 10–20 s of applying each drop of water. At the same time, the contact angles of water and diiodomethane were used to make estimates of surface free energy for various samples according to Fowkes theory [16]. In order to ensure that the results were sufficiently credible, the experimental errors in measuring the θ values were evaluated to be less than ±2°.

2.2. Sample preparation and its surface oxidation

Sample films were prepared by casting 5% P4MS solution in xylene on glass plate and dried in air at 45 °C, then dried under vacuum at 45 °C for 48 h.

Surface oxidation of P4MS films was proceeded using a procedure reported for poly(methylstyrene) latex particles by Li et al. [17]. The P4MS films were suspended in 5×10^{-4} M $CuCl_2 \cdot 2H_2O$ aqueous solution (1:50 mole ratio to *t*-BuOOH). The mixture was heated to 70 °C, and then *tert*-butyl hydroperoxide (0.025 M) was added dropwise to the mixture. The oxidation was carried out under air with continuous stirring. After oxidation samples were floated in deionized water for 24 h, then washed to remove any absorbed chemicals. The sample was then dried with a stream of nitrogen and contact angles were measured after this procedure.

2.3. Determination of carboxylic acid content

The amount of carboxylic acid groups on the surface of the oxidized films was determined by direct potentiometric titrations. A weighted amount of oxidized PMS film was cut into small chips and suspended in 50 ml 0.005 M standard NaOH solution for 20 min and then the suspension was titrated with 0.005 M standard HCl solution with vigorous magnetic stirring. The procedure was the same as that used for the surface-modified poly(methylstyrene) latex particle [17] according to Eq. (1).

$$\begin{aligned}&-\text{COOH content on film surface}\\&\quad = (50 - V) \times 0.005/\text{film surface area}\end{aligned} \qquad (1)$$

where V is the volume of standard HCl solution required for each suspension to reach equilibrium.

2.4. ATR-FTIR measurement

The attenuated total reflectance-Fourier transform infrared spectra (ATR-FTIR) were recorded on a Nicolet 7199 FTIR spectrometer equipped with a mercury–cadmium-telluride (MCT) detector at a resolution of 2 cm^{-1} using a Wilks model 50 ATR attachment and a Ge internal reflection element (IRE) ($52.5 \times 20 \times 2\ mm^3$) with an angle of incidence of 60°.

2.5. XPS measurement

X-ray photoelectron spectroscopy (XPS) experiments were carried out on a PHI-5000C ESCA system (Perkin Elmer) with Al Kα radiation ($h\nu = 1486.6$ eV). In general, the X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54°. The pass energy was fixed at 46.95 eV to ensure sufficient sensitivity. The base pressure of the analyzer chamber was about 5×10^{-8} Pa. The sample was directly pressed to a self-supported disk (10 × 10 mm) and mounted on a sample holder and then transferred into the analyzer chamber. Survey scans (0–1200 eV) and high resolution spectra were both recorded. Calibration was conducted on the C1s peak of the C–C bond at 284.6 eV. The data analysis was carried out by using the PHI-MATLAB software provided by PHI Corporation.

3. Results and discussion

3.1. Characterization of the surface-oxidized P4MS film

The attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrum of surface-oxidized P4MS film showed two small, broad over-lapping bands centered at 1704 and 1724 cm^{-1} (Fig. 1) and the peak intensity increased with

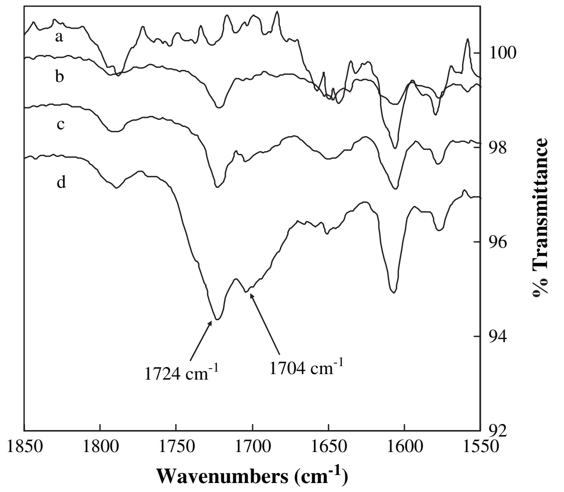


Fig. 1. ATR-FTIR spectra of (a) P4MS (pure), (b) P4MS-ox1 (surface-oxidized for 0.5 h), (c) P4MS-ox2 (surface-oxidized for 3.0 h) and (d) P4MS-ox3 (surface-oxidized for 8.0 h).

