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Frustrated Reconstruction at the Surface of a Glassy Polymer

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ABSTRACT: The introduction of hydrophilic functional groups at the surface of poly(4-methylstyrene) provided a system for studying the thermal reconstruction of the surface of a glassy polymer at temperatures below, at, and above the glass transition temperature (T_g). Partial or "frustrated" reconstruction was observed at temperatures below the T_g of the polymer, and complete reconstruction occurred above it. The frustrated reconstruction indicates that although collective motion of segments entangled in the bulk is governed by the T_g, those segments at the surface are rubbery well below this temperature. In fact, analysis of the initial kinetics of reconstruction as a function of temperature revealed no discontinuity in the activation energy for diffusion at or near the T_g.

Introduction

Organic surface chemistry provides the means for examining the influence of chemical structure at a surface on important interfacial properties.[1,2] We have used these methods to explore the connection between the architecture of a polymer and the composition and dynamics at its surface. For example, we recently reported evidence for the influence of cross-linking on the equilibration of a chemically modified polymer surface against water.[3] Those studies indicated that an elastomer could display surface behavior characteristic of its rubber elasticity. In this paper, we extend our studies to examine the influence of glass-transition temperature of a polymer on the mobility of its surface. At the outset of this work, we identified two specific questions of interest: (1) whether the bulk T_g is a meaningful parameter for describing the mobility of segments at the surface; (2) how entanglements of chains within the bulk of a glassy polymer would restrict the mobility of segments of those chains that reside at the surface. Both of these issues have been the focus of recent theoretical and experimental study by others.[4−20] Theoretical arguments have been made that the surface of a glassy polymer should have an increased amount of molecular mobility, relative to the bulk. This increase in surface motion has been attributed either to an increase in free volume caused by the enrichment of chain ends at the surface[5,9,21] or to a reduction in entanglement density at the surface.[4]

Experimental evidence that the surface of a glassy polymer may be more mobile than the bulk includes the following: atomic-force microscopic,[7] scanning force/lateral force microscopic,[8,9] slow-positron-annihilation spectroscopic,[10,11] ellipsometry,[12,13] Brillouin light scattering,[13,14] and dewetting (or contraction)/X-ray reflectometry[15] studies of polystyrene; X-ray photoelectron spectroscopic studies of poly(styrene-*block*-methyl methacrylate);[16] and grazing-incidence X-ray scattering from a polyimide.[17] While these studies have demonstrated, to one degree or another, the higher mobility of chain segments at or near surfaces, the goal of identifying a unique "surface T_g" has proven problematic, not only experimentally but also conceptually. The central difficulty is in clearly defining the depth into the polymer that distinguishes the surface from the bulk, and the likelihood that any differences between the two regions would change gradually, not abruptly. An added experimental concern is whether the surface properties of a polymeric thin film are different, due for instance to the influence of the underlying substrate,[11−15,17,18] from the surface of a macroscopically thick film.

We have used changes in wetting behavior to evaluate the mobility of chains at or near the chemically modified surface of a glassy polymer. Our choice to monitor wettability by water was motivated, in part, by its extreme surface selectivity—only the outermost 5−10 Å influences wettability[22]—as well as its sensitivity to changes in composition within this "θ-interphase." Our approach is similar to that used previously by us[3,22,23] and by others[24−26] to examine the reconstruction of the surfaces of various polymers:[27] we chemically modified the surface of a hydrophobic polymer to produce hydrophilic functionality. Such surfaces typically reconstruct, via conformational changes of segments and/or diffusion of chains, to produce configurations having lower interfacial free energy.[3,23−27] The kinetics of reconstruction depend on temperature and, presumably also, the glass-transition temperature of the polymer. In the particular case of glassy polymers having a molecular weight above the critical entanglement length (for polystyrene, M_e = 18 000),[28] chains with segments at the surface will also be entangled with those beneath the surface and presumably governed by the bulk T_g. As a result, we expected that the decrease in nearest-neighbor interactions for surface segments, relative to those in the bulk, would allow partial or "frustrated" reconstruction at temperatures below the bulk T_g. Full reconstruction—necessary to reach a *thermodynamic* minimum in free energy—should be possible only above the bulk T_g because any long-range, cooperative movement necessary to remove all hydrophilic functionalities from the surface would be restricted by the remainder of the segments embedded within the glassy interior of the polymer (Scheme 1). Furthermore, unmodified chains should be unable to migrate to the surface at temperatures below the T_g, hence removing another mechanism for reconstruction in this temperature regime.

