Surface Mobility of Grafted Hydrogels

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ABSTRACT: Solid-supported hydrogels were prepared by ozone-induced graft polymerization of 2-hydroxyethyl methacrylate (HEMA), diethylene glycol methacrylate (DEGMA), and triethylene glycol methacrylate (TEGMA) onto polypropylene substrates. Angle-dependent ESCA showed a gradient in chemical composition in the near-surface region (thickness 55 Å). The various shapes of the C 1s peaks collected at a takeoff angle of 45° corresponded to what could be expected from the chemical composition of polyHEMA, polyDEGMA, and polyTEGMA, respectively. At a takeoff angle of 15°, all grafted polymers showed a more hydrophobic character with respect to the shape of the C 1s peak. During dynamic contact angle measurements, HEMA-grafted fibers showed the largest contact angle hysteresis, with an advancing contact angle of about 90° and receding contact angle close to zero. A less pronounced contact angle hysteresis for both DEGMA and TEGMA-grafted fibers was explained by a hindered reorientation as a consequence of an increased side chain length of the grafted polymers. A suppressed contact angle hysteresis was also obtained for fibers grafted in a HEMA monomer mixture containing 5% cross-linker (EDMA). Such surfaces also showed good reproducibility when sequential wetting cycles were performed during the dynamic contact angle measurements.

Introduction

Hydrogels are three-dimensional hydrophilic polymer networks that exhibit the ability to swell in water or other liquids without dissolving. In 1960, Wichterle and Lim reported excellent biomedical properties of poly(2-hydroxyethyl methacrylate), PHEMA.[1] After this breakthrough, a wide range of hydrogels have been examined for other biomedical applications, for example as artificial tissues and organs and drug delivery systems.[2−7] Owing to the possibility of preparing hydrogels with tailor-made composition and characteristics, new applications for such polymers are continuously being found. The high water content of hydrogels results, however, in limited mechanical performance, which in some cases also limits the field of applications.[8] One approach to overcome this problem is to fix the hydrogels on a solid support and thereby improve the mechanical properties. Such solid-supported hydrogels can for example be prepared by various grafting techniques.[9−11] We recently used ozone-induced graft polymerization for the preparation of membrane and fiber-supported hydrogels with controlled grafting yield, surface morphology, and swelling properties.[12−15]

The surface properties of hydrogels are of great importance because it is the surface that determines all kinds of interactions with the surrounding environment, for example wetting, adhesion, and biological response. A polymer that consists of segments or groups with various functionalities or polarities may alternate the surface chemical composition in order to minimize the interfacial tension between the surface and the environment.[16−18] This may be done by numerous dynamic processes, for example migration of additives to or from the surface or reorientation of either segments or side groups. Hydrogels exhibit mobile surfaces since the outermost surface layer contains large amounts of water, which acts as a plasticizer. The most quoted example of side-group reorientation is that in polyHEMA surfaces, which exposes CH_3 and CH_2 groups to a hydrophobic environment and the OH groups to a hydrophilic environment. This behavior of polyHEMA was first discussed by Holly and Refojo in 1975,[19] and their results were based on contact angle measurements. After this discovery, the molecular orientation of polymer surfaces has been a subject of investigation, since knowledge of the surface chemistry may help us to understand and predict several surface-related phenomena, for example biocompatibility. Ratner et al. used a refined ESCA technique to study the chemical composition and reorientation of hydrogel surfaces.[20] The surfaces were examined under high vacuum in a frozen form at liquid nitrogen temperature in order to simulate a wetted surface. Angle-dependent ESCA was used by Ikada et al. for determining chemical composition of surfaces grafted using plasma and UV light technique.[21] Morra et al. discussed the dynamic wetting behavior of photografted hydrophilic acrylic polymers,[22] and Lavielle et al. focused in several papers on the surface properties of polyethylene activated by an electron beam and grafted with a low amount of (1%) acrylic acid.[23−25]

The aim of this study was to investigate the reorganization and mobility of functional groups/segments at the surface of solid-supported hydrogels prepared by ozone-induced graft polymerization. Three different glycol methacrylates with various side-chain lengths were grafted onto polypropylene substrates. Angle-dependent ESCA and dynamic contact angle (DCA) measurements were used to characterize the surfaces. Polypropylene substrates were furthermore grafted in a monomer mixture containing a small amount of a cross-linker. The wettability of such surfaces was also determined by DCA measurements.