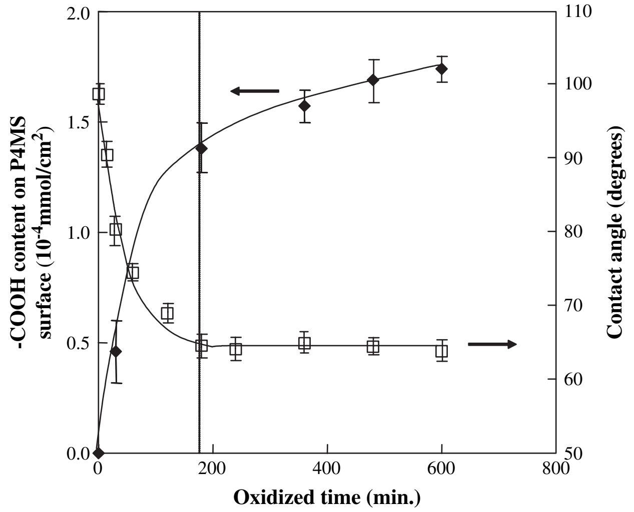


Fig. 2. −COOH content on the surface (◆) and contact angle (☐) of the surface-oxidized poly(4-methylstyrene) film as a function of oxidation time.

increasing oxidation time. These bands were assigned to carboxylic acid and aldehyde groups, respectively [18]. Carboxylic acid carbons and aldehyde carbons could also be characterized by XPS similar to that reported by Rouse [15]. A summary of O/C molar ratios obtained by XPS is shown in Table 1 and the results showed that O/C molar ratios increased with oxidized time, from 0.057 of samples oxidized for 0.5 h to 0.143 of samples oxidized for 8 h.

When the P4MS film was oxidized for 8 h, the water contact angle was 63.4°. The water contact angle on unoxidized P4MS was 98°. As shown in Fig. 2, the contact angles decreased sharply with oxidation time, then reached a constant value in 3 h. At the same time, the results showed that −COOH content on oxidized P4MS film surface increased quickly within first 3 h, then increased very slowly in the next 7 h.

Whiteside and his coworkers [14] divided the functionalized interfacial region of the surface-treated low density polyethylene into three regions based on comparisons of data obtained by experimental techniques having different degrees of surface sensitivity as shown in Scheme 1. The first was the outermost, most closely corresponding to a "surface". This region could be examined by the most surface-sensitive technique − contact angle measurements, which was called "contact angle interphase", namely "θ-interphase". The second was the "near surface" region. Functional groups in this region (together with those in the outermost) can be examined by surface-sensitive instrumental techniques such as XPS. The third one comprised the deeper regions of the polymer. Groups in this region can be detected by ATR-FTIR but are unlikely to influence surface properties. According to our results, when the oxidation time was within 3 h, variation of surface composition of P4MS films mainly took place in the first region, as indicated by contact angle interphases (θ-interphases). The increase of the polar groups, such as −COOH in this region resulted in the decrease of the contact angle. When the oxidation time was from 3 to 8 h, that variation would happen in "near surface" region. This is the reason why the contact angle remained unchanged.

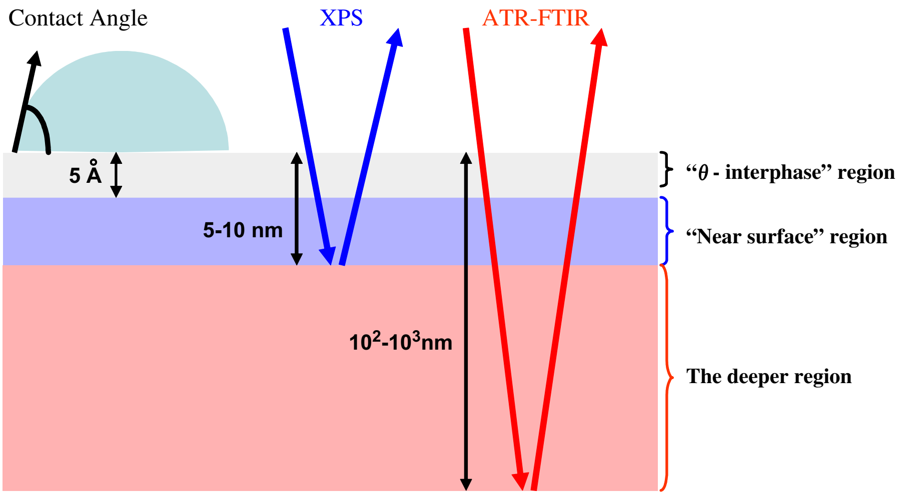
Table 1
O/C molar ratios measured by XPS and surface properties of various surface-oxidized P4MS

