

# Surface Modification of Polyethylene by Photochemical Introduction of Sulfonic Acid Groups

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A photochemical technique for the modification of polyethylene (PE) surfaces was developed. Polyethylene samples were irradiated with UV light in a gas atmosphere containing SO<sub>2</sub> and air to achieve a photosulfonation of the surface. The introduction of sulfonic acid groups (–SO<sub>3</sub>H) onto the PE surface was proved by Fourier transform infrared spectroscopy (FTIR), energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. The influence of the gas composition and the UV irradiation time on the modification reaction were studied by means of contact angle measurements, FTIR spectroscopy, and dyeing with methylene blue. The hydrophilicity of the PE surface increased considerably compared to unreacted PE. The depth of photomodification amounted to several micrometers. A patterned surface modification was obtained by mask projection. The presented method of surface modification is carried out under atmospheric pressure and is considered to be an inexpensive alternative to plasma modification techniques. Because of the large depth of modification, the process may also be useful for the modification of membranes and—in combination with projection lithography—for the manufacture of gratings in thin polymer films (as required for holographic recordings and distributed feedback lasers).

## Introduction

During the past years, the properties of polymer surfaces have attracted increasing attention.<sup>1,2</sup> While the bulk properties of commercial polymers fulfill numerous mechanical and thermal requirements, the properties of the polymer surface are undesirable in several applications. For example, the low surface energy of polymers such as polyethylene (PE) causes poor adhesion of laquers, coatings, and metallizations. As it would be costly to change the properties of the whole polymer, a treatment of the surface is preferred in many cases.

Several techniques have been developed to obtain PE surfaces of increased polarity. Chemical etching processes (e.g., with solutions of CrO<sub>3</sub>) and treatments of the surface with plasma or corona discharges are well established to achieve a partial oxidation of the PE surface and thus higher polarity and wettability.<sup>1,2</sup> An “activation” of PE surfaces with the short-wavelength UV radiation of excimer lamps in the presence of oxygen

has been described only recently.<sup>3</sup> In addition, the grafting of vinyl monomers onto PE surfaces employing radiation (e<sup>−</sup>, γ, UV) has been widely applied.<sup>4</sup>

The introduction of sulfonic acid groups (–SO<sub>3</sub>H) onto polymer surfaces has been found valuable for biomedical applications. It has been shown that the growth of endothelial cells on polymeric materials (e.g., polyurethanes) is improved if the surface of the polymer contains sulfonic acid groups.<sup>5</sup> Plasma processes employing gaseous sulfur dioxide as the reactive component have been successfully applied to the attachment of sulfonic acid groups to polymer surfaces.<sup>5–7</sup> The sulfonation of polystyrene surfaces has also been achieved with solutions of H<sub>2</sub>SO<sub>4</sub><sup>8</sup> or acyl sulfate complexes.<sup>9</sup> In a similar way, the treatment of PE surfaces with sulfur

(3) Bader, H.; Gessler, M.; Rodler, N. *Kunststoffe* **1997**, *87*, 636.

(4) Ranby, B. *Macromol. Symp.* **1992**, *63*, 55.

(5) Klee, D.; Villari, R. V.; Höcker, H.; Dekker, B.; Mittermayer, C. *Mater. Sci. Mater. Med.* **1994**, *5*, 592.

(6) Giroux, T. A.; Cooper, S. L. *J. Appl. Polym. Sci.* **1991**, *43*, 145.

(7) Höcker, H.; Klee, D. *Macromol. Symp.* **1996**, *102*, 421.

(8) Siqueira-Petri, D. F.; Wenz, G.; Schunk, P.; Schimmel, T.; Bruns, M.; Dichtl, M. A. *Colloid Polym. Sci.* **1999**, *277*, 673.

(9) Orler, E. B.; Yontz, D. J.; Moore, R. B. *Macromolecules* **1993**, *26*, 5157.

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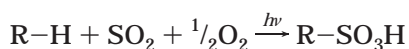
(1) Chan, C.-M. *Polymer Surface Modification and Characterization*; Hansa Publishers: Munich, 1994.

(2) Chan, C.-M.; Ko, T.-M.; Hiraoka, H. *Surf. Sci. Rep.* **1996**, *24*, 1.

trioxide<sup>10</sup> has been found valuable to improve the barrier properties of PE in automotive applications.

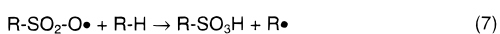
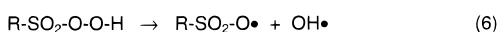
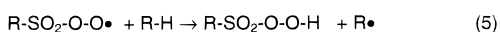
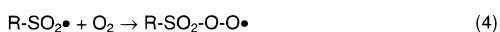
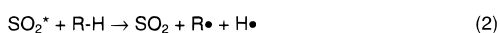
In recent reports the attachment of *specific* functional groups onto polymer surfaces by UV irradiation in the presence of reactive gases has been described. Among these techniques are the photochlorination of polystyrene,<sup>11</sup> the photoassisted introduction of amino groups onto fluorocarbon polymers,<sup>12</sup> the photochemical modification of polystyrene surfaces with CN groups,<sup>13</sup> and the irradiation of polymer surfaces in the presence of gaseous boron compounds.<sup>14</sup> Generally, photochemical techniques appear as an inexpensive alternative to plasma treatments as operation under vacuum is not required.