Experimental Section

Materials. Polypropylene (PP), without additives and in the form of films and fibers, was used as substrates for ozone treatment and grafting. The film substrate was P 120 SA with a thickness of 50 μm, produced by Statoil, Norway. PP fibers with a diameter of ∼20 μm were cut from a spun bond supplied

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by Fiber Web, Norrköping, Sweden. The substrates were surface-purified by extraction prior to use. Methylene chloride, acetone, and water, in that order, were used for purification. The substrates were treated, 15 min in each solvent, in an ultrasonic bath. After extraction, the substrates were dried at 70 °C for 2 h. The monomers were 2-hydroxylethyl methacrylate (HEMA), diethylene glycol methacrylate (DEGMA), triethylene glycol methacrylate, and ethylene glycol dimethacrylate (EDMA). The HEMA and EDMA monomers, as purchased from Fluka Chem. AG., were vacuum-distilled prior to use. DEGMA and TEGMA were supplied by the Institute of Macromolecular Chemistry in Prague. GC measurements confirmed the purity of the monomers.

Ozone Treatment and Graft Polymerization. Ozone treatment of the substrates was carried out in a gas-phase reactor at 32 °C. The substrates were kept in end-open glass tubes during the 75 min treatment. Ozone was generated with a Fischer Ozon 502 ozone generator, which produced an O_2/O_3 flow of 0.250 m^3/h from pure oxygen gas. The ozone concentration was 25 g/m^3. Before it reached the reactor, the gas current was preheated and humidified. A saturated O_2/O_3 mixture at a temperature of 32 °C was then blown into the reactor. Immediately after the ozone treatment, the substrates were placed in a monomer solution. The solution was prepared by diluting 3.0 g of monomer in equal amounts (15 mL) of methanol and deionized water. The water contained 75 mg of dissolved Mohr's salt ($FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$), which forms a redox initiator. The pH of the solution was set to 3.0. The grafting process was performed in a nitrogen atmosphere in sealed glass ampules for 60 min. During the graft polymerization, the ampules were shaken in a water bath at 50 °C. The polymerization was interrupted by opening the ampules and immersing the substrates in water. The grafted substrates were extracted in methanol overnight to remove monomer residuals and then dried at 50 °C for 2 h.

Electron Spectroscopy for Chemical Analysis (ESCA). ESCA was used to determine the chemical composition of the surfaces. The equipment used was a Perkin-Elmer PHI 5500 equipped with an Mg Kα X-ray source. The area analyzed had a diameter of 0.8 mm. The information depth of ESCA was varied by changing the takeoff angle (α) between the photoelectron detector and the solid surface. The mean free path (λ), which is used for calculating the information depth (d), was determined from eq 1. M represents the molecular weight of the repeat unit, E_k is the kinetic energy (eV), ρ is the density of the polymer, and n is the number of valence electrons in the repeat unit.[26] At a takeoff angle of 90°, 3λ is by definition the depth (d_{95}) from which 95% of the C 1s signal arises, whereas 63% of the signal comes from a depth (d_{63}) equal to λ. The information depth (d_{95}) then decreases with decreased takeoff angle (α) between the surface and the detector. The reason is that the detected electrons will travel different distances in the material at a changed α before leaving the surface, eq 2.[26] Samples were analyzed at takeoff angles (α) of either 15° or 45° with alternate order for each sample. Three samples were analyzed for each grafted monomer and takeoff angle, respectively.

$$\lambda = (ME_k/\rho n)/(13.6 \ln(E_k) - 17.6 - 1400/E_k) \quad (1)$$

$$d_{95} = 3\lambda \sin \alpha \quad (2)$$

Dynamic Contact Angle Measurements (DCA). The instrument used for dynamic wettability measurements of the polypropylene fibers was a Cahn 322 dynamic contact angle analyzer operating at a stage speed of 20 μm/s. The lowest possible stage speed was chosen in order to reduce kinetic effects. The length of the fibers determined the immersion depth during the measurements. Wettability measurements were performed in deionized water (γ =72.8 mN/m). Immediately after the measurements in water, each fiber perimeter was determined using a liquid that provides complete wetting, hexadecane (γ = 27.6 mN/m). Since the test liquid completely wets out the fiber, the contact angle (θ) is zero, and the fiber perimeter can thus be calculated by using eq 3. The new perimeter was used when calculating the advancing and receding contact angles of water.

$$P = F/(\gamma \cos \theta) \quad (3)$$

where P is the perimeter (m), F is the force (mN), and γ is the surface tension of the test liquid (mN/m).

