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Trialkylsilanes as reagents for the UV-induced surface modification of polybutadiene

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Abstract

A photochemical process for the modification of polymer surfaces using organosilane compounds has been developed. The process is based upon the UV irradiation of polybutadiene in the presence of liquid ethyldimethylsilane $(C_2H_5)(CH_3)_2Si$–H and gaseous trimethylsilane $(CH_3)_3Si$–H. UV irradiation was carried out with a medium pressure Hg lamp and a 193 nm ArF* excimer laser. The modified polymer surfaces were investigated by infrared (FTIR) and X-ray photoelectron spectroscopy (XPS), contact angle measurements and atomic force microscopy (AFM). It is found that the photoassisted surface modification with trialkylsilanes leads to the introduction of trialkylsilyl groups onto the surface of the target polymer. From quantitative XPS data the composition of the modified polymer suface (C, O and Si) was determined. The surface modification with trialkylsilanes results in a significant lowering of surface tension γ of polybutadiene. The silane/UV process was found to be very sensitive to small amounts of oxygen in the process gas. Summing up, it is demonstrated that UV irradiation in the presence of gaseous silane compounds is a convenient way to introduce organosilicon groups onto the surface of technical polymers.

Keywords: Polybutadiene; Photochemistry; Trialkylsilanes

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1. Introduction

Most technical polymers can be tailored to meet specific mechanical and technical requirements. However, in many cases the hydrophobic nature of most polymer surfaces causes problems related to adhesion, wetting and coating. Over the past decades extensive work has been carried out to modify and to improve the chemical and physical properties of polymer surfaces. Properties such as chemical composition, hydrophilicity, conductivity and crosslink density of polymers can be altered by a variety of techniques. Surface modification techniques based upon wet-chemical etching, corona and plasma discharges and radiation induced grafting are well established [1].

In addition to this, processes based on UV light in the presence of reactive gases have been developed over the past years. Examples for such techniques are UV induced photo-oxidation [2], photochlorination and photobromination [3], the photomodification of PTFE with hydrazine [4] as well as the introduction of sulfonic groups onto polyethylene via photosulfonation processes using mixtures of SO_2 and O_2 [5]. In general, UV processes do not require costly equipment and offer the advantage of patterned surface modification by use of lithographic techniques.

It was interested to see if organosilicon groups can be introduced onto polymer surfaces by photochemical techniques. The hydrosilylation process is well known in organic chemistry. Over the past years hydrosilylation of alkenes, carbonyl compounds and alkynes in the presence of free radical initiators (e.g. azo-bis-isobutyronitrile) has been investigated thoroughly. Compounds such as tris(trimethylsilyl)silane ($(Me_3Si)_3Si$–H, TMSS) are now used as hydrosilylation reagents and also as reducing agents in the synthesis of organic fine chemicals [6–8].

The Si–H bond dissociation energy (BDE) of trialkylsilanes R_3Si–H and the reactivity of trialkylsilyl radicals $R_3Si^{\cdot}$ has been subject of numerous studies. While the BDE of simple trialkylsilanes is similar (trimethylsilane: 378 kJ mol^{-1} [9]; triethylsilane: 380 kJ mol^{-1} [10]), the BDE of triphenylsilane amounts to 350 kJ mol^{-1} [10]. Successive substitution with trimethylsilyl groups at the Si–H unit weakens the Si–H bond

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strength significantly and thus increases the hydrogen donor ability of alkylsilanes. So the BDE of *tris*(trimethylsilyl)silane (TMSS) amounts to 330 kJ mol^{-1} [11,12] and consequently TMSS is an excellent hydrogen donor.

Considering free radical chemistry, trialkylsilyl radicals $R_3Si^{\cdot}$ belong to the most reactive species towards various functional groups [13,14]. Radicals $R_3Si^{\cdot}$ add to olefins and also to aromatic rings at high rate constants. As an example, for the addition of $Et_3Si^{\cdot}$ to cyclohexene a rate constant of 9.4×10^5 M^{-1} s^{-1} has been reported. The addition of radicals $R_3Si^{\cdot}$ to olefines is a strongly exothermic reaction with an estimated value of $\Delta H = -125$ kJ mol^{-1} [14]. So it is not surprising that the addition of trimethylsilyl radicals $Me_3Si^{\cdot}$ to 1-hexene is practically irreversible up to temperatures of 140 °C. In contrast to this, the addition of TMSS radicals $(Me_3Si)_3Si^{\cdot}$ to many alkenes proceeds in a reversible manner and can induce *cis–trans* isomerizations following the so-called *Schenck* mechanism [14]. Generally, the hydrosilylation of olefins is described as a radical chain reaction, with the crucial chain carrying step, the hydrogen abstraction by an alkyl radical from the silane R_3Si–H, being exothermic. For the hydrogen abstraction step the ΔH values amount to -27 kJ mol^{-1} for trialkylsilanes and to -80 kJ mol^{-1} for TMSS [10]. Thiols can be used as catalysts for the radical chain hydrosilylation by introducing more rapid propagation steps [15].

From this point of view trialkylsilanes appear to be promising reagents for the surface modification of C=C unsaturated polymers such as polybutadiene. While the reagent TMSS is very common in the hydrosilylation of organic chemicals, the vapour pressure of TMSS (bp = 82 °C at 16 mbar) turned out to be too low for a surface photomodification process based on gaseous reagents. Instead, ethyldimethylsilane (EDMS), a low-boiling liquid, and trimethylsilane (TrMS), available as a liquified gas, were chosen as reagents. *Cis*-1,4-polybutadiene with 98% *cis*-content was selected as target polymer for the present investigation.

In the following, the surface modification of *cis*-1,4-polybutadiene with the organosilanes EDMS and TrMS under UV radiation of a Hg lamp and a 193 nm ArF* excimer laser will be described. Surface analysis is carried out with various techniques, among them infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and contact angle measurements.

The compounds ethyldimethylsilane (EDMS) and trimethylsilane (TrMS) have high vapour pressures, are easy to handle, non-toxic and almost odourless. Although they are flammable compounds, they do not tend to self-ignition upon contact with moisture or oxygen (in contrast to silane SiH_4). These beneficial properties facilitate handling of the reagents both in laboratory experiments and in technical processes.