The aim of the present investigation was to examine if photochemical techniques can be employed to attach sulfonic acid groups onto polymer surfaces. The photosulfonation of long-chain alkanes (C<sub>6</sub>–C<sub>24</sub>) and alkylbenzenes is carried out on a commercial scale to obtain alkane sulfonates which are employed as detergents.<sup>15</sup> The overall process may be written according to



The mechanism of this reaction is shown in Scheme 1. Gaseous SO<sub>2</sub> absorbs in the UV region 240–320 nm with an absorbance maximum at 285 nm. Irradiation with UV light then leads to the excitation of ground-state SO<sub>2</sub> to its first singlet state (*n*–π\* transition; eq 1). After intersystem crossing (ISC) to its triplet state, the excited SO<sub>2</sub> molecule abstracts H from a hydrocarbon molecule to give alkyl radicals<sup>15,16</sup> (eq 2). Alternatively, an energy transfer from SO<sub>2</sub>\* to R–H via the formation of an exciplex has been proposed.<sup>17</sup> However, the latter mechanism, which implies a direct fission of C–H bonds to give alkyl radicals and H atoms, has been doubted for energetic reasons.<sup>15</sup>

### Scheme 1. Photosulfonation of Alkanes



(R = alkyl)

Chain propagation occurs according to eqs 3–7 in Scheme 1 with persulfonic acid as an intermediate. Finally, alkane sulfonic acids are obtained as the main

reaction product (eq 7). Depending on the reaction conditions, side products such as H<sub>2</sub>SO<sub>4</sub>, monoesters of sulfuric acid, and colored compounds may be formed.<sup>15,17</sup> Generally, only a few reports have been published concerning the amount and the composition of the side products of the photoprocess.

It appeared promising to apply the process of photosulfonation to the modification of the surface of solid-state polymers. To our knowledge, processes of this kind have not been described to date. Initially, we chose PE as the target polymer as the linear hydrocarbon chains can be expected to be of high reactivity in photosulfonation reactions. Summing up, the present paper is concerned with the photomodification of PE surfaces and with surface-analytical investigations by means of X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectroscopy (FTIR).

### Experimental Section

**Materials.** Low-density polyethylene (LDPE) was received from Melitta GmbH (Salzburg, Austria) in the form of blown films of high transparency (35-μm thickness). Sheets (1.0 mm) of ultrahigh molecular weight polyethylene (UHMW-PE; Hostalen GUR from Hoechst, Germany) were received from commercial suppliers. SO<sub>2</sub> (Linde) was of 99.9% purity and compressed air was obtained from AGA (technical grade). Poly(4-styrene sulfonic acid) was prepared from poly(sodium 4-styrene sulfonate) (Aldrich, *M*<sub>w</sub> = 70 000 g·mol<sup>-1</sup>) by acidification with concentrated HCl.

**Physical Measurements.** FTIR spectra were taken with a Bomem M100 spectrometer. For ATR spectra a Spectratech advanced analytical microscope equipped with a ZnSe ATR objective was employed. UV/vis spectra were recorded with a Lambda 9 UV/vis/NIR spectrometer. Contact angles, θ, of water (sessile drop) were measured with a Fibro 1100 Dat MkII dynamic absorption tester (deionized water, 4-μL drop volume, 1-s delay time). The θ values reported are averaged over six individual samples.

**EDX Spectroscopy.** EDX spectra were recorded and evaluated with a Noran Voyager X-ray spectrometer attached to a Zeiss DSM 982 Gemini (5-kV acceleration voltage). Noran Voyager uses top hat filtering for background subtraction and reference spectra for peak deconvolution. All specimens were coated with a thin carbon layer to obtain an electrically conductive surface. The error limit for the sulfur concentrations determined was estimated to ±25% (relative error). Although strong specimen damage was not observed, additional error may be due to the diffusion or evaporation of sulfur compounds.

**XPS Measurements.** X-ray photoelectron spectra were taken with a Kratos XSAM 800 spectrometer (twin anode (Mg, Al) X-ray tube). The acquired photoelectron spectra were excited with Mg Kα radiation. The angle between the X-rays and the detected electrons was fixed to 70° and the samples were aligned such that the analyzer was located along the normal to the sample surface. The depth of XPS analysis was in the range of a few nanometers. The following photoelectron peaks were evaluated: C 1s, O 1s, and S 2p. The binding energy of C 1s photoelectrons was defined to 285.0 eV (reference peak). The shifts of O 1s and S 2p photoelectrons were calculated with reference to the C 1s signal.

**Irradiation Setup.** The polyethylene samples to be irradiated were placed in an irradiation chamber made from steel. The chamber was equipped with a quartz front plate, a gas inlet, and a gas outlet. The distance between the inner face of the quartz window and the sample surface was 2.0 mm. During the irradiation experiment, a gas stream consisting of SO<sub>2</sub> and compressed air was passed through the irradiation chamber. The composition of the gas mixture was adjusted with gas valves and controlled with bubble gauges. The total flow was

(10) Armbruster, K.; Osterhold, M. *Kunststoffe* **1990**, *80*, 11.

(11) Bevington, J. C.; Ratti, L. *Eur. Polym. J.* **1972**, *8*, 1105.

(12) Niino, H.; Yabe, A. *Appl. Phys. Lett.* **1993**, *63*, 3527.

(13) Meyer, U.; Kern, W.; Ebel, M. F.; Svagara, R. *Macromol. Rapid Commun.* **1999**, *20*, 515.

(14) Okoshi, M.; Murahara, M.; Toyoda, K. *J. Mater. Res.* **1992**, *7*, 1912.

(15) Braun, M.; Maurette, M.-T.; Oliveros, E. *Photochemical Technology*; John Wiley & Sons: Chichester, 1991; pp 354–396.

(16) Ogata, Y.; Izawa, Y.; Tsuda, T. *Tetrahedron* **1965**, *21*, 1349.

(17) Graf, R. *Liebigs Ann. Chem.* **1952**, *578*, 50.