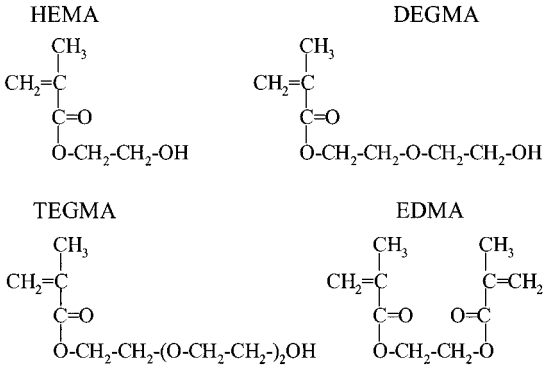

Figure 1. Monomers used for graft polymerization.

Table 1. Chemical Composition of HEMA, DEGMA, and TEGMA Grafted PP Films Determined by ESCA at a Takeoff Angle of 45°

grafted monomer	O/C (ESCA)
HEMA	0.40 ± 0.03
DEGMA	0.41 ± 0.03
TEGMA	0.41 ± 0.03

Results

Surface Chemical Composition. Ozone-induced graft polymerization of HEMA, DEGMA, and TEGMA was performed onto polypropylene films. The structures of the monomers are shown in Figure 1. The figure also includes the structure of EDMA, which was used later in the study. Grafting conditions that were earlier shown to result in a complete coverage of polypropylene substrates during such graft polymerization were selected.[12] It was reported that the graft polymerization was initiated by hydroperoxides that were formed on the substrates during the ozone treatment and then decomposed by a red-ox initiator. The hydroperoxide concentration increased by increasing ozonation time. It was also shown by ESCA that the surface coverage reached a limit when the hydroperoxide concentration was increased, indicating that the surfaces were homogeneously covered with grafted polymers. The chemical composition of the grafted surfaces was determined with ESCA. In Table 1 the ESCA O/C ratio of the grafted films are shown. A takeoff angle of 45° has been used during the measurements. As can be expected from the chemical composition of the monomers used for grafting, the O/C ratio is equal for all grafted surfaces. The obtained values are furthermore in agreement with results reported by Morra et al. for pure polyHEMA. This supports that the PP films are homogeneously covered with grafted polymers and that the grafted layers exhibit a thickness that is at least as thick as the analyzing depth during the ESCA measurements.

In addition to the calculation of O/C ratio, the appearance of the C 1s peak was studied as a function of takeoff angle (α) between the photoelectron detector and film surface. Film substrates were used in order to achieve smooth surfaces, which is a requirement for angle-dependent ESCA measurements. The mean free