Samples	Oxidation time (h)	O/C	Contact angles (°)	γ_S^P	γ_S^D	γ_S
P4MS	0	0	98.0 ± 1	0.2	36.0	36.2
P4MS-ox1	0.5	0.057	80.4 ± 1	2.1	38.2	40.3
P4MS-ox2	3	0.083	63.6 ± 2	5.0	39.8	44.8
P4MS-ox3	8	0.143	63.4 ± 2	9.5	42.0	51.5

In order to compare the surface reconstruction behavior and investigate the surface reconstruction mechanism, three samples with different surface status as shown in Scheme 2 were used and their characteristics are shown in Table 1. The first sample was P4MS-ox1 with slight oxidation in θ-interphase region, the second was P4MS-ox2 with oxidation saturation in θ-interphase region and the third one P4MS-ox3 with oxidation deep into near surface region.

3.2. Parameters of reconstruction of surface-oxidized P4MS film in air

Surface-oxidized poly(4-methylstyrene) (P4MS) films were heated in air at temperatures below, at, and above the T_g of the polymer (110 °C), and their water contact angles were measured. Usually, the contact angle was used to compare the change in surface wettability of the same sample under various conditions. However, it is difficult to compare the extent of surface property recovery when the samples with different surface-oxidation degrees and having different initial contact angles were used. In order to compare the surface reconstruction behavior of various samples, the degree of surface reconstruction (RD) was employed and it could be estimated from the initial contact angle (θ_0), contact angles for the sample heated in air for t minutes (θ_t) and the contact angle obtained after complete reconstruction (θ_c) as



Scheme 1.

$$\mathrm{RD} = \left| \frac{(\theta_t - \theta_0)}{(\theta_c - \theta_0)} \right| \times 100\%$$

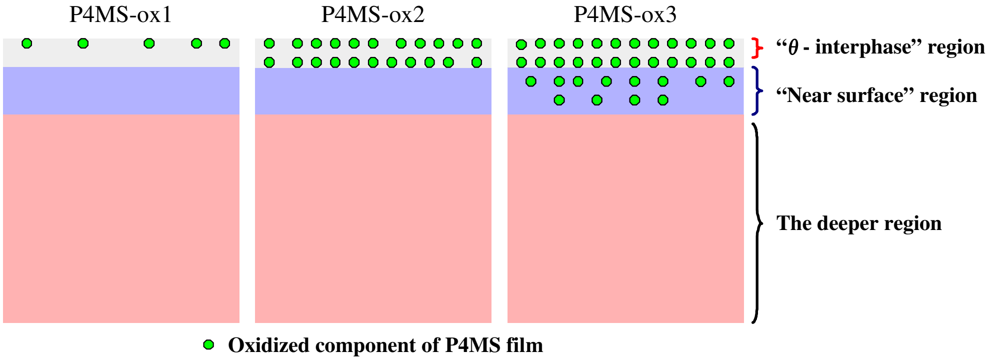
The parameter indicates the extent of hydrophobicity recovery that could be reached when surface-oxidized P4MS film was heated in air. RD of P4MS-ox3 as a function of time is shown in Fig. 3. Almost 100% of RD was only observed for temperatures at or above the T_g, at which surface wettability of P4MS-ox3 film was the same as that of the unmodified polymer. Below 110 °C, the degree of surface reconstruction varied dramatically with temperature. Three temperature regions, above 100 °C, 80–100 °C and 45–70 °C were found according to RD of the samples with heating time. The samples heated in air within the range of 80–100 °C and 45–70 °C appeared to reach a limited degree of surface reconstruction corresponding to RD of about 75% and 25% over a period of 50 h. Similar results were obtained from the other samples P4MS-ox1 and P4MS-ox2.

Fig. 4 compares the degree of surface reconstruction of various samples as the function of temperature. The results showed that RD for P4MS-ox1 was much higher than the other two samples below 120 °C and reached 100% only at 110 °C for 2 h. However, RD for P4MS-ox2 was almost the same as that for P4MS-ox3 within the range of experimental temperatures explored. As shown above, RD was readily used to compare the extent of surface properties recovery of the samples with different surface status.