Our choice of poly(4-methylstyrene) [P4MS] as a model glassy polymer was convenient because oxidation of the *p*-methyl groups near the surface to carboxylic acid and other hydrophilic groups provided a surface whose reconstruction was easily monitored by wetta-

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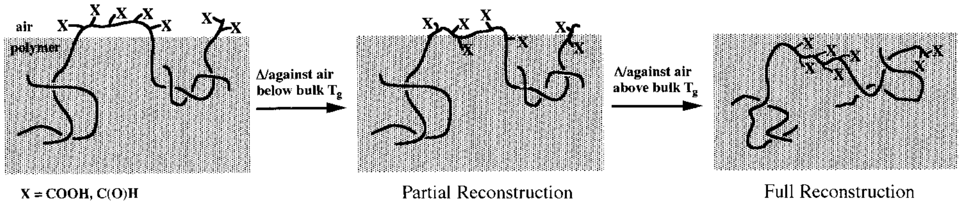
Scheme 1. Schematic Representation of the Surface Reconstruction of a Chemically Modified Glassy Polymer, below and above Its Bulk Glass-transition Temperature (T_g)



bility measurements.[29,30] In addition, the T_g of P4MS is 110 °C, which allowed the convenient measurement of the kinetics of reconstruction both above and below the T_g. We expected that any unique "surface T_g" would be manifested as a discontinuity in the activation energy for reconstruction.

Experimental Section

General Methods. Chloroform (HPLC grade) and acetic acid (glacial, HPLC grade) were purchased from Fisher and used as received. Cobalt(II) acetate tetrahydrate (98%) was purchased from Avocado and used as received. Sodium bromide (99%) and heptane (99%, anhydrous) were used as received from Aldrich. Deionized water with a resistivity of 15−17 MΩ cm was obtained from a Milli-Q-Filtering system (Millipore). Ethanol (190 proof) was purchased from Pharmco and used as received. Ozone was generated using a Welsbach T-23 laboratory ozonator (Welsbach Corp.).

Advancing contact angles were recorded under ambient conditions using a Ramé-Hart Model 100-00 contact angle goniometer. All reported measurements are an average of at least eight different measurements taken within 10−20 s of application of the drop. Differential scanning calorimetry (DSC) was performed using a DSC 2920 (TA Instruments) with a 10 °C/min ramp in temperature. Weight-average molecular weight (M_w) and polydispersity index (PDI) were obtained by gel-permeation chromatography (GPC, Waters) with polystyrene standards. ^{1}H NMR spectra were obtained on a Bruker AMX 360 instrument, and chemical shifts were referenced to the residual proton peak of the solvent. Acetone-d_6 and chloroform-d_3, used as solvents in the NMR experiments as noted, were purchased from Cambridge Isotope Laboratories and used as received. Infrared spectra were collected on a Mattson Polaris FT-112 spectrometer.

Sample Preparation. Poly(4-methylstyrene) ($M_w = 76\,000$, $T_g = 110$ °C, Aldrich), polystyrene ($M_w \geq 1\,000\,000$, $T_g = 107$ °C, Dow), and poly(*p-tert*-butylstyrene) ($M_w = 300\,000$, $T_g = 132$ °C, Scientific Polymer) were purified prior to use by dissolving 2.5 g of the polymer in 40 mL of chloroform and precipitating it from the resulting solution by addition to 400 mL of ethanol at 0 °C. The precipitated polymer was recovered by suction filtration. This process was repeated, and the final precipitate dried in dynamic vacuum at 60 °C (~24 h). Sample films were prepared by pressing the polymer between aluminum plates, using a cardboard spacer to contain the polymer melt, at 145 °C and 2000 psi for 15 min. This procedure was repeated twice more with additional polymer added after the first and second pressings, which resulted in a transparent film ~2 mm in thickness. The film was then removed from the press and annealed at 150 °C in air for 45 min to remove any residual stress and to produce a uniform surface. The side in contact with air during annealing was used for experiments.

