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Nitric Oxide Radical Trapping Analysis on Vacuum-Ultraviolet Treated Polymers

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ABSTRACT: Vacuum-ultraviolet (VUV) radiation causes the dissociation of organic σ bonds such as the C−C and the C−H bonds in polyolefins. The radicals formed in this process were investigated by trapping with nitric oxide. PE, PP, and PS were irradiated in ultrahigh vacuum with the MgF_2-filtered radiation of a hydrogen plasma. After an irradiation period of 1 h and an immediate radical trapping, PE, PP, and PS incorporate 1.4, 0.4, and 0.2 atom % nitrogen, respectively, measured by XPS. These nitrogen concentrations correspond to 5.4×10^{20}, 1.4×10^{20}, and 0.8×10^{20} spins/cm^3, respectively. By the fitting of the XPS-N1s peaks, detailed information about the nitrogen functional groups and about the original radical types was obtained.

Introduction

Vacuum-ultraviolet (VUV) radiation is a typical component of electrical discharges such as low-pressure plasmas.[1] The energy of the photons is sufficient to excite efficiently C−C and C−H σ-bonds of organic compounds such as polyolefins (>7.7 eV). Depending on the absorption spectrum, the electromagnetic radiation can penetrate some 10 nm into the surface. In case of polyethylene (PE),[2] the penetration depth (95% absorption) of the 120 nm VUV radiation amounts to 52 nm.

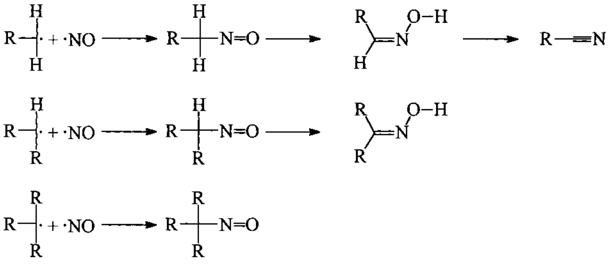
During the VUV irradiation of polymers radicals are formed by bond scissions. In the literature, a number of papers deal with the radical formation in plasma-treated polymers. ESR investigations were done in situ without contact to air[3,4] in a small cylindrical quartz reaction vessel. Other research groups have measured the radical concentration by a post plasma reaction with diphenylpicrylhydrazyl (DPPH).[5−7] However, this liquid phase reaction must be expected to alter the surface only by the influence of the solvent.

In this paper we report results of our investigations on the trapping of long living radical sites with nitric oxide. Nitric oxide is a gaseous, stable, but reactive radical, which can react with carbon radicals. Depending on the type of carbon radical, the reaction is supposed to form different reaction products (Scheme 1). Primary carbon radicals are expected to form nitrile groups, secondary radicals oxime groups, and tertiary radicals nitroso groups. These new nitrogen-containing groups can be distinguished by X-ray photoelectron spectroscopy (XPS) in the N1s region due to their chemical shifts. The concentration of the different radical types can be determined from the concentration of the respective nitrogen functional group. The nitrogen concentration represents the total radical concentration.

Experimental Section

Materials. Nitric oxide (purity 99.5%) and hydrogen (purity 99.999%) were obtained from Linde AG, Germany, and were used as delivered. Polyethylene (PE, Lupolen 2420H, BASF AG Germany) and isotaktic polypropylene (Trespaphan NNA30, Hoechst AG Germany) were commercial materials. The polystyrene (PS, Scopyrol S246P, BUNA AG, Germany) films were casted from a 6.9% PS solution in toluene. All the films were rinsed with absolute ethanol and scraped with a fluff free paper (kimwipe) before treatment. The oxygen surface concentration was at 0.2 atom % for PE and below the detection level (0.1 atom %) for PP and PS.