The rate of surface reconstruction was used to describe how fast the surface reconstruction was and could be conveniently expressed in terms of $1/t_{1/2}$, in which $t_{1/2}$ was defined as the time for the degree of surface reconstruction to reach 50%. All $t_{1/2}$ were obtained at temperatures above 80 °C, since samples heated below this temperature did not reach RD of 50% over the time observed. The results showed that $1/t_{1/2}$ decreased with increase of depth of the functionalized interfacial region and increased sharply at higher temperature. At the same time, the relationship

$$1/t_{1/2} = A\exp(-E_R/RT) \tag{2}$$

between $1/t_{1/2}$ and $1/T$ could be described by an Arrhenius equation (Eq. (2)) and the results are shown in Fig. 5. The apparent activation energies of surface reconstruction (E_R) for various samples were obtained from Fig. 5 and increased with surface-oxidation time as shown in Fig. 6. The surface-oxidized samples with deeper functionalized interfacial region have higher $E_{R,}$ which resulted in lower reconstruction rate and RD under the same treatment conditions.



Scheme 2. Schematic representation of surface status of the various surface-oxidized P4MS samples.

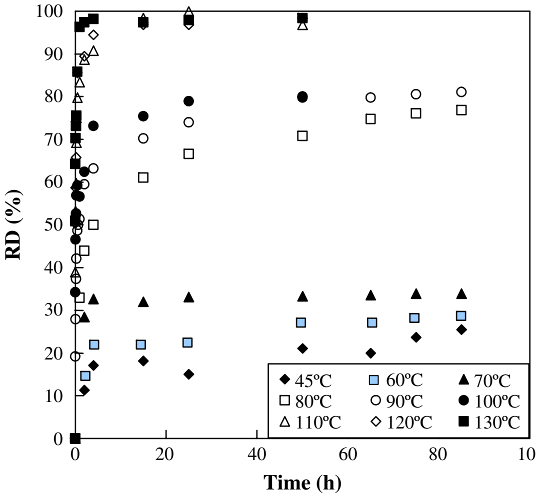


Fig. 3. The degree of surface reconstruction of P4MS-ox3 as a function of time.

3.3. The mechanism of reconstruction of surface-oxidized P4MS film

The water contact angle on various surfaces as a function of temperature is shown in Fig. 7. The results indicated that the contact angles of all three samples increased with increasing temperature until reaching 98°. Complete hydrophobicity recovery was observed when the temperature was above 110 °C. However, the XPS and ATR-FTIR spectra revealed that O/C molar ratios and absorbance intensity of oxygen-containing functionality of P4MS-ox3 did not change after heating in air at 120 °C for 2 h. The reason was attributed to the different depth sensitivities of various analytical tools, contact angle measurement, XPS, and ATR-FTIR [14]. Thus, as functional groups move away from the θ-interphase into the deeper regions of the polymer, they could not be monitored by contact angle measurement. However, the functional groups could be sensed well by XPS and ATR-FTIR techniques with deeper sensitivities. Despite the quantitative uncertainty caused by this observation, the important conclusion certainly valid is that the disappearance of polar, oxygen-containing functionalities from the interface after heating is due to the diffusion of these functionalities into the deeper region.

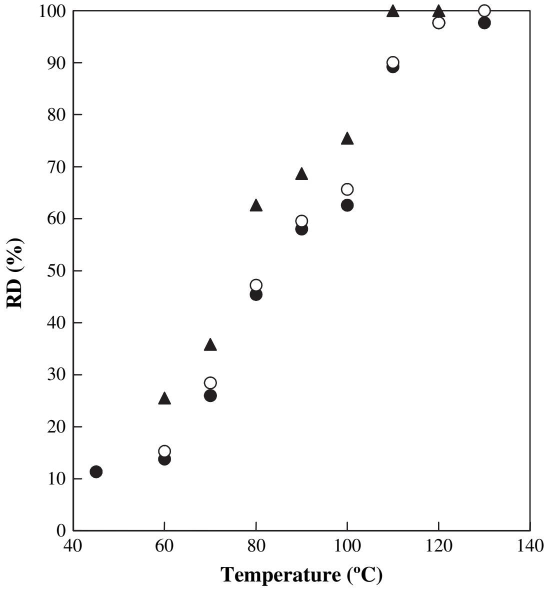


Fig. 4. The degree of surface reconstruction of P4MS-ox1 (▲), P4MS-ox2 (○) and P4MS-ox3 (●) as a function of the temperature heated in air. Time: 2 h.