2. Experimental

2.1. Materials and sample preparation

Ethyldimethylsilane EDMS (bp 46 °C) was obtained from Sigma Aldrich. Trimethylsilane TrMS (bp 7 °C) was purchased from A.B.C.R. (Germany) in the form of a liquified gas. *Cis*-1,4-polybutadiene (98% *cis*) with $M_w \sim 2{,}000{,}000$ g mol^{-1} was supplied by Aldrich. Prior to use the polymer was purified by repeated reprecipitation from toluene/ethanol. Polymer films were prepared by spincasting of polymer solutions (2 wt% in toluene) onto CaF_2 and KBr discs (2 mm thickness, 20 mm diameter). The polymer films were then dried in vacuo (1 mbar) at ambient temperature. Film thicknesses were ca. 250 nm for polybutadiene as measured by ellipsometry.

2.2. UV and FTIR spectroscopy

UV spectra were recorded with a Jasco V-530 UV–vis spectrometer. The absorption spectrum of liquid EDMS was measured with a 1 mm quartz cuvette (QS 110, Hellma, Germany). For TrMS a cylindric gas cuvette (QS 120, Hellma, Germany) with 100 mm pathlength was used. The gas cuvette was purged with N_2 for 10 min and then immediately filled with TrMS gas at a pressure of 1 bar. FTIR spectra were run with a Perkin–Elmer Spectrum One instrment (spectral range between 4000 and 450 cm^{-1}). All FTIR spectra of the polymer samples were recorded in transmission mode.

2.3. UV irradiation experiments

Most UV irradiation experiments were carried out with an unfiltered medium pressure Hg lamp (Heraeus, 1000 W). For these experiments, light intensity (power density) at the sample surface was measured with a spectroradiometer (Solatell, Sola Scope 2000TM, spectral range from 230 to 470 nm). The light intensity was 4.23 mW cm^{-2} (range: 250–254 nm). These values were obtained directly from the polychromatic spectrum of the Hg lamp.

Additional emission spectra of this Hg lamp (covering the range 200–600 nm) were kindly supplied by the manufacturer (Heraeus, Germany).

Laser irradiation experiments were performed with a 193 nm ArF* excimer laser (Lambda Physik LPX 100, 10 Hz repetition rate, pulse duration ~20 ns). The rectangular beam of the excimer laser was expanded by means of two cylindical lenses (focal lengths 63 and 310 mm) made from quartz. For laser UV irradiation, the light intensity was recorded with a pyroelectric detector (Gentec DE-200) being calibrated for 9.68 V J^{-1}. The energy density at the sample surface was 14.3 mJ cm^{-2} per pulse ($\lambda = 193$ nm).

Polymer samples (250 nm films cast onto CaF_2 and KBr discs) were inserted into an irradiation chamber (Fig. 1). The distance between the inner face of the front window (made from CaF_2) and the sample surface was 7 mm. Polymer films were irradiated either with a Hg lamp or a pulsed ArF* excimer laser in the presence of EDMS or gaseous TrMS. Prior to all UV irradiations the sample chamber was purged for 20 min with inert gas (N_2 99.999% from air liquide, flow rate 3 l h^{-1}) to remove all oxygen. Before irradiating the polymer in presence of EDMS (a liquid at ambient temperature) a stream of N_2 was conveyed through a vessel containing EDMS (N_2 flow rate 0.1 l h^{-1}). The N_2 stream loaded with vapours of

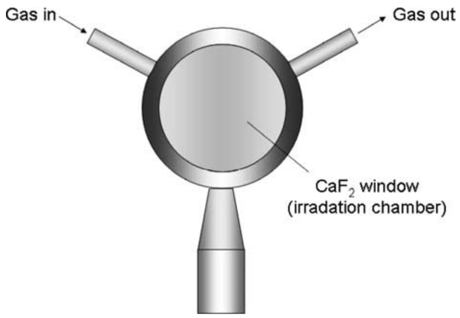


Fig. 1. UV irradiation chamber containing gas inlet, gas outlet and a VUV transparent CaF_2 window (30×2 mm). Behind this CaF_2 window the sample is placed at a distance of 7 mm.

EDMS was then passed through the irradiation chamber. After purging for 5 min, UV illumination was started. This gas stream was maintained during irradiation. For experiments with TrMS, the irradiation chamber was conditioned for 5 min with TrMS gas at a flow rate of $0.1\ l\ h^{-1}$. This gas flow was maintained during subsequent UV illumination. Surplus TrMS and EDMS were absorbed in dodecane. After irradiation the sample chamber was purged with pure N_2 for another 5 min to remove residual silane reagents and volatile reaction products. The modified polymer samples were then stored under inert gas and subjected to characterization within 12 h.

2.4. Surface characterization

Contact angles θ (sessile drop) were determined with a Krüss DSA 100 contact angle tester. 2 μl droplets of test liquids were deposited manually using Hamilton syringes (H 1750), the readout of contact angles occurred 2 s after deposition on the solid surface (tilt angle of the video camera 3°). Contact angles of water (deionized, resistivity approx. 18 MΩ) and diiodomethane (99%, GC) were determined on unmodified and modified polymer surfaces. Data for θ were averaged over 8 individual measurements. The surface tension was calculated referring to Ström's surface tension values for H_2O ($72.8\ mJ\ m^{-2}$) and CH_2I_2 ($50.8\ mJ\ m^{-2}$) [16]. For the calculation of the surface tension γ and its components γ^d (dispersive component) and γ^p (polar component) the method of Owens and Wendt was applied [17].

AFM measurements were carried out using a Nanoscope IIIa instrument from Digital Instruments. Tapping mode was applied to scan the surface. The collected data was analyzed using Nanoscope 5.12r5 analysis program. For interpretation of AFM measurements the z-axis was scaled to a uniform value of 20 nm resolution. Scaling of x and y axis could differ from image to image due to zooming effects of the surfaces. For analysis deflection mode picture was used. To compare the different surface topographies with each other, R_{rms} (average root-mean-square roughness) values were used for calculation. For a detailed description of the algorithm for calculating R_{rms} values, see Ref. [18].

For XPS analysis, polymer films were prepared on copper plates sputter-coated with a thin layer of gold. The polymer samples were then processed in the usual way. 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 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. After the first XPS measurement, polymer samples were kept in the vacuum chamber for 15 h and measured again to examine the stability of the modified surface. The following photoelectron peaks were evaluated: C 1s, O 1s and Si 2p. The binding energy of C 1s photoelectrons was defined to 285.0 eV (reference line). Shifts of O 1s and Si 2p photoelectrons were calculated with reference to the C 1s signal. The surface composition in atomic percent was calculated by a quantitative XPS analysis algorithm based on fundamental parameters [19]. In these calculations, hydrogen is omitted.