Surface Oxidation of Poly(4-methylstyrene). An ozone/oxygen stream was bubbled at a rate of 1.2 L/min through 50 mL of a solution of cobalt(II) acetate (0.1 M) in 1:1 (v/v) acetic acid/water at room temperature for 20 min. Upon reaction of the cobalt species with ozone, the color of the solution changed from light pink to dark green (within the first minute), indicating the conversion of Co(II) to Co(III).[31] Samples of the P4MS film were floated against this solution at 62 °C for a total of 75 min, with rinsing after the first minute, 5 min, and then every 10 min thereafter with ~0.4 M acetic acid to remove any deposited cobalt precipitate(s). After oxidation, samples were floated against deionized water at 55 °C for 24 h to remove any absorbed acetic acid, judged by the disappearance of a carbonyl stretching band at 1714 cm^{-1} in the infrared spectrum of the product in a control experiment. The samples were then allowed to equilibrate at room temperature for ~24 h. All samples had an advancing contact angle of water (pH 1) of 57 ± 2° after this procedure.

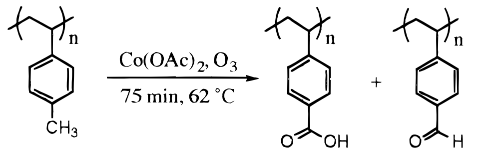
Homogeneous Oxidation of Poly(4-methylstyrene). Poly(4-methylstyrene) (0.25 g) was dissolved in a stirred solution of heptane (35 mL), acetic acid (30 mL), cobalt(II) acetate (0.155 g, 6.2 mmol), and sodium bromide (0.064 g, 6.2 mmol). Oxygen was bubbled at a rate of ~0.5 L/min through this solution at 68 °C for either 2 (partial oxidation) or 9 h (extensive oxidation). The polymer was precipitated by addition to 40 mL of cold methanol (0 °C), and the precipitate was recovered by suction filtration. To remove any residual cobalt salts, evidenced by the loss of color (light orange to off-white), 0.1 g of the dried precipitate was dissolved in 20 mL of 50% (v/v) heptane/acetic acid and reprecipitated by addition to 40 mL of 30% (v/v) ethanol/water. The polymeric product was collected by suction filtration and the process repeated. The final product was then dried in a vacuum (~24 h).

X-ray Photoelectron Spectroscopy (XPS). X-ray photoelectron spectroscopy was performed using a Scienta ESCA300 (Uppsala, Sweden) with monochromatic Al−Kα X-rays and at a working pressure of 10^{-8}−10^{-9} mbar. Survey spectra were collected with a pass energy of 300 eV (0.5 eV steps), and high-resolution spectra were collected with a pass energy of 150 eV (0.05 eV steps), at a takeoff angle between the surface of the sample and the detector of either 6 or 90°. Under our experimental conditions, peak resolution was limited by the inherent sample line width and not by instrumental factors. All spectra were referenced to the main C 1s peak, set at 285.0 eV.

Samples were mounted on a stainless steel stub by pressing both ends of the sample against double-sided sticky tape. A Scienta flood gun was used to compensate for sample charging, by exposing the sample to low-energy electrons (~3 to ~9 eV). An optimal C 1s line shape was obtained by adjusting the flood gun to yield the minimum value for the full width at half-maximum (typically 0.9−1.2 eV). Using the Scienta ESCA300 system software[32] and a published procedure,[33] curve fitting was performed by describing each peak as a series of Gaussian and Lorentzian functions, assuming a linear baseline. All fits had reasonable mixing ($m \geq 0.80$) and asymmetry ($A \leq 0.16$) ratios, as well as acceptable line widths (1.1−1.5 eV, fwhm, C 1s region). High-resolution spectra of the unoxidized polystyrene and poly(4-methylstyrene) surfaces were compared to those published by Beamson and Briggs to ensure proper line shape and position.[33] The following sensitivity factors were used for quantitative analysis: O 1s, 2.8370; C 1s, 1.00; Si 2p$_{1/2}$, 0.955.[34]

Results and Discussion

The surface of P4MS was oxidized using a modified version of procedures reported for the oxidation of substituted toluenes[31,35] and the bulk oxidation of P4MS (eq 1).[36,37] To avoid dissolution, minimize swelling, and thereby maximize selectivity for reaction at the polymer surface, we used a 1:1 (v/v) mixture of acetic acid and water as the solvent in these oxidations. Use of glacial



(1)

acetic acid has been reported to swell poly(4-methylstyrene).[36] With sufficient rinsing, a cobalt-free (vide infra), hydrophilic surface was obtained, with a limiting advancing contact angle of water (pH 1) of 57°. The strong dependence of this angle on the pH of the contacting drop (θ_a = 32° at pH 13) indicated the presence of ionizable carboxylic acids at the polymer surface.[1] The advancing contact angle of water (pH 1) on unoxidized P4MS was 91°.