Scheme 1. Reaction Scheme of Different Carbon Radicals with Nitric Oxide



Experimental Setup (Figure 1). A microwave ECR source (Roth & Rau, Germany) operating at 300 W with a hydrogen feed of 40 sccm and a pressure of 0.23 mbar was used as the radiation source. (For a VUV emission spectrum of a H_2 microwave plasma, see ref 8.) The H_2 plasma radiation was coupled into the ultrahigh vacuum (UHV) sample chamber by a magnesium fluoride window with a diameter of 36 mm and a cut off wavelength of 113 nm. The base pressure of the UHV sample chamber was kept at 1.5×10^{-8} mbar or below by a turbomolecular pump. The PE, PP, and PS sample strips were placed at a distance of about 18 cm from the window of the light source. A second chamber (derivatization chamber) was attached to the UHV chamber and was separated by a gate valve. The derivatization chamber was pumped by a turbomolecular pump and operated at a base pressure better than 1.5×10^{-7} mbar. A nitric oxide source was connected directly to the derivatization chamber. For transferring the samples to the XPS, a load lock was mounted on the derivatization chamber. The pressure never raised above 1×10^{-5} mbar during transfer.

XPS. All the XPS spectra were recorded with an AXIS 165 spectrometer (Kratos Analytical, U.K.) equipped with a monochromator (Al $K\alpha$) and a magnetic lens in hybrid mode (magnetic and electrostatic lenses used).

Treatment Procedure. The intensity of the light source was checked routinely by measuring the fluorescence light of two different sodium salicylate sheets positioned in the middle of the UHV sample chamber. When necessary the intensity was corrected by adjusting the power input of the microwave

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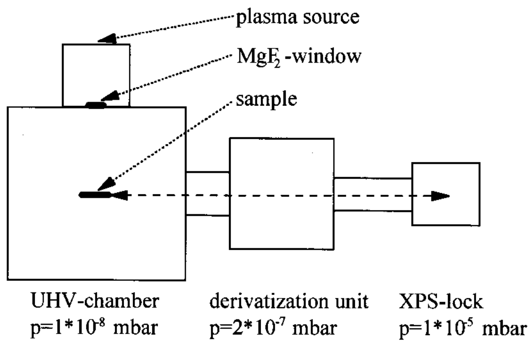


Figure 1. Experimental setup.

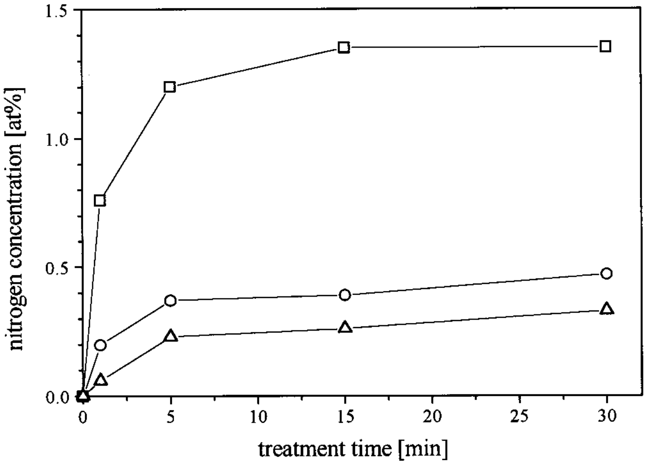


Figure 2. Nitrogen surface concentration as function of treatment duration with nitric oxide (60 min of VUV irradiation, 100 mbar NO, vacuum transfer; (□) PE, (○) PP, (△) PS).

source. The samples were VUV irradiated for various periods of time. Immediately after the light was switched off, the samples were transferred into the derivatization chamber (transfer takes about 20 s) and treated with nitric oxide for various times (1−30 min) at various pressures (5−100 mbar). Then the samples were transferred into the XPS in a vacuum by use of the XPS lock (transfer takes about 20 min). Immediately after the sample transfer they were analyzed by XPS.

Results and Discussion

Preliminary Investigations. Because of the high reactivity of radicals with traces of oxygen we took great care for a low base pressure in the treatment chamber (better than 1.5×10^{-8} mbar). In the first experiments, the quality of the reaction conditions were checked in order to make sure that there is no reaction of radicals with residual oxygen and water. Therefore, PE, PP, and PS were VUV irradiated for 45 min and then transferred in a vacuum without any posttreatment into the XPS system. The small increase of the oxygen concentration [O] by this treatment (PE 0.26 atom %, PP 0.09 atom %, PS 0.35 atom %) demonstrates the good quality of the vacuum conditions. Similar experiments with a sample transfer via air showed a much higher [O]: PE 5.32 atom %, PP 0.91 atom %, PS 0.70 atom %.

