Investigations on Surface-Modified Bulk Polymers. 1. Copolymers of Styrene with a Styrene Moiety Containing a Sugar Monomer

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ABSTRACT: Copolymers containing vinyl sugar units were synthesized by copolymerizing 2,3;4,5-di-*O*-isopropylidene-1-(4-vinylphenyl)-D-gluco(D-manno)pentitol (**1**) with styrene. Films and plates of the copolymers and blends were prepared by casting solutions on glass plates or by hot-pressing. Isopropylidene groups, the hydrophobic protecting groups of the sugars (**1**), were hydrolyzed only in the sample surface layers by treating the films and plates with aqueous acid. The surfaces showed hydrophilic properties afterward and were studied by water contact angle measurement. The accumulation and reorientation of the hydrophilic sugar segments at the surface was demonstrated by a decrease of the receding contact angle and found to depend on the copolymer composition and on sample preparation. The surface compositions of the solution-cast copolymer films were investigated by means of X-ray photoelectron spectroscopy (XPS). The results clearly showed that the isopropylidene groups at the surfaces were removed and the percentage of the sugar carbon at the surfaces accordingly increased. Angle-dependent XPS measurements indicated that the hydrolysis took place evenly to a depth of 10 nm. The surface conductivity of the copolymer plates increased by several orders of magnitude owing to adsorption of water on the hydrolyzed, hydrophilic surfaces under defined air humidities.

Introduction

Considerable interest has been drawn to hydrophobic−hydrophilic properties of polymer surfaces, since they are essential in many applications such as for adhesion and in textiles, pharmaceuticals, composite materials, and biomaterials. In order to impart hydrophilic properties to the surface of hydrophobic polymers, a number of techniques for surface modification have been used, including plasma treatment,[1,2] surface grafting,[3] chemical modification,[4] surface-modifying additives,[5,6] ion-beam treatment,[7] and adsorption and polymerization of amphiphiles.[8] Surface modification also can be achieved by introducing hydrophilic segments into hydrophobic polymers during a copolymerization.[9,10] The advantage of surface modification by a copolymerization is that a copolymer with defined surface composition and structure may meet the requirement of specific applications. A variety of copolymers such as polyurethane-*g*-polyether, polyurethane-*b*-polysiloxane, polyurethane-*g*-polysiloxane, polyurethane-*g*-polyamine, poly(vinyl alcohol)-*g*-poly(dimethylsiloxane), poly(vinyl alcohol)-*g*-poly(tetrahydrofuran),[10−14] polystyrene-*b*-poly(methyl methacrylate), poly(ethylene oxide)-polystyrene−poly(ethylene oxide),[15] and poly(ethylene terephthalate)/perfluoropolyether,[16] and copolymers containing polystyrene, poly(4-octylstyrene), or polyisoprene as a hydrophobic segment and (2,3-dihydroxypropyl methacrylate) as a hydrophilic segment[9] have been investigated by several research groups. All these studies indicated that hydrophobic or hydrophilic segments may be enriched by environmentally induced rearrangement at polymer surfaces.

Recently, poly(vinyl saccharide)s attracted much attention because vinyl sugars can be easily copolymerized with various comonomers, and the resulting copolymers have a chemically stable C−C backbone and hydrophilic side chains. Klein et al.[17−19] studied the synthesis and solubility of poly(vinyl saccharide)s. Nakamae et al.[20,21] copolymerized 2-(glycosyloxy)ethyl methacrylate with methyl methacrylate or styrene and investigated the surface properties of cast films. In our laboratory, Wulff et al.[22,23] investigated the synthesis of C-glycosyl compounds containing polymerizable double bonds without protecting groups, for example, poly(vinyl saccharide)s with *N*,*N*-dimethylbarbituric acid as linker between the sugar and styrene. Other types of vinyl sugar monomers and polymers have been reviewed elsewhere.[24−27] Since poly(vinyl sugar)s constitute polymers of a new structural type, they may have high potentials in modifying the surface of conventional polymer materials and improve the antistatic property, dyeability, adhesion, printability, and biocompatibility of bulk polymers.