$\approx 5 \text{ L}\cdot\text{h}^{-1}$  in all cases. Before entering the irradiation chamber, the gas mixture was passed through a tube containing  $\text{P}_4\text{O}_{10}$  as the desiccant. The volume fraction  $\chi = \text{volume}_{\text{SO}_2} / (\text{volume}_{\text{SO}_2} + \text{volume}_{\text{air}})$  was applied to characterize the composition of the gas mixture. For irradiation, the unfiltered light of a 1300-W Hg lamp (Heraeus) was employed. The distance between the Hg lamp and the PE surface was 15 cm. During irradiation, the PE samples were at a temperature between 50 and 60 °C. The intensity of the 254-nm line was  $1.5 \text{ mJ}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$  at the sample surface as determined with a ferrioxalate actinometer solution<sup>18</sup> in combination with a 254-nm interference filter (Melles Griot). For patterned illuminations, a chromium pattern on a quartz plate was projected onto the sample surface. For this purpose, the optical setup was equipped with a condenser lens ( $f = 200 \text{ mm}$ ), a light stop, and a projection lens ( $f = 50 \text{ mm}$ ). The mask pattern was reduced by a factor of 5.

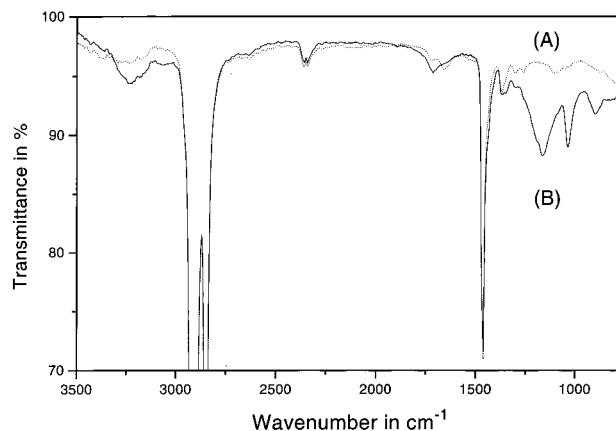
**Irradiation Procedure.** PE samples (size  $10 \times 10 \text{ mm}$ ) were purified by immersion into a mixture of acetone and water (1:1 v/v) employing an ultrasonic bath (10 min, 30 °C). After being dried in vacuo (20 mbar, 30 min at 20 °C), the PE samples were placed in the irradiation chamber and kept in the desired gas atmosphere for a defined period of time (conditioning time  $t_c$  without UV irradiation) to allow diffusion of the gases into the polymer. Subsequently, the samples were irradiated in this gas atmosphere for a period of time,  $t_i$ . After being removed from the chamber, the PE samples were purified by immersion into acetone/ $\text{H}_2\text{O}$  (1:1 v/v) in an ultrasonic bath (10 min, 30 °C). This extraction process ensured the removal of soluble reaction products and excess  $\text{SO}_2$ . After being dried in vacuo (20 mbar, 30 min at 50 °C), the samples were subjected to analysis.

**Dyeing of Irradiated Samples.** After UV irradiation and extraction with acetone/ $\text{H}_2\text{O}$ , the PE samples were immersed into a dye bath for 120 s. The dye bath contained 1.0 wt % of methylene blue (MB) in a mixture of methanol and 1,4-dioxane (3:1 v/v). After being dyed, the samples were washed with acetone and water and finally dried in vacuo (30 min, 50 °C).

## Results and Discussion

In contrast to the industrial photosulfonation of alkanes, which is carried out in the liquid phase, the photomodification process was performed as a gas/solid reaction at a polymer (PE) surface. Prior to irradiation, the PE samples were kept in an atmosphere containing  $\text{SO}_2$  and  $\text{O}_2$  for a defined period of time,  $t_c$ , to allow diffusion of  $\text{SO}_2$  and  $\text{O}_2$  into the polymer. After this conditioning period, the samples were irradiated with the unfiltered light of a Hg lamp for a period of time,  $t_i$ . Subsequent extraction of the polymer surface with acetone/ $\text{H}_2\text{O}$  ensured the removal of soluble reaction products and excess  $\text{SO}_2$ .

The surface analysis of the PE samples was concerned with the detection of sulfonic acid groups as irradiation products. Figure 1 shows ATR-FTIR spectra of an LDPE film (35  $\mu\text{m}$ ) before and after photomodification in the presence of  $\text{SO}_2$  and  $\text{O}_2$ . In this case, the gas mixture contained 50 vol %  $\text{SO}_2$  ( $\chi = 0.5$ ) and the irradiation time  $t_i$  was 5 min ( $t_c = 2 \text{ min}$ ). Besides the typical IR bands of PE (2916 and  $2850 \text{ cm}^{-1}$  (C–H valence vibration),  $1460$  and  $1371 \text{ cm}^{-1}$  (C–H deformation vibration), and  $736 \text{ cm}^{-1}$  (– $\text{CH}_2$ – rocking vibration)), new bands around  $3200 \text{ cm}^{-1}$  and at  $1038$  and  $1156 \text{ cm}^{-1}$  were detected after UV irradiation. The signal at  $1038 \text{ cm}^{-1}$  is attributed to the symmetric stretching vibration of  $\text{SO}_3$  units, and the band at  $1156 \text{ cm}^{-1}$  originates from



**Figure 1.** ATR-FTIR spectra of an LDPE film (35- $\mu\text{m}$  thickness). (A) Before irradiation and (B) after UV irradiation in the presence of  $\text{SO}_2$  and air followed by extraction with acetone/ $\text{H}_2\text{O}$ .

the asymmetric vibration mode of  $\text{SO}_3$  units.<sup>19</sup> The position of these bands is typical of sulfonic acids, which can be distinguished from sulfinic acids, organic sulfates, and sulfones by means of FTIR spectroscopy.<sup>19</sup> The broad signal around  $3200 \text{ cm}^{-1}$  is then assigned to the O–H units of the sulfonic acid groups. The intensities of the IR bands at  $1038$  and  $1156 \text{ cm}^{-1}$ , which were measured after washing with acetone/ $\text{H}_2\text{O}$ , were  $\approx 30\%$  lower than those in the spectra taken immediately after UV irradiation. This suggests that soluble components were extracted during the washing procedure. The ATR-FTIR spectrum in Figure 1 does not suggest significant photooxidation of LDPE as only weak signals evolved in the carbonyl region.