An X-ray photoelectron (XPS) spectrum of the oxidized P4MS film showed a pronounced increase in oxygen photoemission, relative to the unoxidized film (Figure 1). No photoemission due to cobalt was observed, though there was a small amount of silicon (103.3 and 150.3 eV, 1.6 at. %), and trace amounts (~0.1 at. %) of zirconium (184.6 eV),[38] chlorine (200.6 eV), and organic nitrogen (400.3 eV) indicated in the survey scan. A high-resolution spectrum (90° takeoff angle) of the carbon 1s region (Figure 1, inset) contained a peak at 289.4 eV and a shoulder at 287.4 eV, due to oxidized carbon, in addition to the peak for unoxidized carbon at 285.0 eV and shake-up satellite at 291.6 eV. The peak at 289.4 eV is characteristic of carboxylic acid carbons, and the shoulder at 287.4 eV is assigned to aldehyde carbons.

As a starting point for fitting this spectrum, we used optimized parameters for the main peak (285.0 eV) and the shake-up satellite taken from a separate fit of a spectrum of unoxidized P4MS. To these parameters, we added peaks at 287.4 and 289.4 eV and fit the entire spectrum using the following constraints: the full widths at half-maximum (fwhm) of the peaks at 287.4 and 289.4 eV were linked to the main C 1s peak, and the asymmetry factor (A) was fixed at zero for all peaks except the main C 1s peak (A = 0.15). After the initial fitting had converged, all constraints were relaxed and the fit refined. The result indicated an ~1.6:1.0 ratio of acid to aldehyde, with the sum of these intensities representing ~5.4% of the total photoemission in this region. This fraction suggests oxidation of the methyl group in ~49% of the repeat units in that portion of the polymer giving measurable photoemission under our experimental conditions (top ~11–12 nm).[39] This calculation of yield assumes that the peak centered at 285.0 eV contains all of the unoxidized carbon atoms, including the *ipso* aromatic carbon in the oxidized repeat units, an assignment consistent with those published for poly(diallyl phthalate) and poly(ethylene terephthalate).[33] A high-resolution spectrum of the oxygen 1s region (not shown) contained one broad envelope with a full width at half-maximum of 2.7 eV, consistent with the presence of at least two types of oxygen. The O: C ratio calculated from a survey spectrum collected at a 6° takeoff angle (top ~1 nm)[39] was 0.11, the same as that from the survey spectrum at 90° angle and indicating approximately homogeneous oxidation within the top ~11–12 nm of the polymer film.[40] The ratio of oxygen to *oxidized* carbon from the high-resolution spectrum (90° takeoff) was 1.2, consistent with a mixture of acids and aldehydes.

Samples of surface-oxidized P4MS were heated against air at various temperatures below, at, and above the T_g of the polymer (110 °C), and their contact angles of water (pH 1) were then measured (Figure 2). Fast, complete reconstruction, to produce a surface whose wettability was the same as that of the unmodified polymer, was only observed for temperatures at or above the T_g. Below 110 °C, the rate of reconstruction varied dramatically with temperature, but the samples heated at 55–95 °C appeared to reach a limiting *extent* of reconstruction corresponding to a contact angle of water of about 80–84° over a period of 12 d. Even after 36 d, the contact angles on samples heated at 55 and 95 °C were still only 86 and 87°, respectively. This partial reconstruction is consistent with our hypothesis that entanglement with chains on the interior of the polymer prevent the complete reconstruction of those with segments at the surface at temperatures below the bulk T_g (Scheme 1).