At the same time, contact angle vs. temperature was recorded for all three samples in three temperature ranges, below 80 °C, 80–100 °C and above 100 °C, as shown in Fig. 7. Surface free energies of oxidized P4MS films used in this study were estimated from contact angle measurements described by Fowkes [16]. According to Fowkes' theory, surface free energy (γ_S) was composed of dispersive (γ_S^D) and polar (γ_S^P) components. As shown in Table 1, surface free energy increased from 36.2 to 51.5 mN/m and its polar components from 0 to 9.5 mN/m within 8 h of oxidation time. The reason was attributed to polar groups produced on P4MS film surface after oxidation. The dispersive (γ_S^D) and polar (γ_S^P) components of the surface free energy vs. temperature were plotted as shown in Fig. 7. The results showed that γ_S^P decreased sharply with temperature increase and reached almost zero at 80 °C, but the dispersive (γ_S^D) components of the surface free energy almost did not change. Within the second temperature range (80–100 °C) there was little change in both the dispersive (γ_S^D) and the polar (γ_S^P) components of the surface. Within the third temperature range (above 100 °C) γ_S^D decreased to about 36 mN/m only within 10 °C increment, which was the same as that of the pure poly(4-methylstyrene) film. It is obvious that the variation in surface free energy with temperature responded to the change in the contact angles. Similar results were obtained for P4MS-ox1 and P4MS-ox2. The results described above indicated that increase in contact angles within the first temperature range was mainly caused by a reduction in polar component of the surface free energy; however, the hydrophobicity recovery within the third temperature range resulted in a reduction in dispersive component.

By comparing the polar and dispersive components of surface free energy as a function of temperature, the samples being heated in air for 2 h (Fig. 8) and 15 h (Fig. 7), it was found that longer time was required for polar component of the samples with deeper oxidation region to decrease to zero. For example, it took 15 h for γ_S^P of P4MS-ox2 and P4MS-ox3 to decrease to zero when the sample was heated in air within the range of 80–100 °C. However, it only required 2 h for γ_S^P of P4MS-ox1 to decrease to zero at 80 °C. At the same time, Fig. 8b shows that γ_S^D of P4MS-ox1 decreased to 36 mN/m within 2 h when the sample was heated at 110 °C. However, longer time was necessary for γ_S^D of P4MS-ox2 and P4MS-ox3 to decrease to this value.

The bulk T_g of the oxidized P4MS increased from 110 to 220 °C with the increase of its oxidation extent measured by DSC, which was attributed to the incorporation of hydrogen-bonding groups into the polymer [15]. Theoretical arguments have been made that polymeric molecules on a glassy polymer