EDX spectra of the modified PE surface showed a signal typical of sulfur at 2.3 keV. To investigate the surface more precisely, XPS was applied. The XP spectrum of the unmodified LDPE surface displayed only a C 1s signal with a binding energy of 285.0 eV. After the irradiation process, additional XPS signals in the O 1s and S 2p region were detected. The position of the O 1s signal in the irradiated LDPE sample was 532.4 eV. This is in good agreement with the O 1s signal of poly(4-styrene sulfonic acid) at 533.0 eV.

Figure 2 displays a detail of the XP spectrum of the modified LDPE surface (S 2p region). For comparison, the S 2p region of poly(4-styrene sulfonic acid) is shown in Figure 3. The S 2p peaks were deconvoluted into the low-energy S  $2\text{p}^{3/2}$  and the high-energy S  $2\text{p}^{1/2}$  signals. The Gaussian fits are displayed as dotted lines in Figure 2 and Figure 3. Theoretically, the relative peak ratio of the S  $2\text{p}^{3/2}$  and S  $2\text{p}^{1/2}$  signals is  $1.15:0.59 = 1.95$ , as calculated from their different cross sections of photoionization.<sup>20</sup>

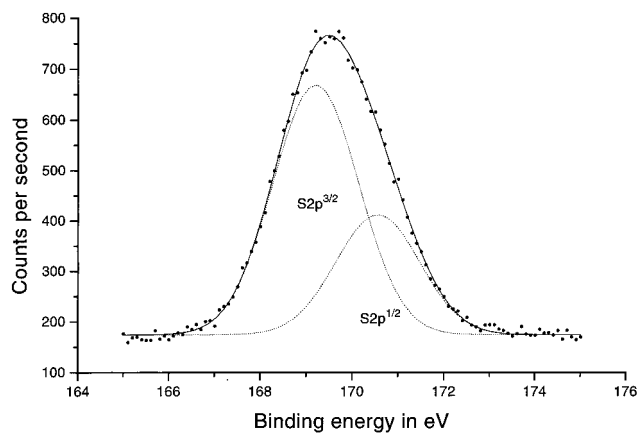
The photosulfonated LDPE surface gave an S  $2\text{p}^{3/2}$  signal at 169.2 eV and an S  $2\text{p}^{1/2}$  signal at 170.6 eV. These values are in acceptable agreement with the S 2p peaks of poly(4-styrene sulfonic acid) (S  $2\text{p}^{3/2}$ , 169.5 eV; S  $2\text{p}^{1/2}$ , 170.8 eV). For comparison, literature data for poly(sodium 4-styrene sulfonate)<sup>8,21</sup> are given. For this polymer, an S  $2\text{p}^{3/2}$  signal at 168.2 eV<sup>21</sup> (ref 8: 168.7

(18) Hatchard, G.; Parker, C. A. *Proc. R. Soc. (London)* **1956**, *A235*, 518.

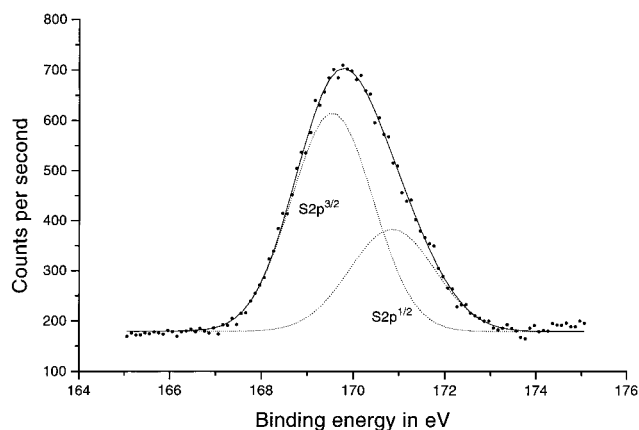
(19) Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley & Sons: Chichester, 1998.

(20) Inagaki, N.; Tasaka, S.; Miyazaki, H. *J. Appl. Polym. Sci.* **1989**, *38*, 1829.





**Figure 2.** Detail XP spectrum (S 2p region) of LDPE after UV irradiation in the presence of SO<sub>2</sub> and air. (●) Experimental data; (...) Gaussian fits for the S 2p<sup>3/2</sup> and S 2p<sup>1/2</sup> peaks with maxima at 169.2 and 170.6 eV.