3. Results and discussion

3.1. Photochemistry with trialkylsilanes

While the plasma-induced polymerization of trialkylsilanes has been utilized for surface modification of polymeric substrates [20,21], comparably little attention has been paid to photoinduced reactions of trialkylsilanes. Considering the UV induced scission of the $R_3Si–H$ bond to give trialkylsilyl radicals, these reagents are of potential interest in photochemical processes at polymer surfaces.

Vacuum UV (VUV) absorption spectra of EDMS and TrMS have been reported in the literature. UV absorption of EDMS and TrMS peaks at three wavelengths in the VUV range (115, 140, and 165 nm) [21,22]. For TrMS, an absorption coefficient of $1.9 \pm 0.5\ L\ mol^{-1}\ cm^{-1}$ has been reported for the wavelength $\lambda = 193$ nm [23]. Investigations on the mercury sensitized photolysis of trimethylsilane TrMS showed that fragmentation into trimethylsilyl and hydrogen radicals is the main photolysis reaction, which then yields H_2 and $(CH_3)_6Si_2$ as reaction products [24]. When UV irradiation of TrMS was carried out with an ArF excimer laser ($\lambda = 193$ nm), also CH_4 and $(CH_3)_4Si$ were detectable by FTIR [25]. From this it can be concluded that Si–H scission is the predominant photolytic reaction for TrMS and EDMS, while Si–C fragmentation occurs to a minor extent.

UV spectra of liquid EDMS and gaseous TrMS were recorded in the range 190–250 nm, Fig. 2. It is seen that UV absorption extends up to 230 nm for EDMS and up to 210 nm for TrMS. Fig. 2 also displays the emission spectrum of a medium pressure Hg lamp. It can be seen that the continuum below 240 nm extends to wavelengths $\lambda < 200$ nm. Thus the UV emission of the Hg lamp should be capable of exciting EDMS and TrMS molecules. With regard to the bond dissociation energy of the Si–H unit ($380\ kJ\ mol^{-1}$), the energy of photons with wavelengths $\lambda < 315$ nm would be sufficient to cleave this bond.

In *cis*-1,4-polybutadiene, the C=C double bonds cause UV absorption up to $\lambda = 220$ nm (similar to low-molecular-weight olefines). Therefore also the target polymer will be excited

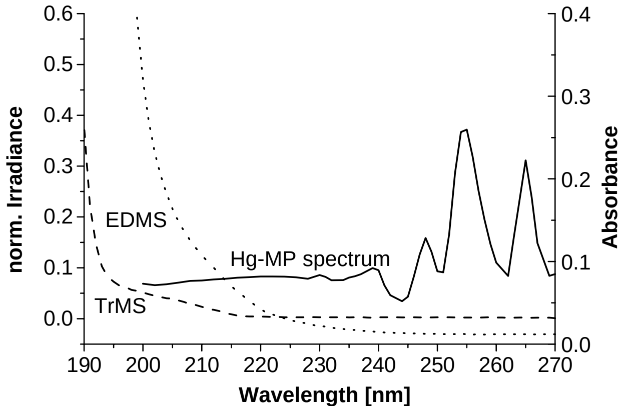


Fig. 2. Emission spectrum of the medium pressure Hg lamp (solid line) in comparison to the absorption spectra of ethyldimethylsilane (EDMS; dotted line) and trimethylsilane (TrMS; dashed line).

during UV irradiation with a Hg lamp and a 193 nm ArF* excimer laser. Indeed it has been shown that substituted olefins can be excited with monochromatic 214 nm light to undergo isomerizations and dimerizations [26]. It should not be overlooked that defect sites, trace impurities and residual catalysts in polymers may also act as a source for radicals during UV illumination [27].

3.2. Hg lamp assisted surface modification of cis-1,4-polybutadiene with EDMS and TrMS

Cis-1,4-polybutadiene films were cast onto CaF_2 plates and UV irradiated in presence of the trialkylsilanes EDMS and TrMS under exclusion of oxygen. Investigation was started with EDMS, as it shows more intense absorption up to a wavelength of 230 nm. Referring to Fig. 2 the absorption spectrum of EDMS matches with a low-wavelength emission of a Hg lamp.

FTIR spectra of *cis*-1,4-polybutadiene were recorded at different stages of UV irradiation under EDMS atmosphere. Figs. 3 and 4 display FTIR spectra recorded after 0, 5, 20 and 45 min of UV illumination (spectral range 700–1800 cm^{-1}).

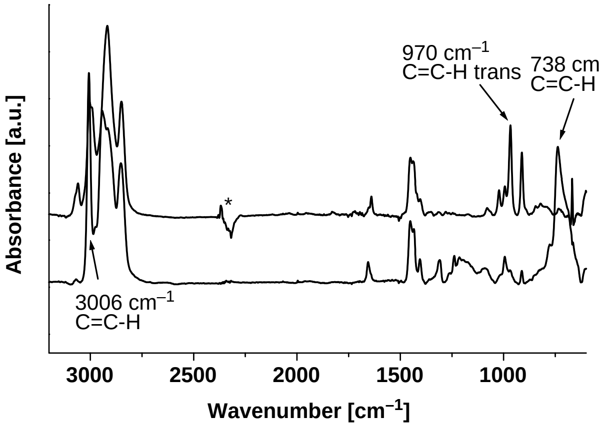


Fig. 3. FTIR spectra of a polybutadiene film prior to UV irradiation (lower figure) and after UV irradiation (upper figure) under EDMS atmosphere (Hg lamp, 5 min).

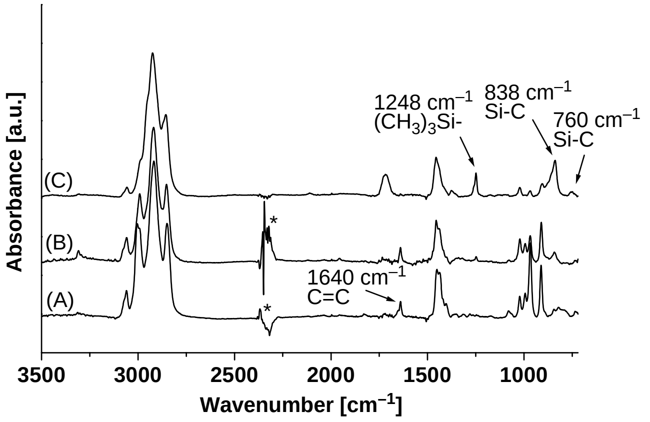


Fig. 4. FTIR spectra of a polybutadiene film recorded after UV irradiation under EDMS atmosphere (Hg lamp) for 5 min (A), 20 (B) and 45 min (C).