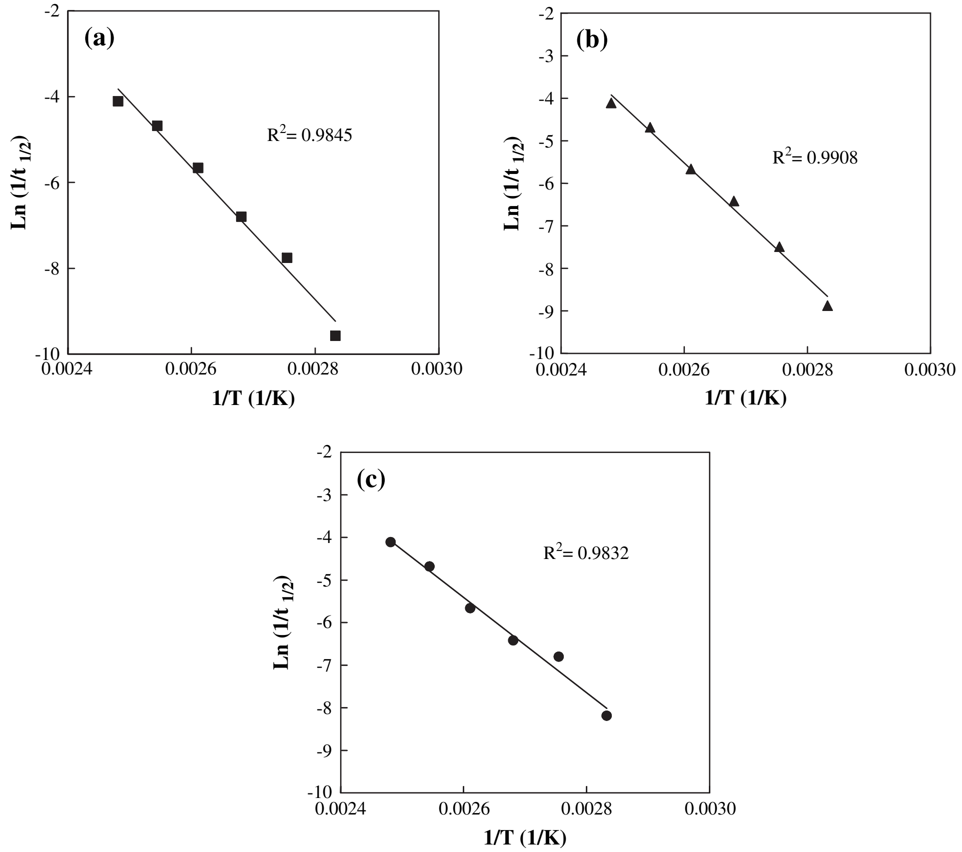


Fig. 5. Arrhenius plot of $1/t_{1/2}$ vs. $1/T$ for P4MS-ox3 (a), P4MS-ox2 (b) and P4MS-ox1 (c) films. The solid line is a linear least-squares fit to the data with a slope indicating an activation energy of 30.1, 26.4 and 21.8 kcal/mol, respectively.

surface should have higher mobility relative to those in the bulk. This increase of surface mobility has been attributed either to an increase in free volume caused by the enrichment of chain ends at the surface [19,20] or to a reduction in entanglement density at the surface [21,22]. Experimental evidence that the molecules on the surface of a glassy polymer are more mobile than the ones in the bulk has been provided by scanning force/lateral force microscopic examination [19,23]. When the surface-oxidized P4MS was exposed to air, polar side groups turned into the bulk, leaving a relatively nonpolar backbone projecting out of the surface to form a ‘‘hydrophobic conformation’’ (see in Scheme 3). Since the rearrangement of the side groups by the main chain bond rotation is much easier than the diffusion of the main chain, this step will be completed up to 80 °C. As a consequence, the polar component of surface free energy decreases to zero. Since the backbone of oxidized P4MS molecules has higher surface free energy due to carbonyl groups relative to an unmodified one, the migration of P4MS molecular chains to the surface is necessary (as shown in Scheme 3) in order to minimize the interfacial energy between surface-oxidized P4MS film and air. To our knowledge, the diffusion of a molecular chain should happen above the glass-transition temperature (T_g). Therefore, the dispersive component of surface free energy of surface-oxidized P4MS decreased to one of unoxidized P4MS only when the temperature was above T_g of P4MS. Below T_g, a segment of P4MS could not diffuse resulting in contact angle of the samples remaining unchanged in the 80–100 °C range.

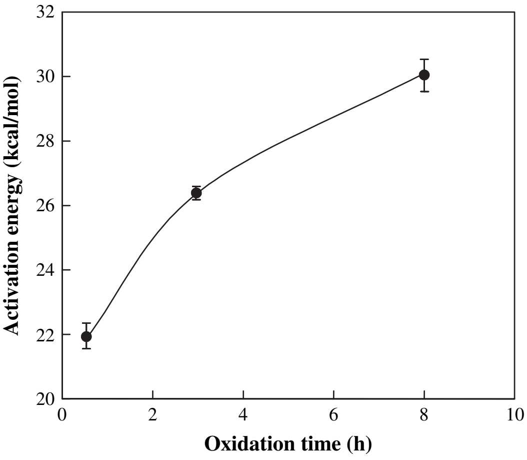


Fig. 6. The relationships between apparent activation energy of surface reconstruction and surface-oxidized time of the P4MS films.

Increased oxidation of P4MS or deeper functionalized interfacial region on surface-oxidized P4MS film resulted in decreasing the mobility of chains due to the strong interaction between the polar groups. Therefore, it is more difficult for polar groups to reconstruct with increasing number.