To establish the reaction conditions for the following investigations, the evolution of the nitrogen incorporation into the surface was investigated in dependence on the reaction time and the pressure of the nitric oxide (Figures 2 and 3). From these experiments the reaction conditions were defined to be 100 mbar of NO pressure and 15 min of treatment duration.

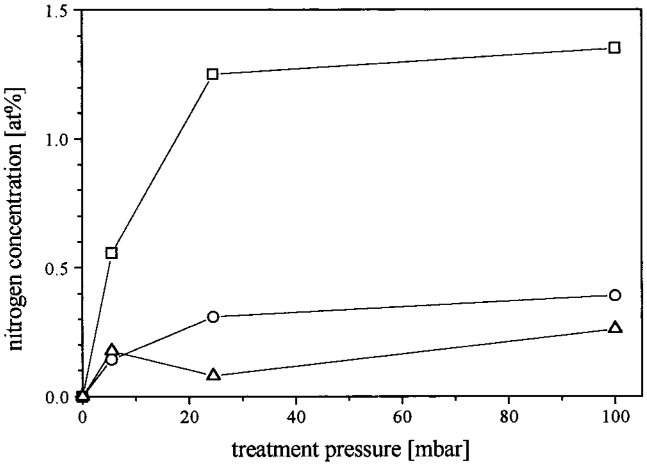


Figure 3. Nitrogen concentration as function of nitric oxide pressure during treatment (60 min VUV irradiation, 15 min of NO treatment duration; (□) PE, (○) PP, (△) PS).

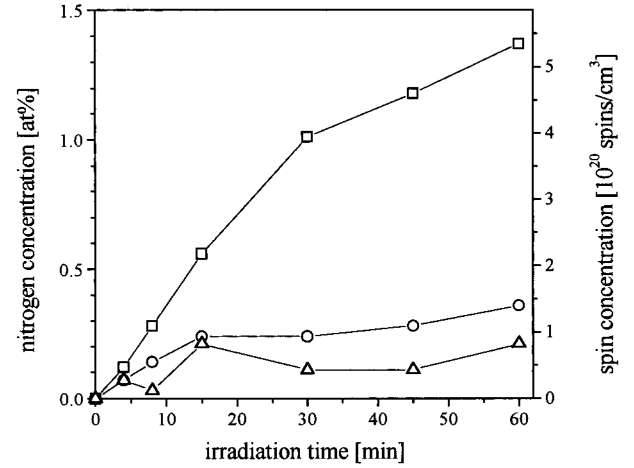


Figure 4. Nitrogen concentration as function of VUV irradiation time (15 min of NO treatment time, 100 mbar NO; (□) PE, (○) PP, (△) PS).

Radical Surface Concentration. Because of the stoichiometry of the trapping reactions (see Scheme 1) the nitrogen concentration can be used to calculate the surface radical concentration. Assuming a polymer density of 0.9 g/cm^3 and a constant surface radical concentration throughout the XPS analysis depth of about 5 nm (this assumption is legitimate because the penetration depth of VUV radiation is much higher than the XPS analysis depth), 1 atom % nitrogen corresponds to a radical concentration of 0.65 mol/L or 3.9×10^{20} spins/cm^3.

Using the conditions mentioned above, the nitrogen incorporation (radical concentration) was studied as a function of the irradiation time (Figure 4). The radical concentration was found to differ considerably between the three polymers. The radical surface concentration which is measured in the trapping experiments is the concentration of radicals at the end of the irradiation. This value is influenced by the formation rate and the decay rate of the surface radicals during irradiation. The surface radical formation depends on the amount of absorbed photons at the surface (that depends on the emission spectrum of the light source and the absorption spectrum of the polymer) and on the quantum yield for bond dissociation. The radical decay can occur in a number of different ways. The first thing that could happen to a freshly formed radical is the recombination within the reaction cage before the two fragments of the bond scission are able to move apart. This is a very probable fate of radicals formed by C−C scission in the backbone of a polymer because their motion is restricted by the bulky rest of the molecule. A recombination of two polymeric radicals is conceivable only at a sufficiently high concentration if they can come close enough to each other for a reaction (by thermal polymer chain movement) in a reasonable period of time. If the radical concentration is low, the cleavage of a hydrogen atom at the neighboring carbon atom and the formation of a double bond is the most likely reaction path. The reaction with small molecules from the surrounding gas phase can be minimized by a low ambient pressure. The low oxygen concentration in the sample surface after the irradiation suggests that the reaction conditions have a sufficient quality to minimize this type of decay reaction.