From Fig. 3 it is seen that within the first five min of irradiation the *cis–trans* isomerization is the predominant photoreaction in polybutadiene. This fact is evident from the disappearance of the signal at 738 cm^{-1} (C=C–H out-of-plane deformation in *cis*-polybutadiene) and the appearance of a band at 970 cm^{-1} (C=C–H out-of-plane deformation in *trans*-polybutadiene). The signals at 912 and 994 cm^{-1}, attributed to out-of-plane C=C–H vibrations of vinyl groups in polybutadienes, increase in intensity as a result of the *cis–trans* isomerization. Noticeable changes are also observed in the C–H region of the FTIR spectrum, as the strong and sharp signal at 3006 cm^{-1} (C=C–H valence vib. in *cis*-polybutadiene) is reduced in intensity. For more detailed band assignments, e.g. Ref. [28].

In Fig. 4 the FTIR spectra recorded after 5, 20 and 45 min of UV illumination are compiled. The spectrum recorded after 5 min is essentially the spectrum of *trans*-isomerized 1,4-polybutadiene. After 20 and 45 min of UV irradiation under EDMS atmosphere additional FTIR signals are observed. The signals evolving at 760 and—more clearly—at 838 cm^{-1} are assigned to Si–C rocking vibrations in $Si(CH_3)_3$ groups [29]. The intense band at 1248 cm^{-1} is attributed to the symmetric $–CH_3$ deformation vibrations in $Si(CH_3)_n$ units [29]. At the same time, the signals typical of C=C bonds in polybutadiene disappear almost quantitatively. This finding is most obvious with the band at 967 cm^{-1} (=C–H in *trans*-polybutadiene) and the bands at 912, 993 and 1640 cm^{-1} (C=C valence vib.). In the spectral region 2800–3100 cm^{-1} of the FTIR spectra the proceeding saturation of the C=C double bonds is evidenced by the disappearance of the signals at 3006 and 3060 cm^{-1} (C=C–H valence vibrations). From these FTIR data it is concluded that (a) polybutadiene is modified with organosilyl groups and (b) that the C=C double bonds are saturated as a result of photochemical processes.

After 20 min of UV irradiation an additional weak FTIR signal around 1720 cm^{-1} was also observed, Fig. 4. These signals may be due to oxygen impurities in the gas stream and can be assigned to carbonyl compounds (C=O stretching vibration). However, the lack of signals at

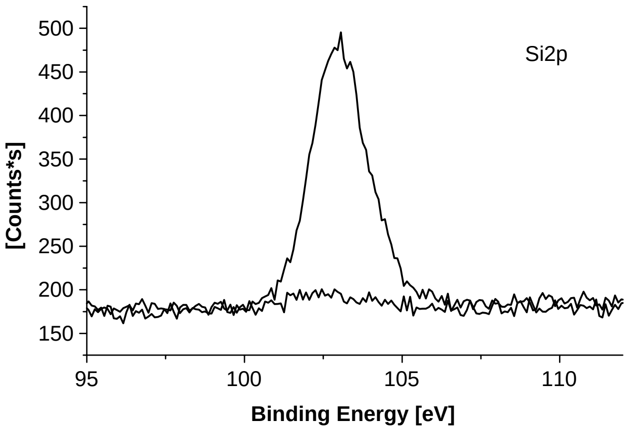


Fig. 5. XPS detail spectra of polybutadiene prior to (lower figure) and after 20 min of UV irradiation (upper figure) with the Hg lamp in the presence of EDMS.

~1100 cm^{-1} (Si–O–Si vibration) shows that siloxane compounds were not produced at the polybutadiene surface during UV irradiation.

To obtain further information on the composition of the polybutadiene surface, X-ray photoelectron spectra were recorded, Fig. 5. XPS spectra taken of pristine polybutadiene showed only trace amounts of silicon at the surface.

After UV irradiation in presence of EDMS for 10 min a XPS signal at 102.8 eV (Si 2p) was detectable. This Si 2p signal is attributed to alkylsilyl groups (Si–C) but cannot be clearly distinguished from silicon attached to oxygen (Si–O) as these lines lie very close to each other (range between 99.3 and 103.3 eV according to literature data). Hence, the Si2p line at 102.8 eV may be a superposition of SiC and SiO lines. Quantitative XPS data for different UV irradiation times are presented in Table 1. Hydrogen (not detectable by XPS) has been omitted in these calculations.

As shown in Table 1, traces of silicon are already present at the polybutadiene surface prior to surface modification with EDMS. After irradiating the polybutadiene sample in presence of EDMS, the amount of silicon increases to a value of 1.7 at.% (after 5 min) and to 4.9 at.% (after 10 min). For oxygen, an increase of the O1s signal after surface modification with EDMS was detected. This phenomenon was also seen in the FTIR spectra (Fig. 4). Although both surface modification and storage of samples were done under inert gas conditions, the amount of oxygen at the *cis*-1,4-polybutadiene surface increased from 2.3 to 9.3 at.% after 10 min of UV irradiation. The incorporation of oxygen may be due to impurities in the gas atmosphere applied during surface modification. It is also possible that trapped radicals and reactive species such as Si–H groups at the modified *cis*-1,4-polybtadiene surface react with ambient oxygen during sample transfer.

Table 1
Quantitative XPS data for polybutadiene modified with EDMS (Hg lamp treated)

	C1s (at.%)	O1s (at.%)	Si2p (at.%)
0 min	95.2	2.3	0.5
5 min	93.2	4.2	1.7
10 min	81.7	9.3	4.9

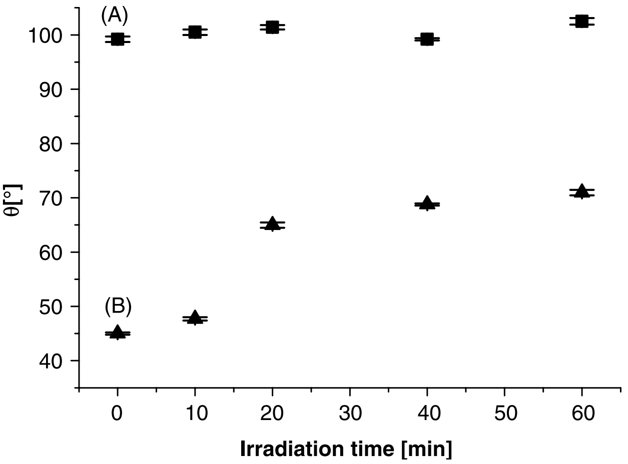


Fig. 6. Contact angle data for polybutadiene after different periods of UV irradiation (Hg lamp) in the presence of EDMS. (A) H_2O and (B) CH_2I_2 as test liquids. The error bars are also indicated.