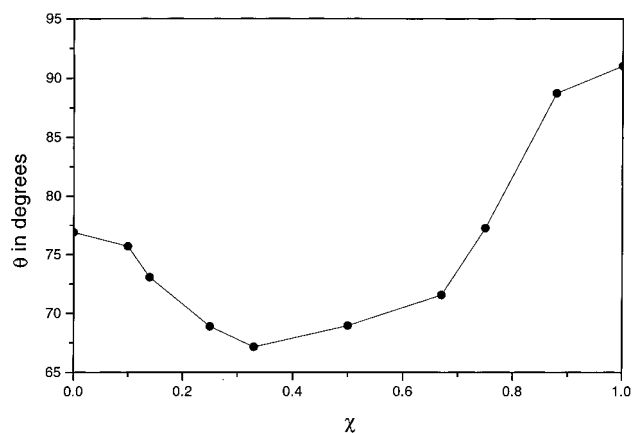


**Figure 3.** Detail XP spectrum (S 2p region) of poly(4-styrene sulfonic acid). (●) Experimental data; (...) Gaussian fits for the S 2p<sup>3/2</sup> and S 2p<sup>1/2</sup> peaks with maxima at 169.5 and 170.8 eV. (eV) and an S 2p<sup>1/2</sup> signal at 169.4 eV<sup>21</sup> (ref 8: 169.8 eV) were reported.

From the XP spectra in Figures 2 and 3 the intensity ratios of the integrated S 2p<sup>3/2</sup> and S 2p<sup>1/2</sup> peaks were calculated. Both for photosulfonated LDPE and for poly(4-styrene sulfonic acid) a ratio of S 2p<sup>3/2</sup>:S 2p<sup>1/2</sup> = 2.1:1 was obtained, which is in good correspondence with the theoretical prediction. This finding indicates that sulfonic acid groups are the main reaction product at the LDPE surface. However, side products such as sulfates and monoesters of sulfuric acid, which are known to be formed during photosulfonation,<sup>15,18</sup> cannot be excluded because these compounds would also give S 2p signals in the high-energy range. Functional groups, where sulfur is attached to one or two oxygen atoms, do not seem to be present. Such groups would be detectable from S 2p signals at lower binding energies (e.g., for poly(hexamethylene sulfone) an the S 2p<sup>3/2</sup> peak at 167.6 eV was reported<sup>21</sup>).

In conclusion, FTIR and XPS data showed that UV irradiation of LDPE in the presence of SO<sub>2</sub> and air leads to the attachment of sulfonic acid groups onto the surface.

**Variation of the Gas Composition.** To determine the optimum volume ratio SO<sub>2</sub>/air for the photomodifi-



**Figure 4.** Photomodification of LDPE in the presence of SO<sub>2</sub> and air. Contact angle  $\theta$  (water) as a function of the volume fraction  $\chi$  of SO<sub>2</sub> in the gas mixture (irradiation time,  $t_i = 3$  min).

cation of LDPE surfaces, the volume fraction  $\chi = \text{volume}_{\text{SO}_2} / (\text{volume}_{\text{SO}_2} + \text{volume}_{\text{air}})$  in the mixture SO<sub>2</sub>/air was varied from  $\chi = 0$  to  $\chi = 1$ . The conditioning time  $t_c$  was 2 min, and the irradiation time  $t_i$  was kept constant at 3 min in these experiments.

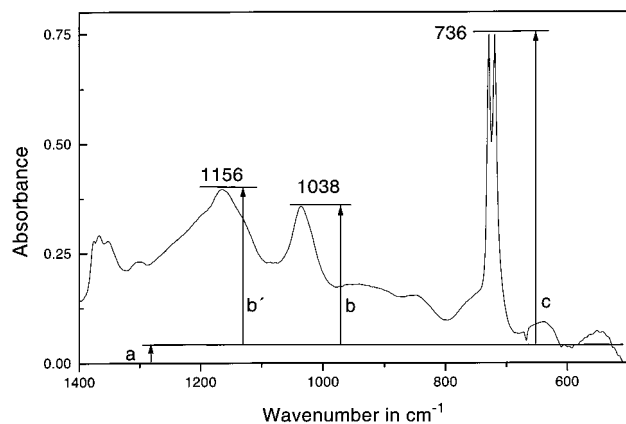
The wetting behavior of the modified LDPE surfaces was examined by contact angle measurements. Figure 4 shows the contact angle  $\theta$  of water as a function of the gas composition. Compared to the contact angle of unmodified PE ( $\theta = 97^\circ$ ),  $\theta$  dropped significantly as a result of irradiation in an SO<sub>2</sub>/air atmosphere. Optimum wetting ( $\theta \sim 67^\circ$ ) was obtained with a gas composition ( $\chi = 0.3$ ) that contained slightly more SO<sub>2</sub> than the stoichiometric amount ( $\chi = 0.285$ ). Irradiation under air ( $\chi = 0$ ) led to a decrease of the contact angle of water to  $\theta \sim 77^\circ$ . This is probably due to some photooxidation of the polyethylene surface. Irradiation in a pure SO<sub>2</sub> atmosphere caused only a small effect on the contact angle ( $\theta \sim 91^\circ$ ).

To obtain information on the relative amount of sulfonic acid groups attached to the LDPE film, absorbance FTIR spectra were recorded. The quantification of the FTIR signals due to the symmetric (1038 cm<sup>-1</sup>) and asymmetric (1156 cm<sup>-1</sup>) vibration modes of -SO<sub>3</sub>H units was performed, as shown in the absorbance FTIR spectrum given in Figure 5. The absorbance at 600 cm<sup>-1</sup> (value  $a$ ) was regarded as the baseline value. The absorbance values at 1038 and 1156 cm<sup>-1</sup> (values  $b$  and  $b'$  in Figure 5) were compared to the absorbance  $c$  at 736 cm<sup>-1</sup> (-CH<sub>2</sub>- rocking vibration). The ratios  $(b/c) \times 100$  and  $(b'/c) \times 100$  were taken as a measure of the progress of the photosulfonation reaction. Figure 6 displays the ratios  $(b/c) \times 100$  and  $(b'/c) \times 100$  as a function of the gas composition ( $t_c = 2$  min and  $t_i = 5$  min in all cases). The maximum amount of sulfonic acid groups was obtained from  $\chi = 0.25$  to  $\chi = 0.5$ . When the LDPE film was irradiated in a pure SO<sub>2</sub> atmosphere ( $\chi = 1$ ), no additional FTIR signals evolved.