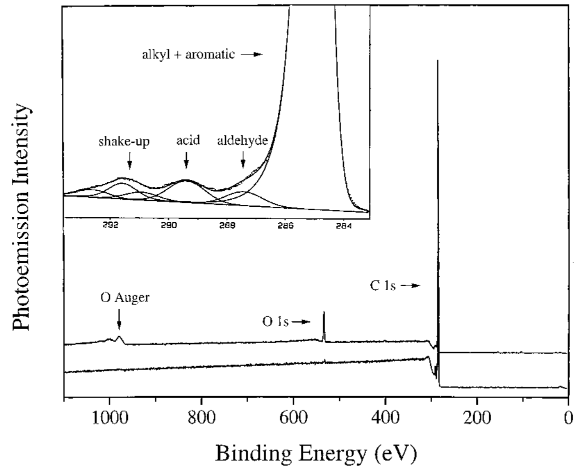


Figure 1. Survey XPS spectra of poly(4-methylstyrene) film (lower) and oxidized poly(4-methylstyrene) film (upper) collected at a 90° take off-angle. Binding energies were referenced to the main C 1s peak at 285.0 eV. In addition to the expected photoemission due to carbon and oxygen, a small amount of silicon (103.3 and 150.8 eV, 1.6 at. %) and trace amounts (~0.1%) of organic nitrogen (400.3 eV), zirconium (184.6 eV), and chlorine (200.6 eV) contaminants were observed. A high-resolution spectrum of the C 1s region (inset) contained a peak at 289.4 eV, characteristic of carboxylic acids, and a shoulder at 287.4 eV, characteristic of aldehydes. The feature at 291.6 eV is a $\pi \rightarrow \pi^*$ shake-up peak.

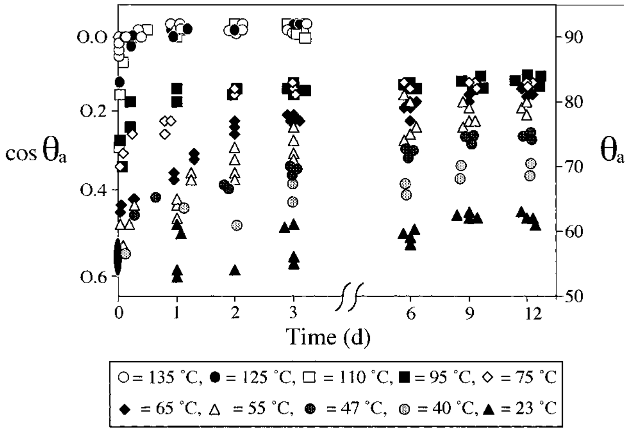


Figure 2. Advancing contact angle of water (pH 1) on oxidized poly(4-methylstyrene) film as a function of the time heated against air, for various temperatures. The filled oval at t = 0 indicates the range of starting contact angles on the samples used in these studies. The largest range in measurements for any sample was ± 3°.

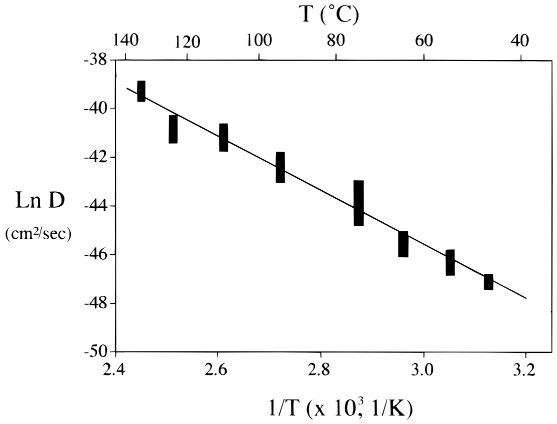


Figure 3. Arrhenius plot of diffusion constant (calculated using eq 3) corresponding to half-reconstruction vs 1/T. The height of the symbols represents the estimated uncertainty in the measurements and corresponds to the range of time ($t_{1/2}$) necessary for the sample to reach a contact angle of 74 ± 2° (i.e., 72 and 76°). The solid line is a linear least-squares fit to the data with a slope indicating an activation energy of 22 kcal/mol.