From the quantitative XPS data in Table 1 it is calculated that—on an average—30% of the polybutadiene monomer units bear a silyl substituent (after 10 min of UV/EDMS modification).

Contact angle measurements were carried out to follow changes in surface tension γ of polybutadiene during progress of surface modification. Pristine *cis*-1,4-polybutadiene is a hydrophobic polymer showing a contact angle $\theta=99.2°$ (water, sessile drop). As a result of UV irradiation in presence of EDMS, θ increased up to 102.5° within 60 min. For diiodomethane, changes in contact angle θ were more pronounced. The contact angle increased from $\theta=45.2°$ (prior to irradiation) to $\theta=70.8°$ after 60 min of irradiation. Fig. 6 displays the contact angles θ for water and diiodomethane on polybutadiene as a function of the UV irradiation time under EDMS atmosphere.

From contact angle data surface tension γ and its dispersive and polar components (γ^d and γ^p) were calculated following the method of Owens and Wendt. For pristine *cis*-1, 4-polybutadiene a surface tension $\gamma=37.0$ mJ cm^{-2} was obtained which equals the value given in the literature [30]. As a result of the photomodification with EDMS the surface tension of polybutadiene decreased from $\gamma=37.0$ mJ m^{-2} ($\gamma^d=36.90$ mJ m^{-2}, $\gamma^p=0.1$ mJ m^{-2}) to $\gamma=23.2$ mJ m^{-2} ($\gamma^d=23.32$ mJ m^{-2}, $\gamma^p=0.08$ mJ m^{-2}), see Fig. 7.

The surface tension γ of polybutadiene mainly consists of the dispersive component γ^d, while the polar component γ^p of the surface energy is comparably small. UV treatment of polybutadiene with trialkylsilanes mainly affects the dispersive component γ^d, which decreases significantly and causes a drop of the overall surface tension γ. As expected, the polar component (γ^p) remains almost unchanged during this process of surface modification as no polar groups are introduced. Summing up, surface modification of polybutadiene with EDMS results in a low-energy surface with increased oleophobic properties.

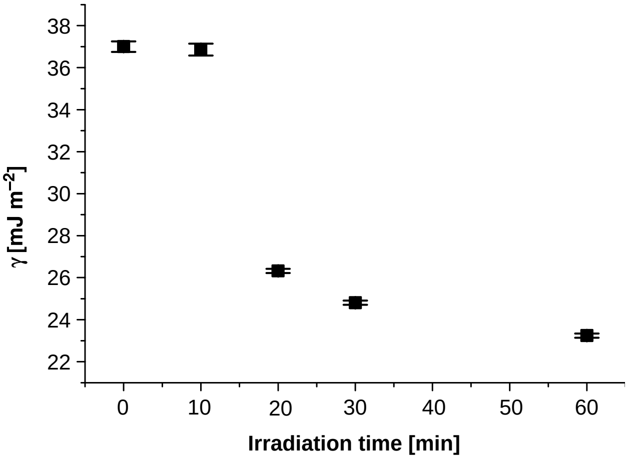


Fig. 7. The surface tension γ for polybutadiene after UV modification with EDMS (γ calculated from H_2O and CH_2I_2 contact angles). The error bars are also indicated.

When *cis*-1,4-polybutadiene was illuminated with a Hg lamp under TrMS atmosphere, changes in the FTIR spectrum were comparable to those observed during the experiments with EDMS. Signals at 1248 and 838 cm^{-1} were observed after 60 min of UV irradiation under TrMS atmosphere and indicated the presence of silyl groups in the polybutadiene film. The *cis–trans* isomerization and also the continuous consumption of the C=C double bonds in the polybutadiene film proceeded in a similar way as described for the reaction with EDMS. However, with TrMS as modifying agent, only a slow decrease of surface tension γ of the polybutadiene surface was detectable within 60 min of UV lamp irradiation. This may in part be explained by the low UV absorbance of TrMS within the spectral range 190–215 nm. Consequently, UV irradiation with a Hg lamp does not seem to be very effective with TrMS for changing the surface properties of polybutadiene.

It is well known that surface roughness can exert a significant influence on the observed contact angles θ. To clarify this, AFM investigations of polymer surfaces prior to and after UV irradiation were carried out to determine variations in surface roughness. For pristine films of *cis*-1,4-polybutadiene a surface roughness $R_{\mathrm{rms}}=0.102$ nm was found. After 60 min of UV irradiation in the presence of trialkylsilane (TrMS) a slight increase of surface roughness to $R_{\mathrm{rms}}=0.143$ nm was detected. Obviously the Hg lamp UV treatment does not cause a significant change in surface topography. Thus the observed variations in the contact angles θ reflect changes in the surface tension γ of the polybutadiene surface and are not influenced by variations in surface roughness.

Moreover, two control experiments were conducted. When polybutadiene was UV irradiated under pure nitrogen (99.999%), only a *cis–trans* isomerization was observed by FTIR spectroscopy. The contact angle (water and diiodomethane) did not change significantly after 10 min of UV irradiation under inert gas conditions. Second, we investigated if trialkylsilanes would react with polybutadiene in the absence of UV light. No incorporation of Si was detectable (XPS, FTIR) for polybutadiene samples that had been stored under trimethylsilane for 10 min in the dark.

3.3. 193 nm ArF* laser assisted modification of cis-1,4-polybutadiene with trimethylsilane (TrMS)

As discussed in the preceding section, both with EDMS and TrMS the use of a medium pressure Hg lamp required rather long irradiation times to achieve a significant modification of the polybutadiene surface. While TrMS provides advantages due to easier handling, the low UV absorption (Fig. 2) causes poor reactivity under Hg lamp irradiation and surface modification with TrMS turned out to be inefffficient under these conditions.

Excimer lasers provide powerful and practically monochromatic radiation at selected UV wavelengths. A 193 nm ArF* excimer laser is an appropriate light source to excite TrMS molecules (Fig. 2).