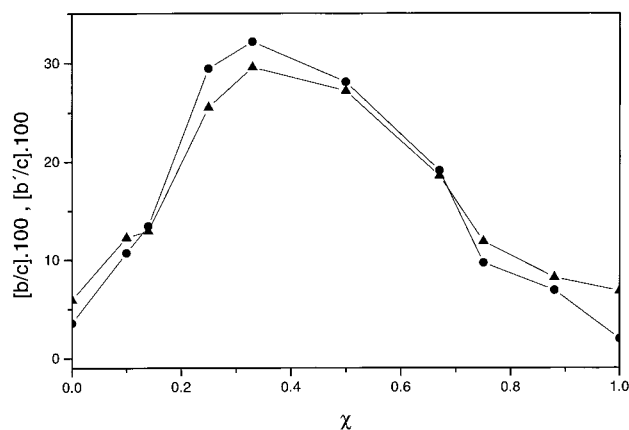
Methylene blue (MB), a cationic dye, is commonly employed for the quantitative analysis of alkane sulfonates and related compounds.<sup>22</sup> The modified LDPE films were dyed with MB to obtain another measure of the amount of sulfonic acid groups introduced. MB will

(21) Beamson, G.; Briggs, D. *High-Resolution XPS of Organic Polymers*; John Wiley & Sons: Chichester, 1992.

(22) Longwell, J.; Maniece, W. D. *Analyst* **1955**, *80*, 167.



**Figure 5.** Absorbance FTIR spectrum of LDPE after UV irradiation in the presence of  $\text{SO}_2$  and air. Quantification of the signals at 1038 and 1156  $\text{cm}^{-1}$  characteristic of sulfonic acid groups.

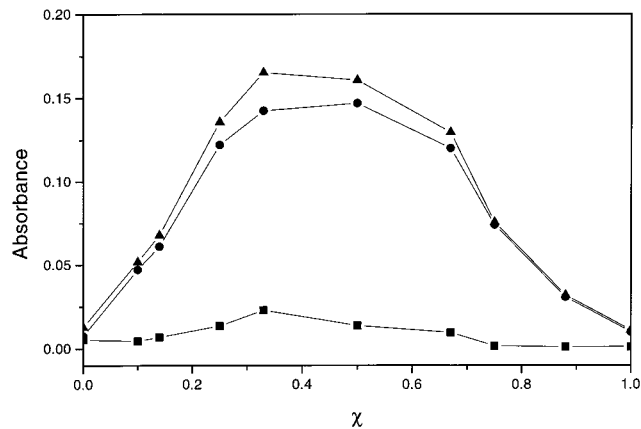


**Figure 6.** Photomodification of LDPE in the presence of  $\text{SO}_2$  and air. Relative intensity of the IR signals typical of sulfonic acid groups as a function of the volume fraction  $\chi$  of  $\text{SO}_2$  in the gas mixture (irradiation time,  $t_i = 5$  min). ( $\blacktriangle$ )  $(b/c) \times 100$  (signal at 1038  $\text{cm}^{-1}$ ); ( $\bullet$ )  $(b'/c) \times 100$  (signal at 1156  $\text{cm}^{-1}$ ).

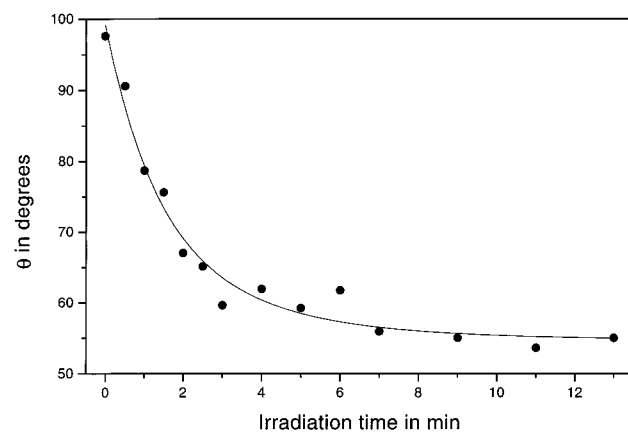
also form complexes with carboxylic acids, which may be present as photooxidation products. Consequently, dyeing with MB rather reflects the amount of ionizable groups at the LDPE surface.

The conditioning time  $t_c$  was 2 min and the irradiation time  $t_i$  was 5 min in these experiments. Figure 7 displays the absorbance at 600 nm of UV-irradiated LDPE films before and after the dyeing process. A slight brownish coloration of the LDPE films was observed as a result of the UV irradiation. This gave rise to some absorbance at 600 nm before the dyeing step. The coloration was most pronounced when a gas composition with  $\chi = 0.33$  was employed. The differences between the absorbance values at 600 nm measured before and after dyeing, which reflect the binding of MB to ionizable groups, is also plotted in Figure 7. Maximum MB dyeing was found between  $\chi = 0.25$  and  $\chi = 0.5$ . This finding is in correspondence with the results from contact angle and FTIR measurements.

Irradiation under air ( $\chi = 0$ ) produced only negligible amounts of ionizable groups (e.g., carboxylic acids) at the LDPE surface as no MB dyeing was obtained in this case. Similarly, UV irradiation in pure  $\text{SO}_2$  ( $\chi = 1$ ) generated only minute amounts of ionizable groups at the polymer surface. A similar result had been obtained



**Figure 7.** Photomodification of LDPE in the presence of  $\text{SO}_2$  and air. Absorbance at  $\lambda = 600$  nm as a function of the volume fraction  $\chi$  of  $\text{SO}_2$  in the gas mixture (irradiation time,  $t_i = 5$  min). ( $\blacksquare$ ) After UV irradiation and ( $\blacktriangle$ ) after subsequent dyeing with methylene blue; ( $\bullet$ ) difference of these values.