The generation of static electricity on polymeric materials causes many problems, both during processing and during practical application, for example, deficiencies of photographic materials, destruction or misfunction of electronic instruments, surface soiling of garments, the clinging of garments to each other and to the body, even dangerous situations such as shock, fire, and explosion hazards owing to high-energy discharge in air. Much effort has been made to improve the antistatic properties of polymers by surface treatment with antistatic agents,[28] dispersing conductive particles,[29] depositing a metallic coating onto the surface,[30] and blending with antistatic modifiers.[31,32] One of the easiest methods for antistatic modification of polymeric materials is to incorporate compounds, e.g., poly(ethylene oxide) (PEO) or its derivatives, which are known as host polymers for solid ionic conductors.[33] Poly(vinyl sugar)s may also be used as antistatic materials since the sugar segments are very hydrophilic.[34]

In our latest investigations, we tried to modify the surfaces of bulk polymers by adding 2,3;4,5-di-*O*-isopropylidene-1-(4-vinylphenyl)-D-gluco(D-manno)pentitol (**1**) during the polymerization of styrene. The copolymer carries hydrophobic acetal-protected hydroxyl

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groups on the sugar segments. After acid treatment of the surfaces, polar groups were generated only at the surface of the copolymers, but not in the bulk. Thus, any detrimental effect on the mechanical properties of the polymers would be avoided. The presence of hydroxyl groups at the surface increased its hydrophilicity and water could be easily adsorbed to the surface, which improved its antistatic ability. The copolymer surfaces were characterized by XPS, contact angle measurement, and surface resistance.

Experimental Section

Materials. The preparation of 2,3;4,5-di-*O*-isopropylidene-1-(4-vinylphenyl)-D-gluco(D-manno)pentitol (**1**) was carried out according to the methods described in the literature.[27] Styrene was purified by extraction with 10% sodium hydroxide solution and by distillation. Commercial polystyrene 143 E was supplied by BASF. Azobis(isobutyronitrile) (AIBN) from Fluka was recrystallized from ethanol. Benzoyl peroxide from Fluka was used as initiator for bulk polymerization. Toluene, tetrahydrofuran, and methanol were distilled before use.

Copolymerization of 1 with Styrene in Solution. Different ratios of sugar monomer **1** and styrene (see Table 1) were dissolved in toluene to give a solution containing 33 weight % of monomer. The added AIBN was calculated to an amount of 0.25 mol % referring to the monomer mixture. Oxygen was removed from the solution by freezing in liquid nitrogen, evacuating the flask, warming to room temperature and flushing the flask with nitrogen gas. The procedure was repeated three times. The mixture was copolymerized at 65 °C. Under strict oxygen-free conditions, 0.05 mL samples were taken from the mixture by a syringe and dropped into methanol every 20 min. As soon as polymer traces appeared, the polymerization was stopped by precipitating the mixture in methanol. Yields of about 5% were achieved. The copolymer was precipitated twice by adding the toluene solution to 10 times its volume of methanol. The polymer was dried in vacuum at 80 °C for 48 h. The compositions were characterized by 300 MHz ^{1}H NMR spectroscopy (Varian VXR300) and by elemental analyses (Perkin-Elmer CHNS 10, Analyzer 2400). Average molecular weights were measured by membrane osmometry with a Knauer osmometer.

^{1}H NMR (300 Hz, $CDCl_3$): δ 6.3−7.3 (br m, Ar), 3.65−4.7 (br m, sugar), 2.85 (br d, OH), 0.8−2.4 (br m, CH_2CH), 1.2−1.4 (br m, CH_3).

Copolymerization of 1 with Styrene in Bulk. Sugar monomer **1** in varying ratios (see Table 2) of the monomer mixture was dissolved in styrene together with benzoyl peroxide (0.25 mol % of monomer mixture). The solution was enclosed in a glass tube and kept at 65 °C for 8 h. The resulting copolymers were precipitated twice from toluene into methanol and dried at 80 °C in vacuum.

Determination of Detatched Sugar by Periodate Oxidation. The sensitivity of periodate toward free sugar was checked by addition of defined amounts of periodate to solutions of free arabinose with different concentrations in 50 mL of 1 N HCl. The mixtures were stirred for 48 h without light before the remaining periodate was determinated by iodometric titration.[35] The decrease of periodate was proportional to the dissolved amount of sugar. This method gave reliable results down to a limit of 2×10^{-4} mol of sugar in 50 mL of 1 N HCl.

To analyze the sugar being detached from the surfaces, 10 g of copolymer powders with different compositions were stirred in 50 mL of 1 N HCl with 2% THF at 70 °C for 4 h. The powder was removed from the liquid. Sodium periodate (1.3 g, 6×10^{-3} mol) was added to the aqueous mixture, and the solution was treated as described above. In no case was the amount free sugar found in the hydrolysis mixture more than 2×10^{-4} mol. The sugar being released by 10 g of copolymer during acid treatment obviously stayed under this limit. During hydrolysis, the majority of the sugar on the surfaces must have remained on it.

Table 1. Composition of Copolymers for the Determination of Reactivity Parameters

copolymer	monomer **1** (feed) (mol fraction)	monomer **1** (anal.) C %[a]	monomer **1** (anal.) mol fraction[b]
S1	0.01	91.09	0.01
S2	0.05	87.96	0.06
S3	0.16	82.66	0.17
S4	0.33	77.54	0.33
S5	0.50	74.03	0.49
S6	0.67	71.47	0.67
S7	0.84	68.48	0.96

[a] Mass percent of carbon in polymer was measured by elemental analysis. The error of mass percent of element is in the range of ±0.2%. [b] The molar fractions of **1** in the copolymers were calculated from the results of elemental analysis.