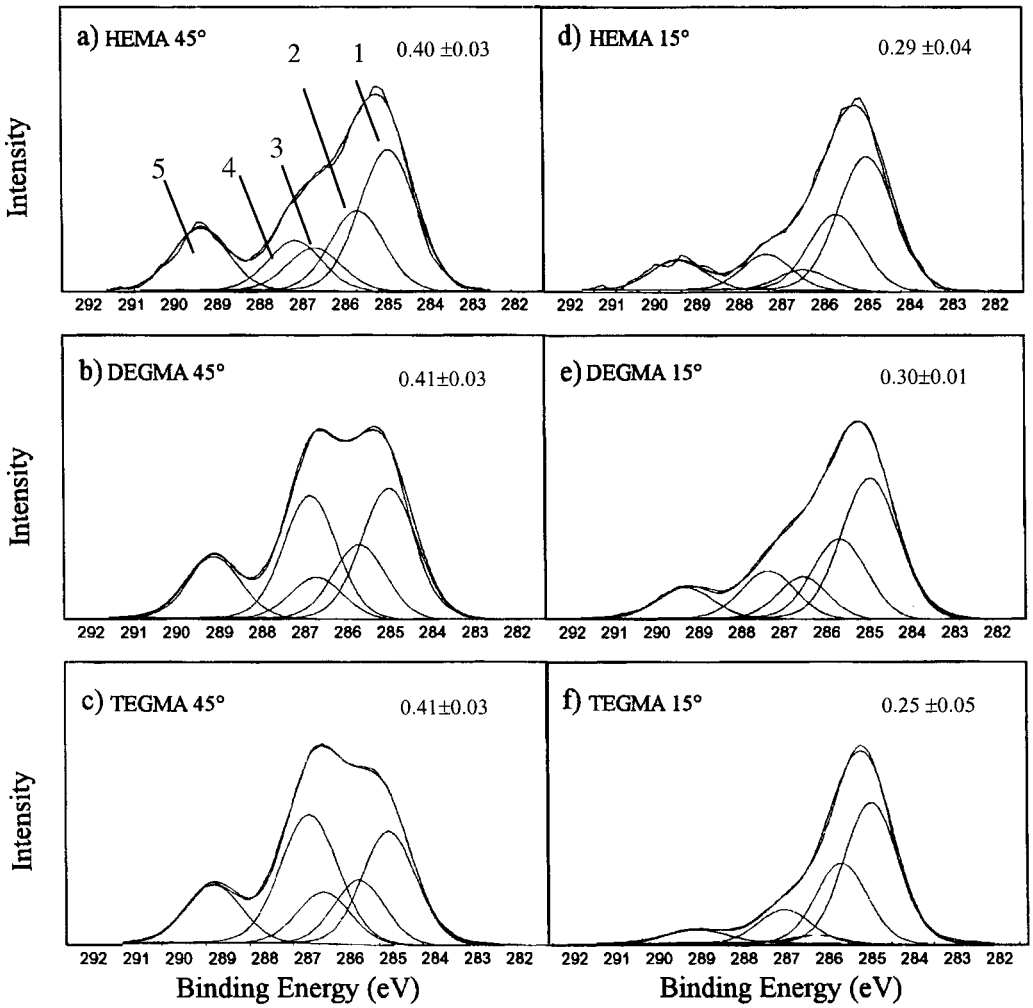

Figure 2. ESCA C 1s peaks collected at takeoff angles of 15° and 45° for HEMA, DEGMA, and TEGMA-grafted surfaces: C−*C*−C (peak 1−2), C−*C*−O−R (peak 3−4), C−*C*OO−R (estergroup, peak 5).

path (λ), which is used for calculating the information depth (d), was determined to be ≈26 Å for all polymers using eq 1. Two takeoff angles, 15° and 45°, were used in the ESCA analyses. By applying eq 2, we found that 95% of the signal at $\alpha = 45°$ is roughly collected from the outermost 55 Å for all three polymers. Thus, the thickness of the grafted layers discussed above is at least 55 Å. At $\alpha = 15°$, the corresponding information depth is about 20 Å. Figure 2 shows the carbon peaks of HEMA, DEGMA, and TEGMA-grafted PP films at the two takeoff angles. The shapes of the C 1s peaks collected at 45° (Figure 2a−c) correspond to what can be expected from the chemical composition of polyHEMA, polyDEGMA, and polyTEGMA, respectively. The C 1s peak for polyHEMA has relatively the smallest signal at 287 eV. At this binding energy, the contribution from C−*C*−O−R appears. The peak at 287 eV then increases as a function of the side chain length of the grafted polymer. Consequently, polyTEGMA has the largest signal at this binding energy. When the surface is investigated by collecting spectra at a takeoff angle of 15°, the signal at 287 eV is smaller for all grafted polymers, which indicates a more hydrophobic nature (Figure 2d−f). It can be observed that the shape of the C 1s peaks at $\alpha = 15°$ is quite similar for the three grafted polymers despite the difference in chemical composition. Figure 2 also includes the calculated O/C ratio at α equal to 45° and 15°. It can be observed that the O/C ratio decreases when α is changed from 45° to 15° for all grafted surfaces. The changed chemical composition, in terms of decreased O/C ratio, is in accordance with the changed appearance of the C 1s peaks. The ESCA measurements show that there is a composition gradient in the near-surface layer of all grafted polymers, although it is difficult to obtain information about the chemical composition of the outermost atomic layers since the information depth at a takeoff angle of 15° is still 20 Å. The difference between the takeoff angles of 15° and 45° may be an effect of the orientation of functional groups/segments toward the bulk when the samples are placed in a "hydrophobic" environment such as air or in a vacuum. A proposed model of the difference between the grafted layer in wet state and in the dry state is shown in Figure 3. The grafted layer is probably swelled in the wet state, and the grafts are relatively stretched. The drying process results in collapsing of the grafted layer, while

Figure 3. Proposed model of grafted layers before and after drying.