We have analyzed these kinetic data assuming that the reconstruction involves thermally activated diffusion of oxidized segments away from the polymer/air interface and that the kinetics are describable by an Arrhenius relationship (eq 2).[25] While the process is clearly

$$D = A_{D} \exp(-E_{a,D}/RT) \tag{2}$$

more complex than assumed, this approach has proven useful in extracting meaningful activation parameters in the reconstruction of surface-modified polyethylene.[41] Evaluation of this equation, assuming that segments more than 5 Å beneath the surface of the polymer do not influence wettability,[22] yields eq 3, where $t_{1/2}$

$$D = 2.725 \times 10^{-15}\ \mathrm{cm}^2/t_{1/2} \tag{3}$$

represents the time required for the surface to reconstruct halfway. Since the starting contact angle on these samples was 57° and increased to 91° upon complete reconstruction (only actually reached for temperatures above the T_g), the value of the $t_{1/2}$ in this system corresponds to the time required to reach a contact angle of 74° at a particular temperature. Only the samples aged at 25 °C did not reach this level of reconstruction over the time observed. Figure 3 shows an Arrhenius plot for the reconstruction of the samples at temperatures in the range from 47 to 135 °C. The data in Figure 3 were fit by a straight line with a slope indicating an activation energy for diffusion ($E_{a,D}$) of 22 kcal/mol. The linearity of the data *over the entire range of temperatures investigated* is striking, and the absence of a discontinuity in the plot indicates no change in activation energy associated with a glass-transition temperature. Since this range spans temperatures from well above to far below the T_g of the polymer, we conclude that the mobility of chains near the surface relevant to our wettability measurements are influenced neither by the bulk T_g nor by any "surface T_g" within this range.

This activation energy corresponds to the initial regime of reconstruction and is common to the samples at all temperatures represented. We attribute it primarily to the chain segments actually at the interface, which have greater flexibility than those in the bulk due to their reduced number of van der Waals contacts with other chains. Consistent with this conclusion, the observed activation energy is much lower than that reported for the self-diffusion of polystyrene (M_w = 43 700) in the melt (40 kcal/mol, 170−190 °C).[42] The lower activation energy in our reconstruction studies may also reflect the small scale of length (5−10 Å) relevant to measurements of wettability.[22] Thus, local mobility and conformational changes that do not require diffusion of entire chains could have a dramatic effect on these measurements. In control experiments, we have also addressed two alternative explanations for the high level of mobility at the surface of this glassy polymer: (i) although unlikely, it is possible that oxidation of the methyl groups of P4MS gives a polymer with a lower T_g and thus more flexibility than P4MS itself; (ii) oxidation at the benzylic position in the backbone of the polymer could lead to chain cleavage and increased mobility due to a decrease in molecular weight and a corresponding increase in the number of chain ends at the surface.

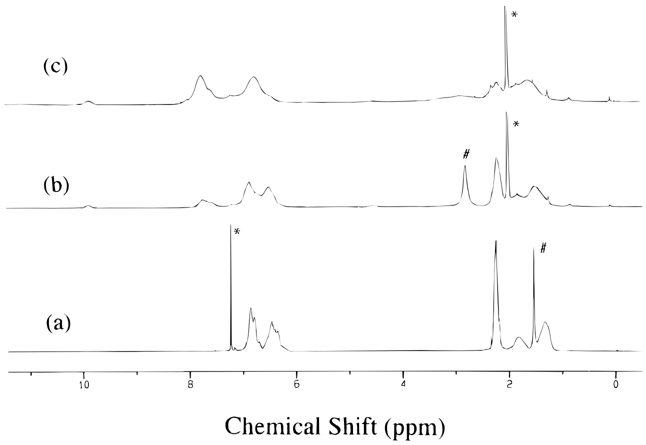
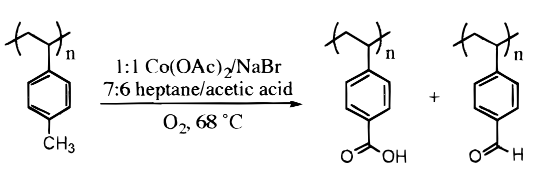


Figure 4. ^{1}H NMR of (a) P4MS (chloroform-d_3), (b) P4MS oxidized to 33% conversion of repeat units (acetone-d_6), and (c) P4MS oxidized to 93% conversion (acetone-d_6). The peaks labeled with an asterisk (*) are due to residual protons of the solvent, and those labeled with a pound sign (#) are due to water.