In general, organic polymers show a typical absorption between 60 and 160 nm where C−C and C−H σ-bonds absorb. PE and PP comprise only these types of bonds. The absorption coefficients of PE[2] (penetration depth $\kappa = 52$ nm at $\lambda = 121.5$ nm) and PS[9,10] ($\kappa = 58-64$ nm at $\lambda = 121.5$ nm) were reported in the literature. For PP, however, the absorption coefficient was determined only in the region between 170 and 240 nm,[11] which is not important for the investigations reported here because of the very much stronger absorption below 160 nm. But on the basis of the absorption coefficients of some organic vapors,[12] the absorption coefficient can be estimated. Assuming a density of the organic compounds of $\rho = 0.9$ g/cm^3 and the same molecular absorption cross section in gaseous and in solid state, the penetration depth κ of ethane, propane, butane, pentane, and 2-*cis*-butene ranges from 62 to 67 nm (at $\lambda = 121.5$ nm). Considering the amount and the type of valence bonds per volume unit in the system, there is almost no difference between PE and PP and the absorption spectra can be expected to be very similar. The absorption in the wavelength region below 160 nm can result in dissociation and ionization. The VUV light source that we used had a cut off wavelength of 113 nm (11 eV) due to the MgF_2 window. Therefore, photoionization can be neglected in our experiments.[12] Photodissociation results in the formation of radicals. The PS spectrum shows, beside the σ absorption, also an absorption in the region between 150 and 285 nm, which are caused by forbidden and allowed transitions in the phenyl ring.[10] These excited states usually relax thermally or by fluorescence.[13]

Considering these absorption characteristics and the emission spectrum of the hydrogen plasma light source which emits most of the photons at $\lambda < 160$ nm (Lyman and Werner Bands),[8] the amount of electronic excitation in the topmost surface layer is very similar for PE, PP, and PS. The excitation state and the relaxation path, however, seem to differ considerably.

For PS we found the lowest radical concentration of the three polymers. The absorbed energy seems to be dissipated rather thermally or by fluorescence than by bond scission. The fluorescence is observed visually in the experiment. The cage effect as discussed above and an energy transfer to the aromatic system as reported in ref 13 can explain the data. A similar behavior of this polymer (and other aromatic polymers) is well-known for γ irradiation.

Table 1. XPS N1s Positions of Different Nitrogen-Containing Functional Groups

groups	structure	position (eV)	peak	ref
nitriles	C−CN	399.1−399.5		15
oximes	C=NOH	400.5	N1	*a*
nitroso compds	C−N=O	403.7	N2	16
nitro compds	$C-NO_2$	405.5−406.3	N3	16
nitrates	$C-ONO_2$	408.2	N4	15

[a] Determined from poly(methyl vinyl ketoxime) in our laboratory.

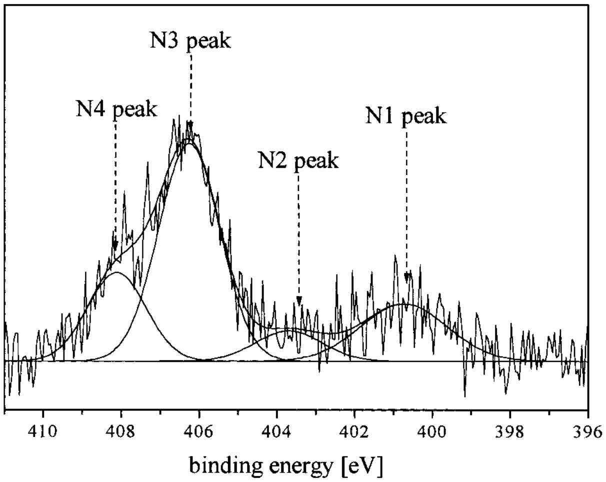


Figure 5. Exemplary N1s peak deconvolution of PE after 30 min VUV irradiation and nitric oxide posttreatment.