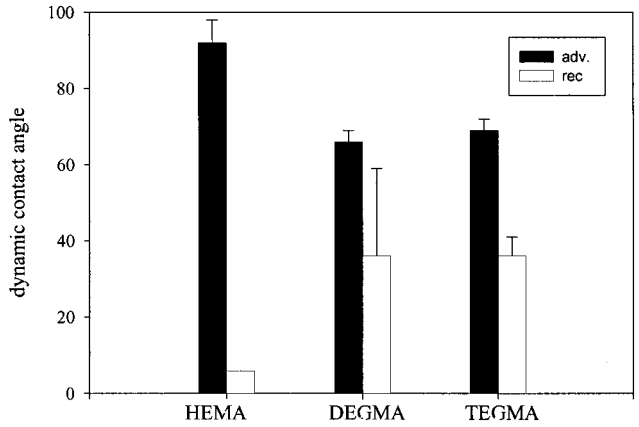

Figure 4. Dynamic contact angles for HEMA, DEGMA, and TEGMA.

at the same time the more hydrophobic parts of the polymer backbones are oriented to the hydrophobic environment.

Dynamic Contact Angle Measurements. Ozone-induced grafting was also performed onto polypropylene fibers. The dynamic wettability of fibers grafted with HEMA, DEGMA, and TEGMA was studied using a Cahn 322 dynamic contact angle analyzer. Such measurements are very surface-sensitive, with an information depth of a few angstroms. Both advancing and receding contact angles were determined for the grafted fibers, and the mean values of at least 15 measurements are shown in Figure 4. As earlier reported, θ_{adv} for HEMA grafted fibers is about 90° whereas θ_{rec} is close to zero.[12] The pronounced hysteresis, i.e., the difference between θ_{adv} and θ_{rec}, is believed to be a result of the mobility of functional groups (−OH) in the surface layer of the grafted polymer. Such behavior of polyHEMA, prepared by solution polymerization with a redox initiator, was proposed by Holly and Refojo.[19] The contact angles determined for DEGMA and TEGMA-grafted fibers differ from those obtained for grafted HEMA. Both grafted DEGMA and TEGMA have advancing contact angles of about 65°−70° and receding contact angles of about 35°. The only difference between grafted DEGMA and TEGMA is that the scatter of the receding contact angles for grafted DEGMA is larger. No differences in the contact angles were observed when the fibers were dried for 24 h at higher temperature, 75 °C instead of 50 °C**.** The reduction of hysteresis for grafted DEGMA and TEGMA may be an effect of the increased side chain length of the grafted polymer. The increased side chain length may result in a hindered reorientation ability. The pendent hydroxyl groups are also able to form hydrogen bonds, which may reduce the mobility. In addition to surface mobility, surface heterogenity and surface roughness may cause contact angle hysteresis. However, our recently published ESCA and SEM results confirm that the substrates are covered with chemically homogeneous and smooth grafted layers.[12]

One factor that can reduce the mobility on the molecular scale is the presence of either physical or chemical cross-links between the polymer chains. To investigate the effect of chemical cross-links on the surface mobility, a certain amount (5 mol %) of the HEMA monomer used for grafting was replaced with a bifunctional monomer, EDMA, normally used as cross-linker for hydrogels. The dynamic contact angles for fibers grafted with this monomer composition were then measured and compared with fibers grafted with "pure" HEMA. Figure 5 shows two wetting cycles. The one shown in Figure 5a is obtained for a fiber grafted with HEMA without cross-linker, while the one in Figure 5b is grafted with HEMA containing 5% cross-linker. It can be observed that the shape of the tensiogram is changed when EDMA is added to the monomer mixture used for grafting. The "cross-linked" surface layer shows a suppressed hysteresis effect. The value of the advancing contact angle is in this case 71 ± 6°. Furthermore, the contact angle during receding was equal to 30 ± 9°, which is much higher than the corresponding angle obtained for fibers grafted with HEMA without cross-linker. This may be an effect of a hindered reorientation ability as a consequence of a cross-linked surface. The dynamic contact angles obtained for fibers grafted with HEMA/EDMA are similar to those obtained for pure DEGMA and TEGMA.