Preparation of Copolymer Films and Plates. Solution Casting. Copolymer films were prepared by casting toluene solutions on glass carriers. The concentration of the solution was 10−15 w/w %. The films were first dried in a circulating-air oven at 30 °C for 24 h and then in vacuum at 60 °C.

Extrusion and Hot-Pressing. The copolymer was extruded by means of a single-screw extruder (Brabender 19/25 D) at 200 °C. The resulting granulates were dried in vacuum at 60 °C for 24 h. Plate samples of 1 mm thickness were prepared by hot-pressing with a Schwabenthan Polystat T 200 pressing machine at 160 °C between polished aluminum plates.

Deprotection. Sample films and plates were immersed in a mixture of 1 N HCl and 2% tetrahydrofuran at 70 °C for 4 h. The surfaces were washed with deionized water and dried in air.

Contact Angle Measurement. Water contact angle measurements were carried out in air with an NRL contact angle goniometer (Ramé-Hart, Inc.) and using a sessile droplet technique. Both advancing and receding contact angles were measured, and five to seven measurements were made on each sample.

XPS Measurement. Spectra of the copolymer films were recorded by using an ESCALAB 5 (VG Instruments) X-ray photoelectron spectrometer with a hemispherical analyzer. The Mg Kα X-ray source of the ESCA spectrometer was operated at 300 W (15 kV and 20 mA). A pass energy of 20 eV was used. The pressure in the chamber was less than 1×10^{-7} Pa. All binding energies were referenced by setting the methylene peak maximum in the C1s spectrum to 285.0 eV.

Surface Resistance Measurement. According to the methods described in VDE 0303,[36] concentric silver electrodes were sputtered on both sides of the sample plate at 1×10^{-5} Pa using a Balzers 360 sputtering device. Samples were conditioned under different relative air humidities and the surface resistance was measured at 500 V in a conditioned atmosphere. A Kepco OPS 2000 B was used for the power supply, and the current was measured by a Keithley 616 digital electrometer.

Results and Discussion

Copolymerization reactivity parameters were investigated at low copolymer yield by elemental analysis and ^{1}H NMR spectroscopy and calculated by using the Fineman-Ross method.[37] The results of elemental analysis are shown in Table 1. A reactivity ratio $r_1 = 0.89$ was found for **1** and $r_2 = 0.87$ for styrene. The average homosequence length could be calculated from the composition of copolymers. For example, the homosequence length of **1** and styrene in a copolymer containing 5 mol % of **1** are 1.05 and 17.45 units, respectively. The reactivity ratios also indicate that the copolymer composition is random. Several polymerization techniques were tested for the preparation of sugar monomer **1**/styrene copolymers. Bulk polymerization in 10-mL glass tubes turned out as the best method.

Table 2. Molecular Weight and Composition of Copolymers from Bulk Polymerization

copolymer	monomer **1** (feed) (mol %)	monomer **1** (anal.)[a] (mol %)	yield	$10^{-5}M_n$[b]	T_g (°C)[c]
B1	0	0	94	8.0	103.6
B2	1	1.6	87	8.5	103.2
B3	2	2.4	93	8.0	102.8
B4	5	6.4	95	7.0	99.0
B5	10	10.0	89	9.5	97.6
B6	16	17.2	85	8.0	95.5

[a] The molar fractions of **1** in the copolymers were calculated from the results of elemental analysis. [b] Molecular weight was determined by membrane osmometry. [c] T_g was measured by DSC.

Table 3. GC Results of Hydrolysis Mixture under Different Hydrolysis Conditions

water/HCl with cosolvent (mass %)	pH	free acetone[a] (mol·m^{-2})
2% THF	1	2.1×10^{-6}
2% THF	0	6.9×10^{-6}
0.2% THF	1	8.3×10^{-7}
0.2% propanol	1	5.6×10^{-7}
2% propanol	1	9.2×10^{-7}

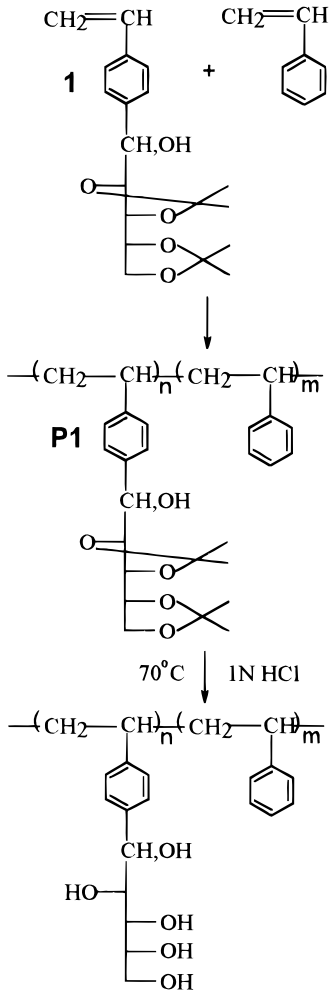
[a] The amount of free acetone was determined by GC.