In the case of PP, the amount of radicals is higher than for PS but still much lower than for PE. We can assume that the radical formation rates do not differ very much for PP and PE. The decay paths, however, seem to be different. As known from quartz microbalance and IRRAS measurements[14] in the case of PP, material is removed from the surface and a new surface is formed steadily while much less material is removed from the PE surface and radicals can accumulate.

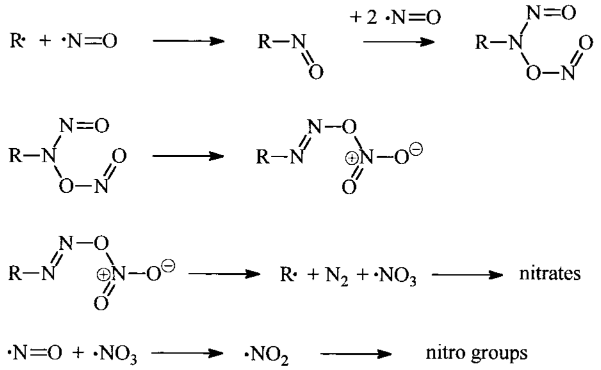
N1s peak analysis. As mentioned above, different radical species can be determined by radical trapping with nitric oxide (Scheme 1). The chemical shifts of various nitrogen-containing functional groups are summarized in Table 1.

PS was not investigated because of the small nitrogen concentration in the surface. The N1s signals of treated PE and PP are deconvoluted with 4 Gaussian peaks N1, N2, N3, and N4 which are positioned at 400.5, 403.7, 406.2, and 408.1 eV, respectively (Figure 5). The peaks N1, N2, and N4 can be assigned clearly to oximes, nitroso compounds, and nitrates, respectively. The peak at 406.2 eV (N3) was assigned to nitro compounds.

The analysis of the N1s peak revealed that the peak shape does not change significantly with the conditions and the duration of the trapping reaction. Thus the measured N1s peak shape is only determined by the polymer and the irradiation conditions, i.e., by the radical type and the concentration of the radicals. It was found that the N1s peak shape changes with irradiation time.

The origin of oxime (N1) and nitroso (N2) functional groups is quite obvious. Oxime groups are formed by the reaction of primary and secondary carbon radicals with nitric oxide followed by a hydrogen migration from the carbon to the oxygen atom (Scheme 1). In the case of the primary radicals, there is still one hydrogen atom

Scheme 2. Oxidation of Nitroso Groups by Nitric Oxide and Formation of Nitro, Nitrite, and Nitrate Functional Groups[17–19]



left at the carbon atom of the oxime group. Whether the dehydration to nitrile groups as shown in Scheme 1 does really take place under the chosen reaction conditions could not be proven. Consequently, the complete absence of nitrile features in the N1s peaks does not necessarily mean that no primary radicals are formed even though it seems to be reasonable (see below). The oxime functional groups seem to be stable because it was found that the amount of oxime groups is constant with nitric oxide trapping time. The reaction of tertiary carbon radicals with nitric oxide forms nitroso groups (Scheme 1). In the literature an oxidation of nitroso groups by nitric oxide is described[17–19] (Scheme 2). Therefore, tertiary carbon radicals form nitroso as well as nitro and nitrate functional groups. Consequently, we can expect the oxime concentration to be a measure of (primary and) secondary radical concentration and the summation of nitroso, nitro and nitrate functional groups to be a representation of the tertiary radicals.