(4)

To assess the effect of oxidation of P4MS on its T_g, we prepared macroscopic amounts of oxidized P4MS following a procedure similar to the one used in the surface modifications (eq 4).[36,37] One sample, oxidized to 33% conversion, contained an ~2.7:1.0 ratio of the corresponding acid to aldehyde, as determined by ^{1}H NMR (Figure 4b, acetone-d_6).[43] A spectrum of the unmodified polymer (in chloroform-d_6) is provided in Figure 4a for comparison. Gel permeation chromatography (GPC) indicated a reduction in weight-average molecular weight (M_w) from 76 000 to ~20 000, with a polydispersity of 1.67. Despite the decrease in molecular weight, the T_g of this sample increased from 110 to 144 °C upon oxidation (Figure 5c). A second sample, oxidized to 93% conversion, contained a higher ratio of acid to aldehyde (~5.1:1.0), determined by ^{1}H NMR (Figure 4c, acetone-d_6). In this case, analysis by GPC indicated even

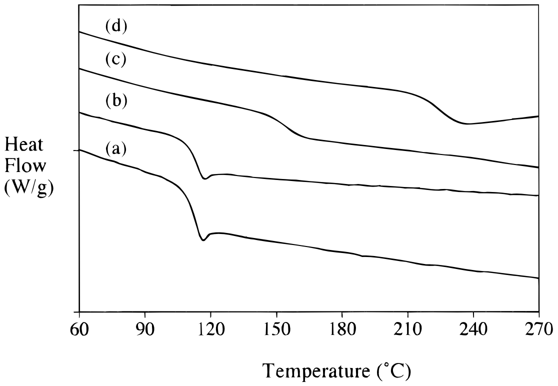


Figure 5. Differential scanning calorimetry scans of (a) unmodified P4MS film, (b) *surface*-oxidized P4MS film, (c) P4MS oxidized to 33% conversion of repeat units, and (d) P4MS oxidized to 93% conversion. The scan rate was 10 °C/min.

more extensive degradation, to a M_w of only 6000 and a polydispersity of 2.09. Nonetheless, the T_g of this sample increased to 222 °C (Figure 5d). Infrared spectra of both the 33%-converted and 93%-converted products showed carbonyl absorptions at 1700 and 1723 cm^{-1} and a broad hydroxyl stretch at 2500−3600 cm^{-1}. We attribute the increase in T_g upon oxidation, even as molecular weight was reduced, to the incorporation of hydrogen-bonding groups into the polymer. This trend is consistent, for example, with the increase in T_g accompanying the conversion of polymethylacrylate (T_g = 10 °C) to poly(acrylic acid) (T_g = 106 °C).[44] Comparison of a *surface*-oxidized sample to the starting material showed no appreciable change in T_g, as expected (Figure 5a,b).

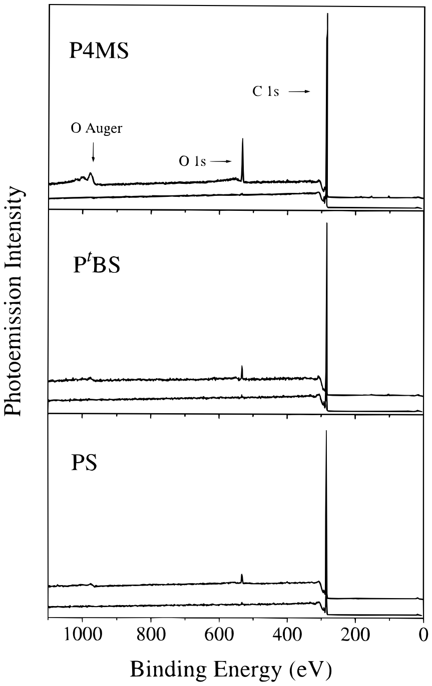


Figure 6. Survey XPS spectra of both untreated and surfaced-oxidized P4MS (top), P^{t}BS (middle), and PS (bottom). Spectra were taken at a takeoff angle of 90°.