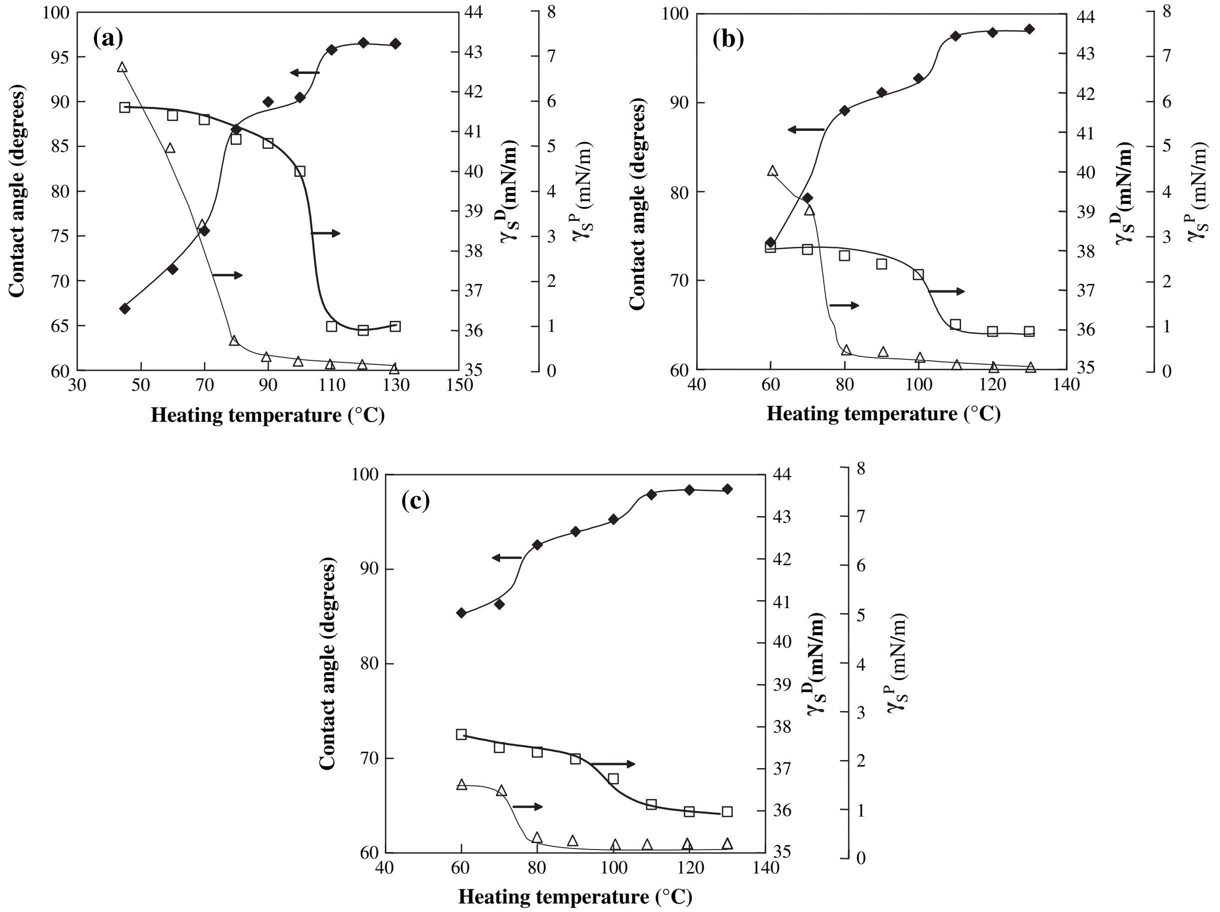


Fig. 7. Contact angles (◆) and the dispersive (γ_S^D, □) and polar (γ_S^P, △) components of the surface free energy of P4MS-ox3 (a), P4MS-ox2 (b) and P4MS-ox1 (c) heated in air for 15 h.

Simultaneously, as the depth of oxidized poly(4-methylstyrene) molecules in θ-interphase region increases, it requires unoxidized poly(4-methylstyrene) molecules to migrate longer distances to the surface of surface-oxidized P4MS samples. On the other hand, the mobility of P4MS molecules in "near surface" region is much lower than those in θ-interphase region. This was the reason why the sample with lower depth of functionalized region had higher reconstruction rate and could reach complete hydrophobicity recovery easily. In addition, although P4MS-ox3 has higher oxidation degree than P4MS-ox2, the difference between the two samples is that P4MS-ox3 undergoes a small amount of oxidation in the near surface