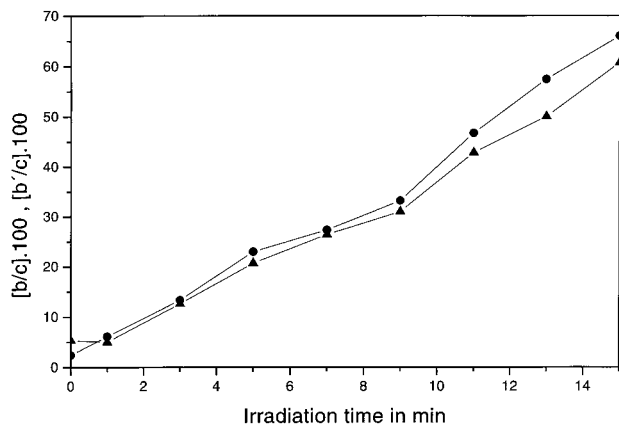
**Figure 8.** Photomodification of LDPE in the presence of  $\text{SO}_2$  and air ( $\chi = 0.5$ ). Contact angle  $\theta$  of water as a function of the irradiation time,  $t_i$ .

from contact angle measurements and FTIR spectra. Although the formation of sulfonic acids during UV irradiation of alkanes in the presence of pure  $\text{SO}_2$  has been reported in the literature,<sup>17,23</sup> the irradiation of LDPE surfaces in the presence of pure  $\text{SO}_2$  did not cause pronounced changes of the surface properties.

Summing up, good wetting and dyeing of LDPE surfaces were obtained by UV irradiation in a gas atmosphere containing  $\text{SO}_2$  and air when the volume fraction  $\chi$  of  $\text{SO}_2$  was  $\approx 0.5$  (this corresponds to a volume ratio of  $\text{SO}_2:\text{O}_2 \sim 5:1$ ). Employing this gas composition, the brownish coloration of the LDPE samples caused by UV irradiation was only moderate.

**Variation of the Irradiation Time.** The efficiency of surface modification processes largely depends on the time required for the particular treatment. Bearing this in mind, the influence of the irradiation time on the extent of the surface modification of LDPE was investigated. For these experiments a gas mixture with  $\chi = 0.5$  was applied. The conditioning time  $t_c$  was 2 min in all cases.

Figure 8 displays the contact angle  $\theta$  of water on the LDPE surface as a function of the irradiation time,  $t_i$ .



**Figure 9.** Photomodification of LDPE in the presence of  $\text{SO}_2$  and air ( $\chi = 0.5$ ). Relative intensity of the IR signals typical of sulfonic acid groups as a function of the irradiation time,  $t_i$ . (▲)  $(b/c) \times 100$  (signal at  $1038 \text{ cm}^{-1}$ ); (●)  $(b'/c) \times 100$  (signal at  $1156 \text{ cm}^{-1}$ ).

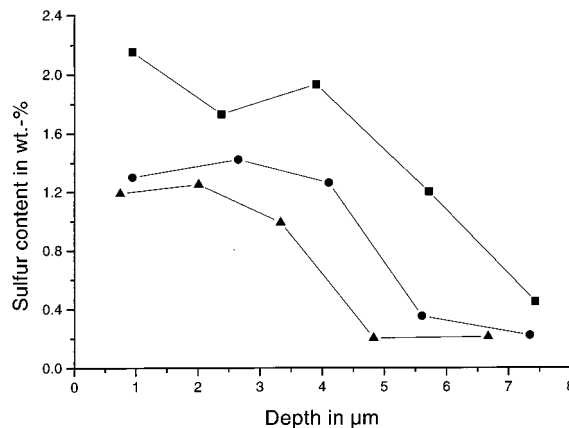
For irradiation times,  $t_i$ , between 0 and 3 min, the contact angle dropped almost linearly from  $\theta = 97^\circ$  (unmodified LDPE) to  $\theta \sim 60^\circ$ . However, at  $t_i > 3$  min, the contact angle remained almost constant in the range  $55^\circ < \theta < 60^\circ$ .

These results were interpreted in the following way: prolonged irradiation leads to the incorporation of an increasing number of sulfonic acid groups at the LDPE surface. Photosulfonation would produce a mixture of mono-, di-, and polysulfonated polyethylene chains of different molecular weights, which have different solubilities. At the same time the polymer chains may undergo cross-linking and chain fragmentation reactions; see, for example, ref 24. Polysulfonated PE chains, low molecular weight reaction products and photofragmentation products in layers near the surface will be preferably extracted during the washing procedure with acetone/ $\text{H}_2\text{O}$ . This may in part account for the invariance of the contact angle  $\theta$  after prolonged UV irradiation.

As mentioned above, the intensities of the IR bands at  $1038$  and  $1156 \text{ cm}^{-1}$  in the modified LDPE films decreased by  $\approx 30\%$  when the samples were extracted with acetone/ $\text{H}_2\text{O}$ . This finding is further indication that surface layers of PE are solubilized as a result of the photosulfonation process.

FTIR spectroscopy was found valuable in following the progress of photosulfonation. Figure 9 displays the band ratios  $(b/c) \times 100$  and  $(b'/c) \times 100$  (compare Figure 5) as a function of the irradiation time,  $t_i$ . The band ratios, considered as a measure for the total amount of sulfonic acid groups in the LDPE film, increased almost linearly with  $t_i$ . This indicates that photosulfonation also proceeds in deeper layers of the LDPE film as  $t_i$  is prolonged (changeover to bulk modification).