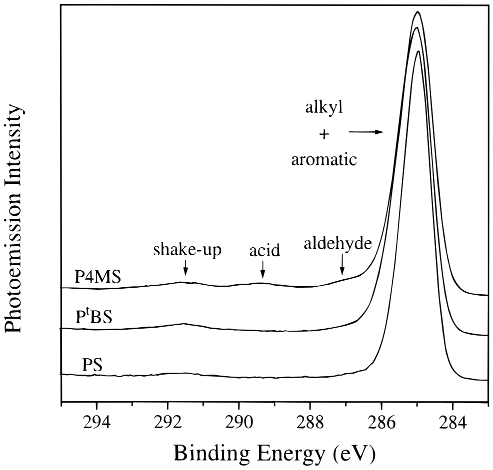


Figure 7. High-resolution XPS spectra in the carbon 1s region of PS, P^{t}BS and P4MS that had been treated with the ozone/cobalt solution. These spectra were collected at a takeoff angle of 90°, and indicate the presence of oxidized carbon for P4MS, but not for the others.

Table 1. Advancing Contact Angles for Polymer Surfaces before and after Oxidation

polymer	pH	before oxidation	after oxidation
P4MS	1	91	57
	13	91	33
P^{t}BS	1	93	89
	13	91	89
PS	1	91	91
	13	91	91

To address the possibility that the reconstruction of P4MS below the T_g reflected increased surface conformational freedom due to chain-end enrichment resulting from oxidative cleavage of the polymer backbone, we examined the chemistry of the backbone under the conditions of our surface reactions. This experiment took on added significance, given the reduction in molecular weight that accompanied the related homogeneous oxidations. To prevent interference in our studies from oxidation away from the backbone, we chose two model polymers having only one oxidizable benzylic carbon, polystyrene (PS) and poly(*p*-*tert*-butylstyrene) (P^{t}BS). Analysis by XPS and contact angle measurements allowed convenient assessment of the amount of backbone oxidation at the surface of these polymers upon treatment with ozone in the presence of the cobalt catalyst. Figure 6 compares the XPS survey spectra (90° takeoff angle) before and after oxidation of PS, P^{t}BS, and P4MS. Although all of the treated surfaces contained oxygen, some of the oxygen could be accounted for by the presence of a small amount of a silicon (as silicate or silica) impurity on the surface. For polystyrene, most of the oxygen could be accounted for in this way, as the ratio of silicon to oxygen was approximately 1:3. After accounting for this source of excess photoemission, we found that the oxidized P4MS contained five times the amount of oxygen found on the oxidized P^{t}BS. High-resolution spectra (90° takeoff angle) in the carbon 1s region confirmed the presence of oxidized carbon for the surface-treated P4MS, but not the other two polymers (Figure 7). In fact, no oxidized carbon was even found in a high-resolution spectrum of “oxidized” P^{t}BS at a very shallow takeoff angle (6°). Consistent with these results, the surface of P4MS became much more hydrophilic upon treatment with the oxidizing solution, whereas those of the other polymers did not. The advancing contact angles of water are summarized in Table 1, for both pH 1 and pH 13. The large difference between the two pHs for P4MS reflects the presence of carboxylic acid groups that are ionized and thus more hydrophilic at high pH. The difference in reactivity among these polymers, evident in the XPS and wettability data, indicate that chain cleavage is much less important than oxidation of the methyl groups in changing the hydrophilicity of P4MS, and, more important, probably is not solely responsible for the mobility of this surface below the T_g of the bulk polymer.

Conclusions

We have examined the reconstruction of a surface-modified glassy polymer above and below its T_g. As expected, complete reconstruction at and above the T_g was observed, though only partial reconstruction occurred at temperatures below the T_g. This partial or "frustrated" reconstruction reflects the covalent attachment of surface segments to chains that are entangled within the interior of the polymer. Only above the T_g can cooperative movement occur, leading to complete reconstruction. The bulk T_g therefore is not a meaningful parameter for describing short-range mobility of surface segments.

Analysis of the kinetics of initial reconstruction below, at, and above the T_g showed no discontinuity in the activation energy for diffusion, which would be an expected consequence of a "surface $T_{g.}$" The observed activation energy of diffusion ($E_{a,D}$) of 22 kcal/mol is much lower than the self-diffusion of polystyrene in the melt, reflecting the greater mobility of surface segments relative to the bulk, as well as the small scale of length relevant to wettability measurements. Control experiments confirmed that the oxidation of P4MS should not lower the T_g of the polymer and that oxidation of the backbone that could produce a lower molecular weight polymer at the surface was probably minimal under the experimental conditions used in the surface modifications.

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