Polymerization in solution gave lower molecular weights because of radical chain transfer to solvent molecules, while the products of suspension polymerization could not be obtained free of surfactant impurities. Bulk polymerization had a high yield and delivered better materials concerning molecular weight, purity, and mechanical stability. Table 2 shows the characterization results of compositions and properties. For surface investigations, copolymers of different compositions were synthesized. No concentrations higher than 16 mol % for **1** were used in bulk polymerization because of its limited solubility in styrene. The glass transition temperature T_g of the copolymers varied from 95.5 to 103.6 °C with changes in composition, and the T_g of the homopolymer of **1** was 85 °C.

The hydrolysis of the isopropylidene groups on the copolymer surfaces was carried out under various conditions. Copolymer powders were used for the determination of optimum hydrolysis conditions. The high specific surface of the powder made it possible to quantitatively analyze the free acetone and the free sugar, obtained in the hydrolysis mixture, by gas chromatography and periodate oxidation. The specific surface area of the powders was measured by nitrogen adsorption using the BET isotherm equation. Polymer **S2** was treated with addition of different cosolvents and acid concentrations. A mixture of 1 N hydrochloric acid and 2% tetrahydrofuran as cosolvent turned out as the best composition. It was generally found that taking THF instead of propanol and using 2% of cosolvent instead of 0.2% removed twice the amount of acetone. A 10 times higher acid concentration removed 2 times more acetone. The results are shown in Table 3.

The fact that no sugar was removed from the polymer surfaces in any case indicated that the C−C linkage between styrene and the pendant sugar was stable. Deacetalation on the copolymer surface took place easily in an acidic environment. The depth of hydrolysis could be calculated from the removed amount of acetone per m^2 as being more than 10 nm. The same hydrolysis conditions were used for the deacetalation at the surfaces of copolymer films and plates. Under these conditions the hydroxyl groups were generated at the surface of the copolymer, but not in bulk. As will be discussed later, angle-dependent XPS measurement showed that the hydrolysis occurred completely, at least to 10 nm from the surface. The procedure of copolymerization and hydrolysis is shown in Scheme 1.

Scheme 1



For copolymer films, it is difficult to quantitatively analyze the free acetone produced during hydrolysis, due to the very small specific surface area of the films and the low amount of free acetone being generated compared to powders. After hydrolysis, the presence of hydroxyl groups caused the surface of the copolymers to become more hydrophilic. Therefore, the hydrophilicity of the surface can be an indicator of hydrolysis efficiency. Contact angle measurement as a simple, surface-sensitive technique has long been widely used for surface characterization. Contact angle hysteresis is, consequently, a useful probe of the hydrophobic/hydrophilic property of a solid surface, e.g., wettability, heterogeneity, and surface mobility.[38−40] For investigating the rate of hydrolysis at copolymer surfaces, the water contact angle of a copolymer film was measured after different hydrolysis times. The receding angle, as a good measure of the high-surface-energy parts,[41] should be more characteristic of OH groups generated on the surface by hydrolysis. Figure 1 shows the receding contact angles for a copolymer film containing 2 mol % of **1**. With increasing hydrolysis time, the contact angle decreased steeply within 5 min and afterward varied very little. This indicated that the hydrophobic surface of the copolymer easily became hydrophilic after hydrolysis. Most isopropylidene pro-

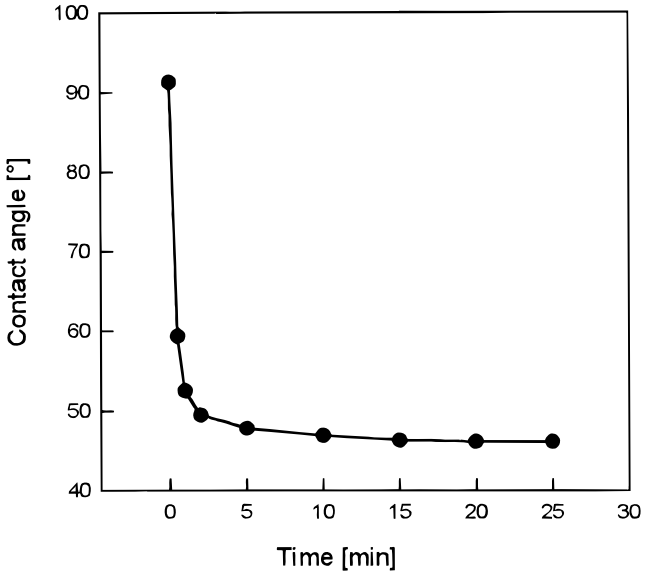


Figure 1. Dependence of contact angles on hydrolysis time. The copolymer film was hydrolyzed in 1 N HCl at 70 °C.