The UV reaction of *cis*-1,4 polybutadiene films with TrMS under 193 nm radiation was followed by FTIR spectroscopy, see Fig. 8. Again the initial *cis–trans* isomerization and—at later stages—the evolution of signals at 1249 and 840 cm^{-1} were observed which indicate the introduction of trimethylsilyl groups. Simultaneously the C=C double bond at 1655 cm^{-1} disappeared. FTIR spectra remained constant after 60 s of 193 nm irradiation under TrMS atmosphere. With a pulse energy of 14.3 mJ cm^{-2} at a frequency of 10 Hz, this equals an energy density $E=8.6\ \mathrm{J\,cm}^{-2}$ delivered to the polymer surface. As an excimer laser delivers intense and monochromatic light, UV modification of polybutadiene proceeds much faster than under the light of a medium pressure Hg lamp. No signals in the spectral region of carbonyl species (1650–1750 cm^{-1}) were detectable after UV irradiation.

XPS measurements of the modified *cis*-1,4-polybutadiene sample evidenced a Si2p peak at 102.6 eV, Fig. 9. Quantitative data on the composition of the surface are presented in Table 2. Also in this case traces of silicon were detected at the surface of pristine *cis*-1,4-polybutadiene films (probably impurities from contact with ambient atmosphere). After 350 s of irradiation

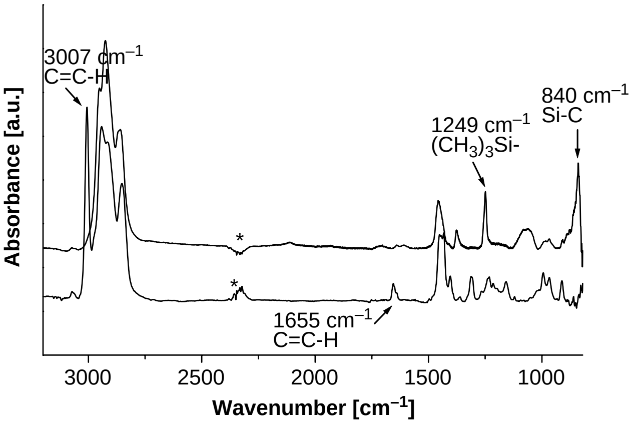


Fig. 8. FTIR spectra of a polybutadiene film recorded prior to (lower figure) and after 60 s of UV irradiation with the 193 nm excimer laser in presence of TrMS (upper figure).

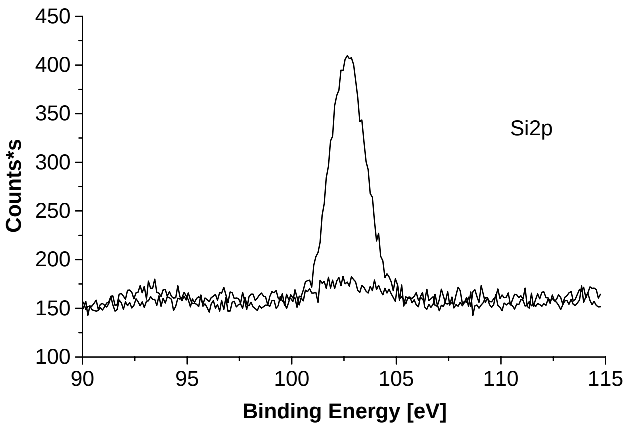


Fig. 9. XPS detail spectra of polybutadiene before (lower figure) and after 350 s of UV irradiation with the 193 nm excimer laser in the presence of TrMS (upper figure).

the silicon content increased from 0.8 to 2.8 at.%. Simultaneously the oxygen content increased from 2.3 to 6.2 at.% after 350 s of 193 nm UV irradiation. From the data in Table 2 it is calculated that—on an average—13% of the butadiene monomer units were modified with silyl groups (after 5 min of 193 nm ArF* irradiation in presence of TrMS).

Cis-1,4-polybutadiene treated with TrMS in presence of a 193 nm ArF* excimer laser incorporated less alkysilyl groups than *cis*-1,4-polybutadiene treated with a Hg lamp in the presence of EDMS. Also in this case the Si 2p line may be a superposition of the lines for Si–C and Si–O functions (an unambiguous discrimination is not possible).

Parallel to the FTIR and XPS measurements contact angles θ of water and diiodomethane on the polybutadiene surface were recorded. Fig. 10 displays the variation in θ as a function of the energy density E at $\lambda = 193$ nm. The contact angle of water increased from 100.6° (unirradiated sample) to 112.4° ($E = 1.70$ J cm^{-2}; 12 s of laser irradiation). At the same time, the contact angle of diiodomethane increased from 54.8 to 89.6°, see the data in Fig. 10.

The variation in surface tension γ as a function of E is plotted in Fig. 11. Irradiation of the polybutadiene surface with energy densities E up to 1.7 J cm^{-2} resulted in a continuous decrease in surface tension from $\gamma = 34.80$ mJ m^{-2} ($\gamma^d = 34.75$ mJ m^{-2}, $\gamma^p = 0.05$ mJ m^{-2}) to $\gamma = 13.23$ mJ m^{-2} ($\gamma^d = 13.18$ mJ m^{-2}, $\gamma^p = 0.05$ mJ m^{-2}). These results show that a low energy-surface is obtained when polybutadiene is irradiated with 193 nm light under TrMS atmosphere. The situation is comparable to the irradiation under EDMS atmosphere.

Again the surface topography of polybutadiene films prior to and after UV irradiation was investigated by AFM.

Table 2
Quantitative XPS data for polybutadiene modified with TrMS (193 nm ArF* treated)

	C1s (at.%)	O1s (at.%)	Si2p (at.%)
0 s	95.2	2.3	0.5
350 s	91.0	6.2	2.8

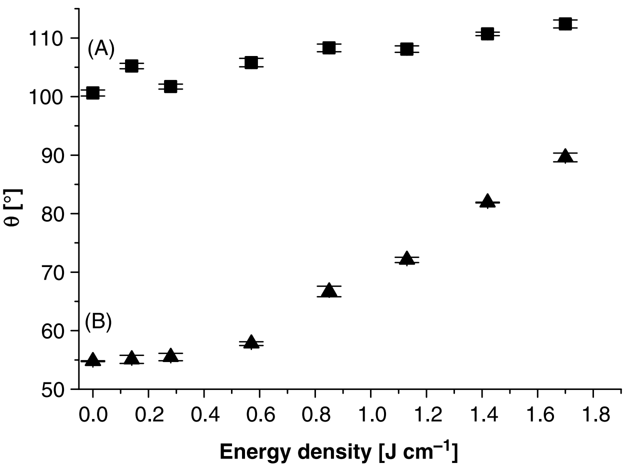


Fig. 10. Contact angle data for polybutadiene after different periods of UV irradiation with the 193 nm excimer laser in the presence of TrMS. (A) H_2O and (B) CH_2I_2 as test liquids. The error bars are also indicated.