**Depth Profile of Photomodification.** The results obtained so far suggest that the photosulfonation of solid PE is not restricted to the surface and that deeper layers are also modified when  $t_i$  is increased. Clearly, the depth of photomodification will depend on the diffusion of  $\text{SO}_2$  and  $\text{O}_2$  into the polymer and also on the UV light intensity in deeper layers of the polymer. To obtain



**Figure 10.** Photomodification of UHMW-PE in the presence of  $\text{SO}_2$  and air ( $\chi = 0.5$ ). Sulfur content as a function of depth. (▲)  $t_c = 0$  min,  $t_i = 5$  min; (●)  $t_c = 2$  min,  $t_i = 5$  min; (■)  $t_c = 2$  min,  $t_i = 10$  min.

**Table 1. Depth Profile of the Photomodification of Polyethylene (UHMW-PE) after UV Irradiation in the Presence of  $\text{SO}_2$  and Air**

sample	$t_c$ (min)	$t_i$ (min)	approximate depth of modification ( $\mu\text{m}$ )
1	0	5	4
2	2	5	5
3	2	10	7

depth profiles of the photomodification, we analyzed cross sections of photosulfonated polyethylene. To facilitate sample preparation, sheets of UHMW-PE were investigated in this case. However, it should be noted that UHMW-PE and LDPE are different with respect to diffusion and general behavior.

Three samples of UHMW-PE were irradiated in an  $\text{SO}_2$ /air atmosphere with  $\chi = 0.5$ . The times of conditioning ( $t_c$ ) and UV irradiation ( $t_i$ ) were varied; see Table 1. After the samples were washed with acetone/ $\text{H}_2\text{O}$  and dried, cross sections were prepared and investigated by means of EDX. EDX spectra (point scans) were taken at five positions at distances between 0 and  $8 \mu\text{m}$  beneath the PE surface. From the intensity of the EDX signal at  $2.3 \text{ keV}$  the sulfur content of the PE sample was calculated.

Figure 10 shows the distribution of the sulfur content (in wt %) as a function of depth (estimated error limit for the sulfur contents:  $\pm 25\%$  relative error). It can be seen that the photomodification process extends to several micrometers beneath the PE surface and that both the conditioning time,  $t_c$ , and the irradiation time,  $t_i$ , have a pronounced influence on the result. At irradiation times of  $t_i = 5$  min ( $t_c = 0$  and  $2$  min, respectively) a sulfur content of  $\approx 1.2$  wt% was determined in the outer layers. Figure 10 shows that the thickness of the modified layer increased from  $\approx 4$  to  $\approx 5 \mu\text{m}$  when the PE samples were conditioned for  $t_c = 2$  min prior to irradiation. With  $t_i = 10$  min the penetration depth increased to  $\approx 7 \mu\text{m}$ . In this case the sulfur content in the PE layers near the surface amounted to  $\approx 2$  wt%. This corresponded to an incorporation of about one  $\text{SO}_3\text{H}$  unit per 100 carbon atoms.

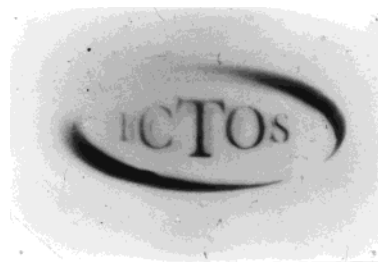
The UV absorbance ( $254 \text{ nm}$ ) of the UHMW-PE employed was  $\approx 0.3$  for  $10\text{-}\mu\text{m}$  films. This corresponds to an attenuation of the incident UV light by  $50\%$  after a  $10\text{-}\mu\text{m}$  penetration depth. Therefore, it can be concluded

that diffusion of  $\text{SO}_2$  and  $\text{O}_2$  into the polymer, rather than the attenuation of the UV light intensity, is the limiting factor for the photosulfonation process. It is also probable that the photoreaction occurs to a different extent in crystalline and amorphous regions of PE.

The depths of modification obtained by the presented photochemical process are in distinct contrast to those obtained with other techniques of surface modification. For example, corona and plasma treatments usually give modification depths in the nanometer range.

**Patterned Photomodification.** An unique feature of photochemical surface modifications is the possibility to carry out patterning processes. To demonstrate this, a chromium pattern on a quartz plate was projected onto a LDPE surface positioned in an atmosphere containing  $\text{SO}_2$  and air ( $\chi = 0.5$ ). The optical setup ensured a reduction of the mask pattern by a factor of 5. After undergoing UV irradiation ( $t_c = 2$  min;  $t_i = 5$  min) and being washed with acetone/ $\text{H}_2\text{O}$ , the sample was dyed with methylene blue to make the irradiated zones visible. Figure 11 shows the emblem of our institute on the LDPE surface (original size  $\approx 6 \times 3$  mm). This experiment demonstrates that such photomodifications can be applied to obtain patterns containing sulfonic acid groups at PE surfaces. When projection lithography is employed, even finer structures such as gratings and so forth should be possible.

The photosulfonation of solid PE is another example for a photomodification of polymer surfaces employing



**Figure 11.** Patterned photomodification of LDPE. The mask pattern projected onto the surface was made visible by dyeing with MB (original size:  $6 \times 3$  mm).

UV-sensitive gases. Additional experiments are in progress to achieve a transformation of the sulfonic acid groups to sulfochlorides, sulfonamides, and so forth. The application of the described modification process to polymers other than polyethylene is also under investigation.

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