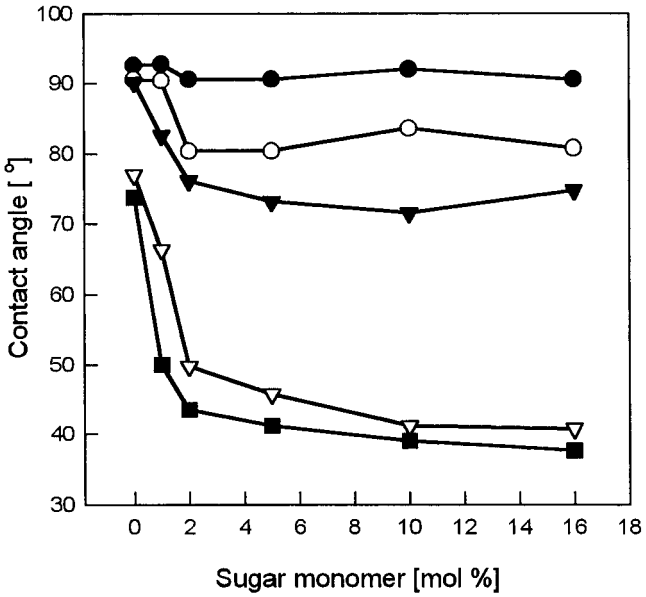


Figure 2. Contact angles of the copolymers hydrolyzed in HCl: (●) advancing angle of untreated polymer; (○) receding angle of untreated polymer; (▼) advancing angle of treated sample; (▽) receding angle of treated sample; (■) receding angle of hot-treated sample.

tecting groups on the surface were obviously removed within 5 min. It was also proved by XPS.

As mentioned before, the addition of a cosolvent may improve the contact between the copolymer solid phase and the acidic liquid phase and therefore increase the hydrolysis efficiency. Besides hydrochloric acid, sulfuric acid was also used because it is less corrosive and is therefore preferred in industrial applications. It was used at the same equivalent concentration. The samples treated with H_2SO_4 at 70 °C showed receding angles similar to those treated with HCl. The surfaces hydrolyzed with HCl at different temperatures showed small differences in receding contact angles, while the difference for the surfaces hydrolyzed with H_2SO_4 are obvious (see Figures 2 and 3). It may suggest that H_2SO_4 at 70 °C had the same hydrolysis efficiency as HCl, although at lower temperatures it was less efficient.

Before hydrolysis, the copolymer surfaces were significantly hydrophobic. Both advancing and receding

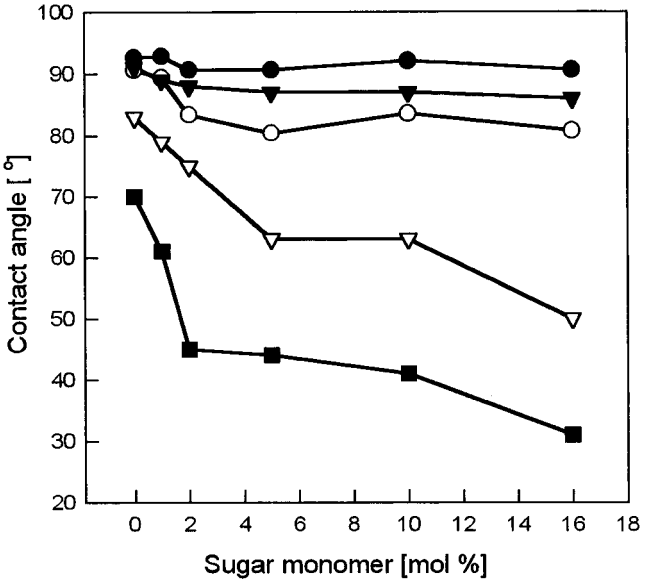


Figure 3. Contact angles of the copolymers hydrolyzed in H_2SO_4: (●) advancing angle of untreated polymer; (○) receding angle of untreated polymer; (▼) advancing angle of treated sample; (▽) receding angle of treated sample; (■) receding angle of hot-treated sample.