We also performed sequential scanning loops during the DCA measurements. It was shown by Morra et al. that such measurements can be used to detect water adsorption onto HEMA surfaces prepared by dip coating.[27] They concluded that a shift of the advancing force position line for the second loop toward the receding force in the first loop was due to the fact that the water front in the second loop advances over an already wetted surface whose cracks and crevices are filled with water. Figure 6 illustrates three typical sequential wetting cycles obtained for HEMA/EDMA grafted PP fibers. Since both advancing and receding are equal for all loops, neither fiber swelling nor the presence of pre-

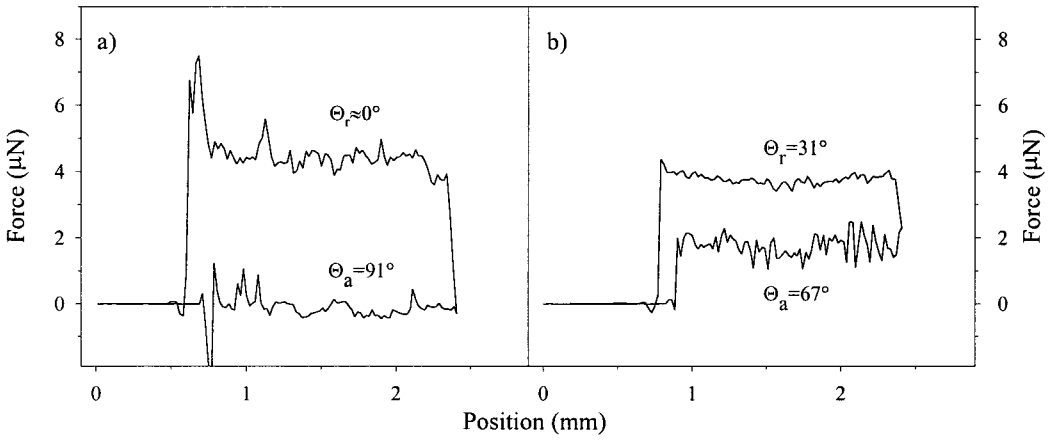

Figure 5. DCA tensiogram of HEMA-grafted polypropylene fibers: (a) fiber grafted in a HEMA mixture without cross-linker; (b) fiber grafted in a HEMA mixture containing 5 mol % cross-linker.

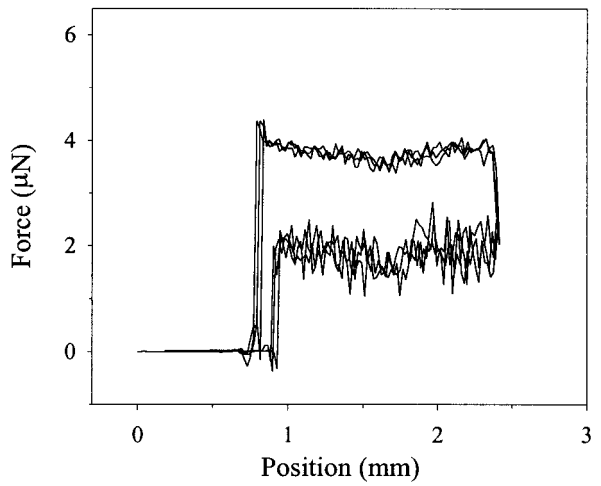

Figure 6. Sequential wetting cycles obtained for HEMA/EDMA grafted PP fibers.

served functional groups (−OH) in the absolute surface as a result of the previous wetting cycle can be assumed.

The constant hysteresis effect also confirms that no substantial amount of water is adsorbed as a consequence of the first wetting cycle. In such cases the second advancing loop would have resulted in much lower contact angle. The good reproducibility for all loops confirms that the surface properties did not change during the contact angle measurements.

Conclusions

Ozone-induced graft polymerization of HEMA, DEGMA, and TEGMA was performed onto polypropylene films and fibers. ESCA showed that the polypropylene surfaces were covered with the grafted polymers, and angle-dependent ESCA furthermore showed that a gradient in chemical composition existed in the near-surface region of the grafted polymers. A more hydrophobic character with respect to the shape of the C 1s peak was obtained when the takeoff angle was decreased from 45° to 15°. During dynamic contact angle measurements, HEMA-grafted fibers showed a large contact angle hysteresis. For both DEGMA and TEGMA-grafted fibers, a less pronounced contact angle hysteresis was obtained. This was explained by a hindered reorientation as a consequence of an increased side chain length of the grafted polymers. A suppressed contact angle hysteresis was also obtained for fibers grafted in a HEMA monomer mixture containing 5% EDMA, normally used as cross-linker for hydrogels. Such "cross-linked" surfaces also showed good reproducibility when sequential wetting cycles were performed during the dynamic contact angle measurements. This confirms that smooth surfaces were obtained as a result of the grafting process.

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