The surface roughness (R_{rms}) of untreated polybutadiene films had a value of $R_{rms} = 0.105$ nm and increased to $R_{rms} = 0.379$ after 60 s of 193 nm laser irradiation ($E = 8.6$ J cm^{-2}). The increasing surface roughness is visualized by 3D AFM micrographs in Fig. 12. Obviously the laser UV irradiation of polybutadiene under TrMS atmosphere does not only lead to the introduction of trialkylsilyl groups but also increases the roughness of the surface. Surface corrugation of polymers is common under the pulsed light of UV lasers. This might also influence the observed contact angles θ in a way similar to the well-known 'lotus effect'. Yet it can be concluded that the introduction of organosilicon groups onto the polybutadiene surface is the main reason for the increase of contact angles θ and the decrease in surface tension γ derived from the θ values.

3.4. Possible mechanisms for the photoreaction of cis-1,4-polybutadiene with trialkylsilanes

The direct UV excitation of the C=C double bond in *cis*-1, 4-polybutadiene (and olefines in general) can proceed by a π–π^*

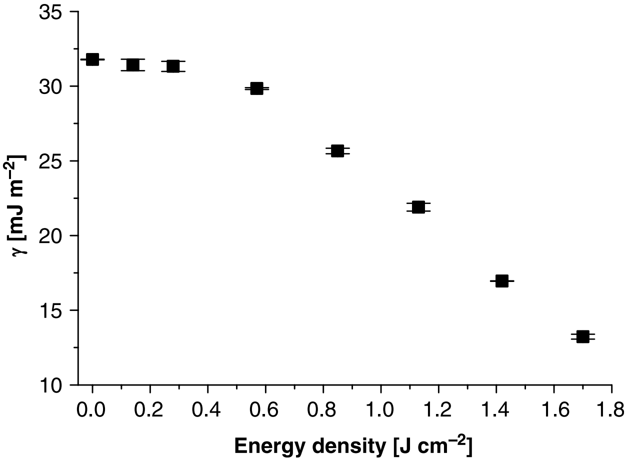


Fig. 11. The surface tension γ for polybutadiene after UV modification with TrMS (γ calculated from H_2O and CH_2I_2 contact angles). The error bars are also indicated.

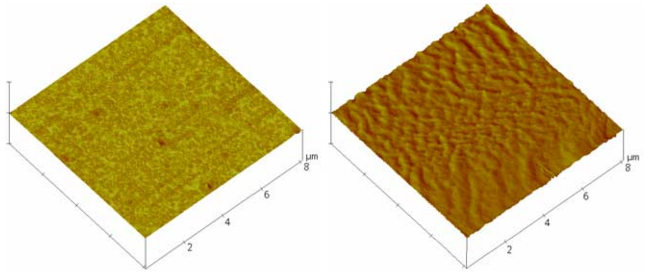


Fig. 12. Atomic force microscopy (AFM) micrographs of polybutadiene prior to (left figure) and after UV irradiation with the 193 nm excimer laser in the presence of TrMS (right figure).

transition. With *cis*-substituted olefines and *cis*-1,4 polybutadiene an isomerization to the *trans*-configuration is then observed as the main reaction. However, *cis*–*trans* isomerizations are also mediated by reversible attachment of radicals to the C=C double bond (*Schenck* mechanism). Indeed, this isomerization in *cis*-1,4-polybutadiene during UV irradiation has been observed in the absence of trialkylsilanes and also during the initial stages of UV irradiation in the presence of EDMS and TrMS. The isomerization was readily detectable by FTIR. This shows that under the present irradiation conditions (Hg lamp and 193 nm excimer laser) the C=C bond in *cis*-1,4-polybutadiene is directly excited. Regarding the highly exothermic ($\Delta H = -125$ kJ mol^{-1}) and thus practically irreversible addition of radicals $R_3Si^{\cdot}$ to olefines, it cannot be assumed that a Schenck mechanism is operative during the observed *cis*–*trans* isomerization of polybutadiene.

In the preceding section it has been shown that UV irradiation of *cis*-1,4-polybutadiene in the presence of trialkylsilanes R_3Si–H leads to an introduction of silyl groups which is accompanied by an almost complete saturation of C=C double bonds. Considering the photoinduced reactions of trialkylsilanes R_3Si–H, which lead to radicals R_3Si and $H^{\cdot}$, it can be assumed that the surface modification of *cis*-1,4-polybutadiene proceeds via radical intermediates as depicted in Fig. 13. A silyl radical $R_3Si^{\cdot}$ is generated in the primary photolysis (line I) and adds irreversibly to the C=C double bond in polybutadiene (line II). Subsequent hydrogen abstraction by the alkyl macroradical from R_3Si–H then completes the hydrosilylation reaction (line III).

This reaction may proceed as a chain reaction as has been proposed for the radical mediated addition of silanes to a variety of olefines [14]. It is clear that recombination reactions of allyl type radicals in the polybutadiene chain with trialkylsilyl radicals are another way of incorporating silyl substituents (line IV).

At the same time, main chain alkyl radicals generated by other reacions will participate in H abstraction from the silane. Generally, alkyl radicals $RCH_2^{\cdot}$ will attack trimethylsilane at the Si–H group in 95% and at the methyl group in 5% of the cases (triethylsilane: 60 and 40%, respectively) [14].