contact angles were considerably high, and the difference between the advancing and receding contact angles was approximately 10°. Because both monomer units were hydrophobic, no enrichment of one of them was expected at the surfaces of the copolymers in contact with water until the hydrolysis had been carried out. The contact angle hysteresis could be caused by various surface imperfections, such as roughness, heterogeneity, deformation, and suface mobility.[42,43] When the protecting groups were removed from the pendant sugar by hydrolysis, the sugar segments became hydrophilic owing to the presence of hydroxyl groups. Contact angle measurements then showed a large difference of about 40° between the advancing and receding contact angles. The large hysteresis is caused by the reorientation of the hydrophilic and hydrophobic segments on changing the environment. Hydrophobic segments are supposed to be oriented toward the surface in air, while there will be a preference for the hydrophilic sugar segments to be exposed at the surfaces when the surfaces are wetted with water.[38]

With increasing amounts of sugar in the copolymer, the advancing contact angles showed smaller changes since the hydrophobic segments preferred the presence on the copolymer surfaces in air to minimize the surface free energy and stabilize the copolymer surface. The receding contact angles first fell steeply at 2 mol % concentration, and then decreased very gradually with the concentration of the sugar monomer up to 16 mol % (Figure 2). By introduction of sugar monomers and induction of the wet environment, the hydrophilic segments partly covered the surface of the copolymer to the extent that the receding contact angle reached the saturation value at around 2 mol %. This might indicate that the modified surfaces were typical heterogeneous surfaces,[42] and the introduction of sugar monomer **1** effectively modified the copolymer surface and made it more hydrophilic.

As another method, we used a commercial polystyrene and a copolymer containing 16 mol % of monomer **1** for blending in solution. The resulting blends contained 0, 1, 2, and 5 mol % sugar monomer **1** like the copolymers.

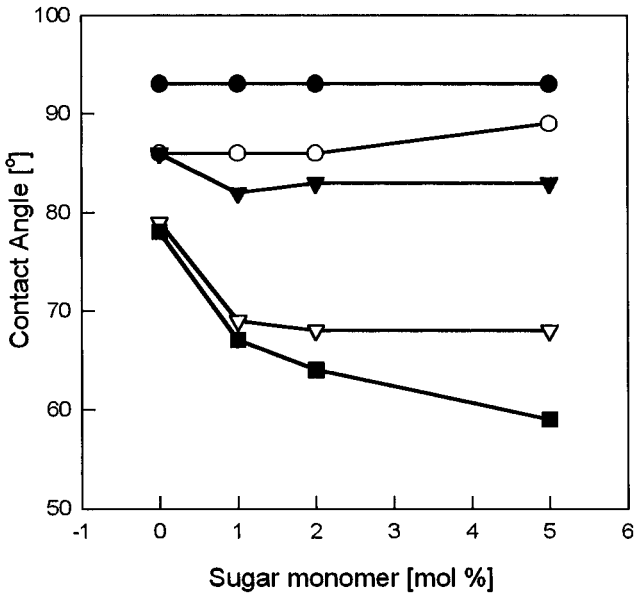


Figure 4. Contact angles of the blends hydrolyzed in HCl: (●) advancing angle of untreated polymer; (○) receding angle of untreated polymer; (▼) advancing angle of treated sample; (▽) receding angle of treated sample; (■) receding angle of hot-treated sample.

Table 4. Contact Angles of Samples Containing a Total Amount of 2 mol % Sugar Monomer 1

		contact angle (deg)	
sample	preparation[a]	advancing	receding
copolymer	cast from solution	71	43
copolymer	extruded and hot pressed	67	25
blend	blended in solution	83	63
blend	blended by extrusion and hot pressed	86	33

[a] All samples were hydrolyzed in 1 N HCl at 70 °C.

The cast films were hydrolyzed under the same conditions as the copolymer films. The contact angle measurement results are shown in Figure 4. These results demonstrated that the hydrolyzed surfaces of the blends had a lower hydrophilicity than the corresponding copolymers. The differences in hydrophilic/hydrophobic character for the blends compared to the copolymers might be an effect of the different mobility of chain segments in copolymers and of macromolecules in blend matrices. The surface character of blends was affected not only by the mobility of sugar segments, but also by the interaction between molecules of polystyrene and of the copolymers. The latter would affect the diffusion and orientation of copolymer molecules to the surfaces of the blends.[44,45] The reason for the lower hydrophilicity could be the lower accumulation of copolymer chains at the surfaces of the blends. Contact angles of samples containing 2 mol % of monomer **1** were compared under different methods of sample preparation. We found that the samples of the copolymer and the blends prepared by extrusion and hot-pressing were more hydrophilic than those prepared by casting from solution. It seemed that the mobility and accumulation of sugar monomers were different in the melt and in solution. The substrates used for sample preparation might also influence the orientation of sugar segments. The results are shown in Table 4.