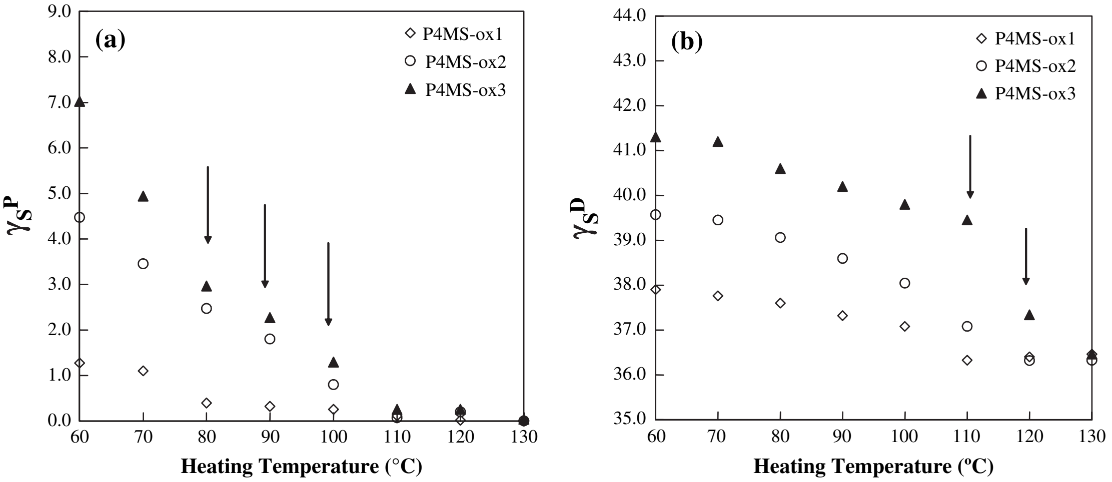
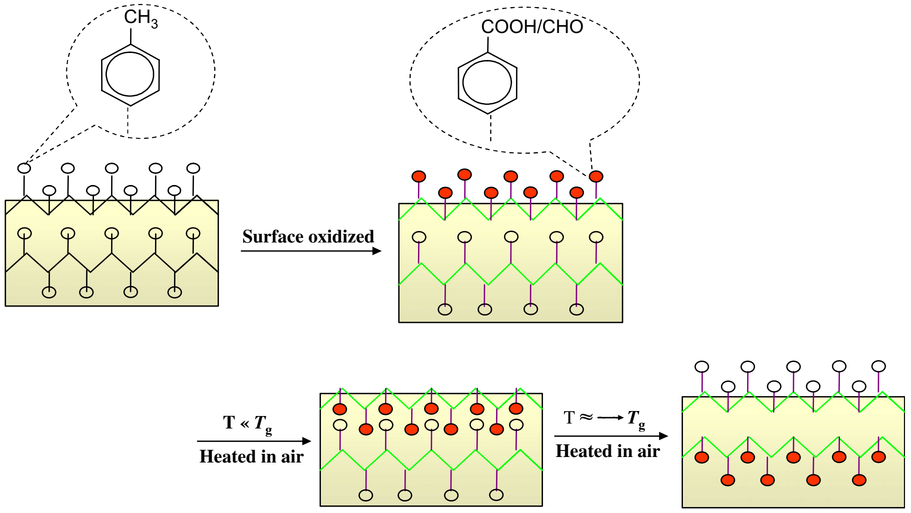


Fig. 8. The polar component (a) and dispersive component (b) of surface free energy vary with heating temperature. Heating time: 2 h.



Scheme 3. Schematic representation of the surface reconstruction of surface-oxidized P4MS, below and above its bulk glass-transition temperature (T_g).

region, resulting in similar RD values of P4MS-ox2 and P4MS-ox3 after heating in air for 2 h (shown in Fig. 4).

4. Conclusions

In this paper, the degree of surface reconstruction (RD) and the rate of surface reconstruction were employed to describe polymer surface reconstruction behavior. The degree of surface reconstruction was defined as $(\theta_t - \theta_0)/(\theta_c - \theta_0) \times 100\%$, in which θ_0, θ_t and θ_c were initial contact angles, contact angles for the sample heated in air for t minutes and one at complete reconstruction, respectively. The reconstruction rate was expressed as $1/t_{1/2}$, in which $t_{1/2}$ is the time for RD to reach 50%. The results showed that the relationship between $1/t_{1/2}$ and $1/T$ could be described by an Arrhenius equation for various samples. The surface reconstruction of the surface-oxidized samples became harder and apparent activation energy (E_R) of reconstruction increased as the depth of the functionalized region of oxidized poly(4-methylstyrene) increased.

According to variations of water contact angles and the surface free energy of the samples with temperature, the surface reconstruction of surface-oxidized P4MS samples occurs in two steps. The first step takes place below 80 °C, in which polar side groups turn into the bulk, leaving a relatively nonpolar backbone projecting out of the surface to form a ‘‘hydrophobic conformation’’. The second step occurs above the T_g (110 °C) of P4MS, in which P4MS molecular chains migrate to the surface in order to minimize the interfacial free energy between surface-oxidized P4MS film and air since the backbone of oxidized P4MS molecules containing carbonyl groups has a higher surface free energy relative to unmodified P4MS molecules. When the depth of the functionalized interfacial region of surface-oxidized poly(4-methylstyrene) film increased, a longer time was required for polar groups to turn over (the first step) and for unoxidized P4MS molecules to migrate to the surface (the second step) resulting in samples with a deeper functionalized region having lower reconstruction rates and RD under the same treatment.

Acknowledgments

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