Regarding the rapid saturation of the C=C double bonds in polybutadiene, a simple hydrogenation via $H^{\cdot}$ radicals is also possible (line V). Examples for photoinduced hydrogenations may be found in thiol-ene and similar addition reactions, which can be compared to radical-mediated hydrosilylations. As an

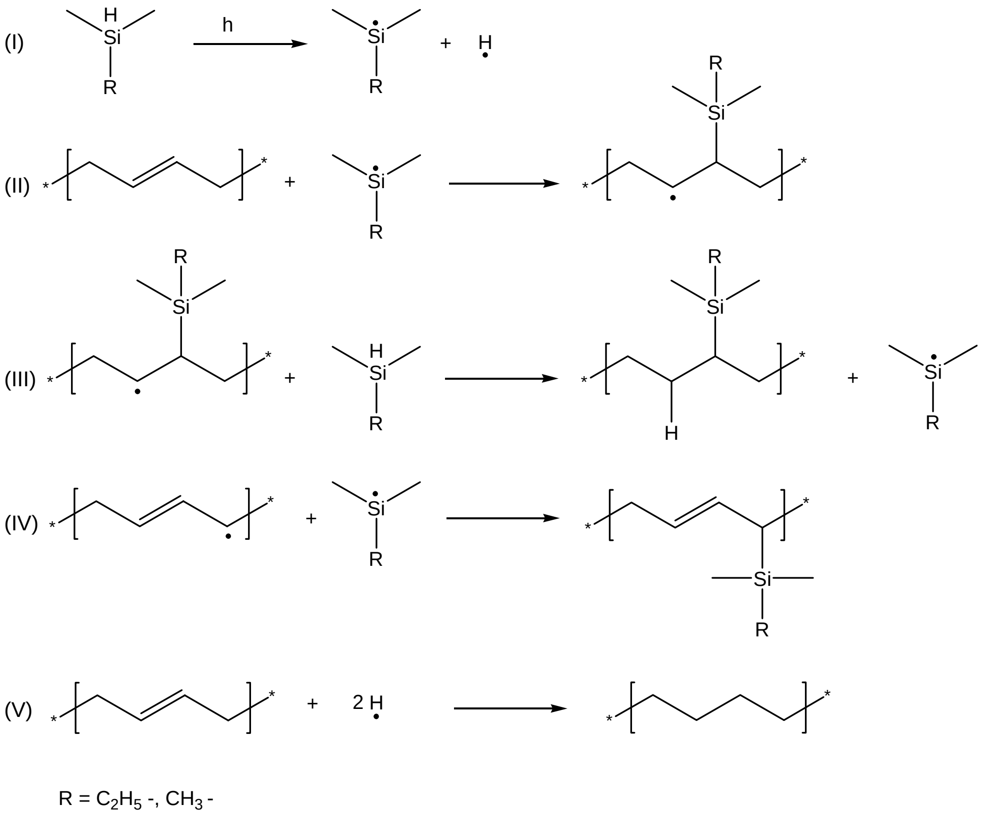
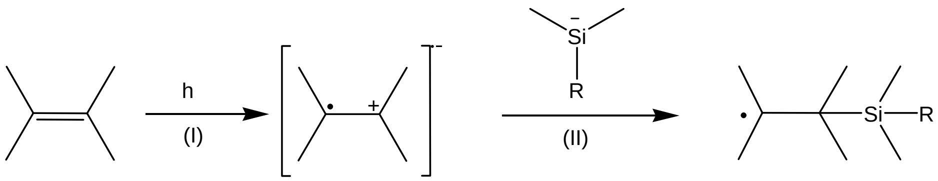


Fig. 13. Proposed free radical reactions of polybutadiene with trialkylsilanes under UV irradiation.



R = C_2H_5-, CH_3-

Fig. 14. A possible reaction of Rydberg excited olefins with trialkylsilyl anions R_3Si^-.

example, the UV reaction of propane-2-thiol with simple olefines (e.g. nonadec-1-ene) produces 90% of the thioether, but also yields 10% of the corresponding alkane. Another example is the UV assisted reaction of 1,2-diphenylethene (stilbene) with benzeneselenol C_6H_5Se–H. Instead of the addition reaction a photochemical hydrogenation proceeds, and 1,2-diphenylethane is produced in almost quantitative yield [31]. Therefore, it should not be ruled out that reactions between trialkylsilanes and olefines yield alkanes as side products.

Upon direct UV excitation of olefines, Rydberg transitions are also known to occur [26]. These π–σ^* transitions (with distinct lines in the UV absorption spectrum) transform the C=C bond into a radical cation and a loosely bond electron (Fig. 14, line I). The radical cation then undergoes addition reactions with nucleophiles such as alcohols or amines. The UV assisted addition of alcohols to olefines is probably the most prominent reaction of olefines, which proceeds via Rydberg states. Indeed such reactions can be initiated by UV irradiation with medium pressure Hg lamps [32].

Yet it remains uncertain if Rydberg states also participate in the reaction of olefines with silanes. The electron affinity EA of trialkylsilyl radicals $R_3Si^\cdot$ is similar to that of carbon centered radicals ($(CH_3)_3Si^\cdot$: EA = 94 kJ mol^{-1} [33]; $C_6H_5CH_2^\cdot$: EA = 83.2 kJ mol^{-1} [34]). Thus it cannot be ruled out that anions of the type R_3Si^- are formed which then react with the carbocation as depicted in Fig. 14 (line II). However, this mechanism remains highly speculative. Therefore, the UV induced reactions of trialkysilanes with polybutadiene is favoured to be described via free radical processes.

4. Conclusions

It has been demonstrated that trialkylsilanes R_3Si–H can be applied in the photoassisted modification of polymer surfaces. The UV irradiation of polybutadiene surfaces with a medium pressure Hg lamp in the presence of vapours of ethyldimethylsilane (EDMS) results in an attachment of alkylsilyl groups. Similar results are obtained when the UV irradiation of polybutadiene is carried out with monochromatic UV light (193 nm ArF* laser) in the presence of gaseous trimethylsilane (TrMS). The incorporation of silyl groups has been confirmed both by FTIR and X-ray photoelectron spectroscopy.

In both cases low-energy surfaces with reduced wettability are obtained. The surface energy γ of *cis*-1,4-polybutadiene drops from its initial value $\gamma = 37.0$ to 23.2 mJ m^{-2} after Hg lamp irradiation in the presence of EDMS. With 193 nm irradiation under TrMS atmosphere, even lower values for the surface tension ($\gamma = 13.23$ mJ m^{-2}) are found after the surface modification process. It should be pointed out that the pulsed laser irradiation also causes some surface corrugation which may contribute to the reduction in wettability.

The generation of low-energy polymer surfaces by UV treatment in the presence of silanes may be useful to improve their antiadhesive properties. At the same time, uptake and permeation of organic solvents and vapours can be reduced by such techniques.

It has been noticed that UV surface modification with trialkylsilanes is highly sensitive to traces of oxygen in the process gas. On the other hand, UV irradiation of surfaces in the presence of both silane and oxygen may be a way to obtain Si–O surface layers. In a similar fashion, an oxidative conversion of the silylated polymer surfaces into polysiloxane layers would be a strategy to obtain wear resistant and protective surface layers. This topic will be addressed in a forthcoming contribution.

Acknowledgements

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