Contact angle measurements provided much information about the hydrophilic−hydrophobic character of the copolymer surfaces. However, the detailed chemical information about the composition of the copolymer surface was not obtainable from these results. X-ray photoelectron spectroscopy (XPS) was a very useful technique for the analysis of polymer surface compositions. Angular-dependent XPS could reveal the compositions at different sampling depths up to 10 nm. The copolymer films cast from solution were investigated by XPS. Figure 5 shows typical C1s spectra of PS and copolymers 16 mol % of **1**. All spectra had resolved peaks at 284.76, 285, 286.47, 288.06, and 291.5 eV for aliphatic carbon, phenyl carbon, C−O, isopropylidene carbon, and the $\pi-\pi^*$ shake-up satellite component,[46] respectively. Since both comonomers had aromatic rings, we did not show the peak at 291.5 eV in

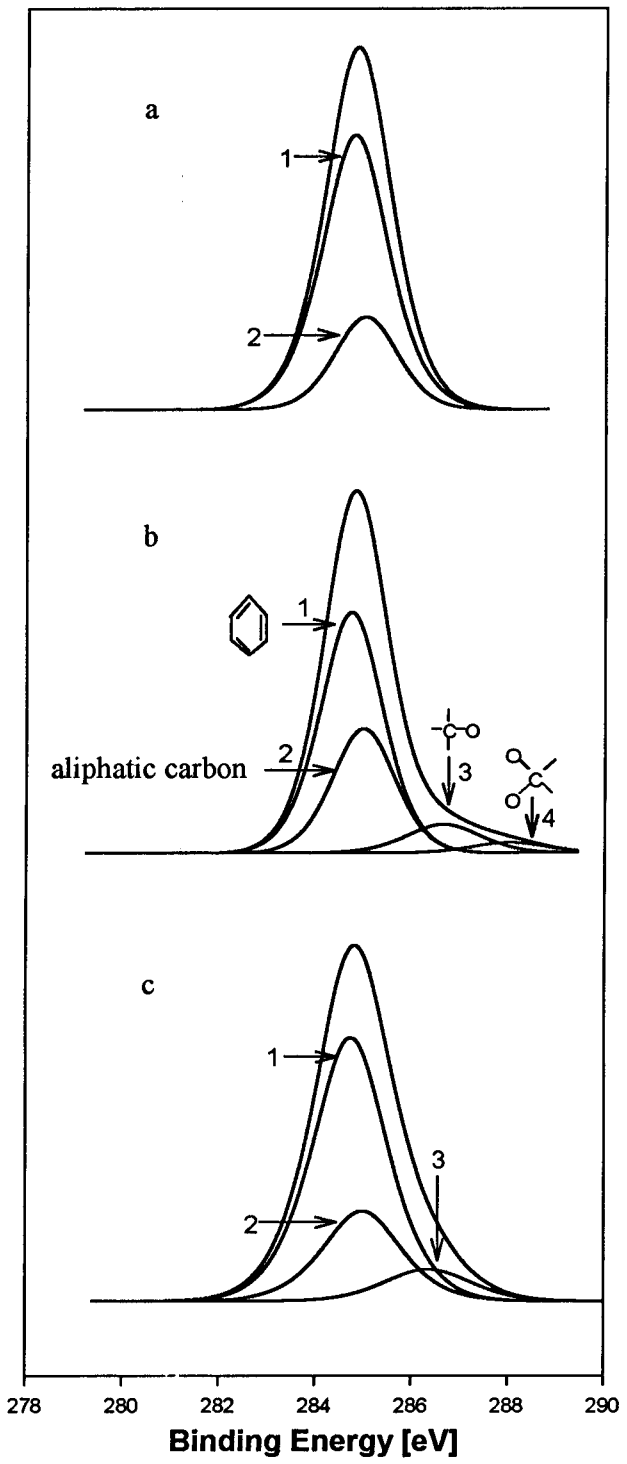


Figure 5. XPS C_{1s} spectra of the polymers cast from solution: (a) polystyrene without treatment; (b) untreated copolymer **B6**; (c) treated copolymer **B6**.

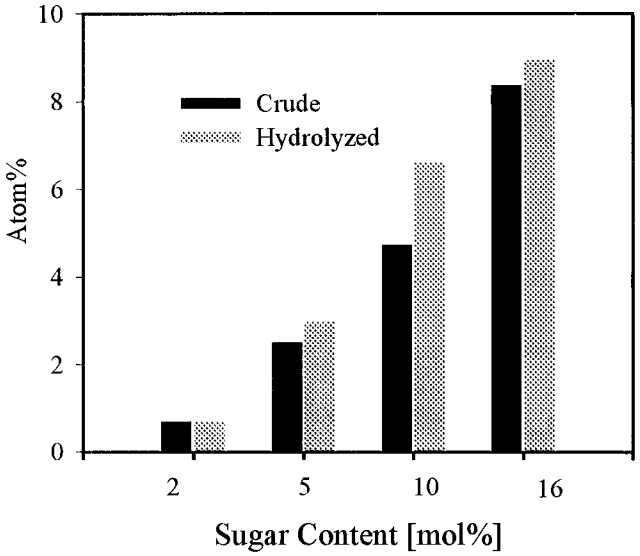


Figure 6. Changes of sugar carbon ratio at the surface.