On the basis of this reaction model, the PE and PP data (Figures 6 and 7) permit some mechanistic conclusions. VUV irradiation of PE causes C–C or C–H σ bond splitting, and primary or secondary radicals are accumulated during the first 15 min of irradiation. The lifetime of primary carbon radicals is expected to be rather short because they are transformed into secondary radicals by a hydrogen rearrangement. The shape of the curves in Figure 6 suggest that these radical sites are an intermediate product. The equilibrium concentration increases during the first 15 min of irradiation up to 0.2 atom %. After their formation, these sites are converted into tertiary radicals. The mechanism of this reaction could be a radical recombination followed by a next excitation or an addition of a radical on a C=C double bond followed by a hydrogen rearrangement. Obviously, the formation of tertiary radicals indicates a cross-linking of the PE.

In the case of PP, primary and secondary radicals are formed in the first 15 min up to an equilibrium concentration of 0.17 atom %. The formation of primary and secondary radicals in case of PP resembles the one of PE. While in PE these radicals are formed by main chain scission and hydrogen cleavage from C–H bonds, in PP also the cleavage of methyl side groups can contribute. The following reaction paths differ significantly between the two polymers. In PP much less tertiary radicals are found compared with PE despite the fact that PP has a large amount of tertiary carbon atoms. However, Iwasaki et al.[20] reported a photoisomerization of γ-generated tertiary radicals in PP to the primary radical at the methyl side group. This process is very likely to occur in a VUV treatment with a nonmonochromatic light source as it was used in our experiments.

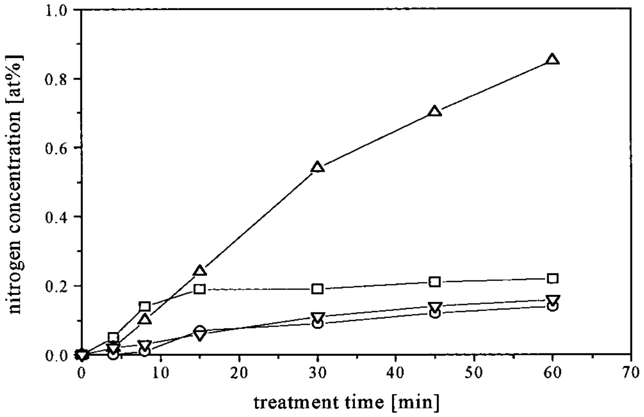


Figure 6. Concentrations of N1, N2, N3, and N4 functional groups on the surface of PE as a function of VUV treatment time (15 min of NO treatment time, 100 mbar NO, vacuum transfer; (□) N1, (○) N2, (△) N3, (▽) N4).

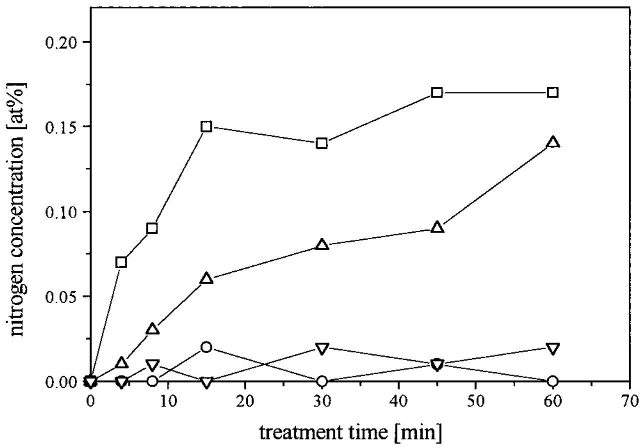


Figure 7. Concentrations of N1, N2, N3, and N4 functional groups on the surface of PP as a function of VUV treatment time (15 min of NO treatment time, 100 mbar NO, vacuum transfer; (□) N1, (○) N2, (△) N3, (▽) N4).

Conclusions

We have been able to show that nitric oxide can be used for trapping radicals on a polymer surface. The nitrogen concentration determined by XPS is a measure for the total radical concentration. In the high-resolution N1s spectra a number of different nitrogen–oxygen functional groups can be distinguished. They originate from different radical types. Oximes are formed by the reaction of nitric oxide with primary or secondary carbon radicals, while nitroso, nitro, and nitrate groups are produced from tertiary radicals.

This radical trapping method is an indispensable tool for the investigation of radicals in the polymer surface and their reactions in and after a plasma or VUV treatment.

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