Table 5. Surface Composition of a Copolymer Film Determined by XPS Measurement

sampling depth (nm)	atom % (after hydrolysis) C1[a]	C2	C3	C4[b]	atom % (before hydrolysis) C1	C2	C3	C4
8.0	69.99	23.39	6.62	≤0.5	68.39	26.87	4.75	2.10
6.8	69.52	23.93	6.55	≤0.5	61.80	30.73	5.21	2.02
3.9	69.16	24.36	6.48	≤0.5	69.94	27.50	4.72	1.96
theoretical	70.6	23.5	5.9	0	65.9	26.4	5.5	2.2

[a] The numbering of carbon atoms is as shown in Figure 5. [b] C4 cannot be observed by the instrument. [c] The sample was made of polymer **S5**.

Figure 5. The spectrum of polystyrene only had two peaks at 285 and 284.76 eV because of its simple structure composed of methylene, methine groups, and aromatic rings (Figure 5a). The C1s spectrum of a copolymer containing 16 mol % of **1** showed a tail, which obviously indicated the existence of C−O bonds and protecting groups in the sugar units (Figure 5b). Figure 5c shows the spectrum of a hydrolyzed copolymer having the same composition as that in Figure 5b. The peak at 288.06 eV for isopropylidene carbon could not be seen. This meant that the protecting groups on the surface were removed successfully and the hydrolysis took place at least within the range of the XPS sampling depth of about 7.5−10 nm. The hydrolysis of acetals in the surface layer also became visible in the decrease of methyl carbon C2 caused by acetone removal and the increase of sugar specific carbon C3. Figure 6 shows the sugar carbon ratio at surface. The integrated area ratio of the different peaks for each untreated polymer approximately accorded with the theoretical results calculated from the bulk compositions. The sugar units in the copolymers did not seem to be enriched at the surface of solution-cast films under dry conditions. This may be explained by the random sequence of the copolymers.[21] Table 5 shows the results of angular dependent XPS for a copolymer containing 10 mol % sugar units. The values of sampling depth were 3.9, 6.8, and 8.0 nm, corresponding to takeoff angles of 30, 60, and 90°, respectively.[7] The data also demonstrated that the aliphatic carbon on the surface decreased and that the sugar carbon increased after hydrolysis. The compositions at the different sampling depths showed no obvious difference.

Table 6. Measured Surface Resistivities (ρ_s)

sample	ρ_s, Ω
PS	2.13×10^{16}
B3	2.85×10^{16}
B4	8.33×10^{15}
B5	3.05×10^{15}
B6	2.06×10^{13}

Because of the presence of hydroxyl groups at the modified copolymer surfaces, water would easily be adsorbed to the surfaces by hydrogen bonding. Furthermore, solid ionic conductors and gases might be hosted by the water and increase the conductivity of the modified surfaces. We measured the surface resistance of commercial polystyrene and the copolymers under different relative humidities. The sample plates were prepared by hot-pressing in order to obtain more hydrophilic surfaces according to the results discussed before. We found that the surface resistance of the copolymers highly depended on the humidity of the environment. When the relative humidity was 75% and 40%, the difference in resistance between the commercial polystyrene and the copolymer could not be detected because of the limitation of our instrument. The results measured at 85% relative air humidity are shown in Table 6. Up to 10 mol % of sugar content, the surface resistivity of the copolymer decreased very gradually. The resistivity difference between PS and the copolymer with 16 mol % sugar content decreased by 3 orders of magnitude.

Conclusions

Copolymers of styrene and **1** were easily synthesized by radical polymerization. Both monomers had comparable reactivity parameters. The highest sugar monomer content for bulk copolymerization was 16 mol % owing to the limited solubility of monomer **1** in styrene. The hydrolysis at the copolymer surfaces was nearly complete after 5 min and reached more than 10 nm in depth. The C−C linkage between the sugar and the styrene moiety in **1** was stable during hydrolysis. After hydrolysis, the isopropylidene protecting groups on the surface of the copolymer were removed effectively, and the surface showed hydrophilic properties. The surface accumulation of the sugar segments in the copolymers and the blends with commercial PS depended not only on the content of sugar but also on the methods of sample preparation. The surfaces prepared by hot-pressing were more hydrophilic than those prepared by solution-casting.

This study demonstrates that a concept for obtaining polymers with an antistatic surface is promising. The presence of hydroxyl groups on the surface enables insulating polymers to adsorb a more conductive moisture layer.

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