

Nitrogenation of linear and branched alkanes by ambient-pressure dielectric-barrier post-discharges: Where goes the nitrogen?

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Abstract: Plasma nitrogenation of alkanes and polyolefins can partly be explained by consecutive reactions with $N_2(A)$ and $N(^4S)$. For a major part of incorporated nitrogen, however, the open question is where, i. e., into what kind of N-functional groups it has gone.

1. Introduction

The introduction of nitrogen into polymer surfaces by exposure to plasmas in pure N_2 or in N-containing gases is known for ca. 50 years. In spite of substantial research, the chemical nature of plasma-nitrogenated polymer surfaces has remained largely unknown. This contribution reports on investigations of polyolefins (polyethylene PE, -propylene PP, -isobutylene PiB) or films (≤ 80 nm) of alkanes (tetracosane n-C24, squalane) after interaction with flowing dielectric-barrier post-discharges (DB-PDs) at atmospheric pressure. At PD delay times beyond 1 ms, ground-state atoms $N(^4S)$ as well as metastable $N(^2P)$ and $N_2(A)$ are the predominant active species [1].

2. Methods

A coaxial N_2 -DBD was fed by pulsed sinusoidal voltage (40 or 80 kHz, 1 ms on : 2 ms off); samples on Au-coated Si substrates were located at ~ 100 ms delay in the PD, perpendicular to the gas flow (Fig. 1a). A 10 lmin^{-1} STP flow of N_2 ($x_{O_2} \leq 0.7$ ppm) was passed through the discharge volume of 1.56 cm^3 , resulting in 12 ms residence time. With 17.8 W power at 80 kHz, the energy deposition was 46 mJ/cm^2 . Sample temperatures were between 200 and 350 K. n-C24 ($T_{\text{fus}} = 324 \text{ K}$) and squalane could thus be treated as liquids, enabling modification of the whole film and providing larger amounts of singly-functionalized material for further chemical operations and analyses. PD-exposed samples were analyzed by X-ray photoelectron spectroscopy (XPS) and infrared reflexion-absorption (IRRAS) spectroscopy, combined with derivatization by 4-trifluoromethylbenzaldehyde (TFBA). Gas chromatography coupled with mass spectrometry (GC-MS) was applied for analysis of nitrogenated alkanes.

3. Results and Discussion

Fig. 1b shows results of XPS analyses for PE, PP and PiB. Significant differences in the T-dependence of nitrogen uptake are provisionally interpreted, in accordance with results from radiation research [2]: $N(^4S)$ and $N(^2P)$ are virtually unreactive with alkanes. With an energy of 6.17 eV beyond $N_2(X)$, $N_2(A)$ is able to excite the lowest triplet states (T_1) of alkanes (5.8 to 6.0 eV). T_1 states of n-alkanes preferably undergo C-H bond cleavage with the highly mobile H atom escaping from the cage of surrounding molecules. The remaining alkyl radical reacts with $N(^4S)$, resulting in a nitrene and, after rearrangement, an imine ($>C=N-R$ or $-H$). T_1 states of branched alkanes, in contrast, mainly fragment by C-C cleavage close to branchings. At low T and low chain mobility, cage recombination

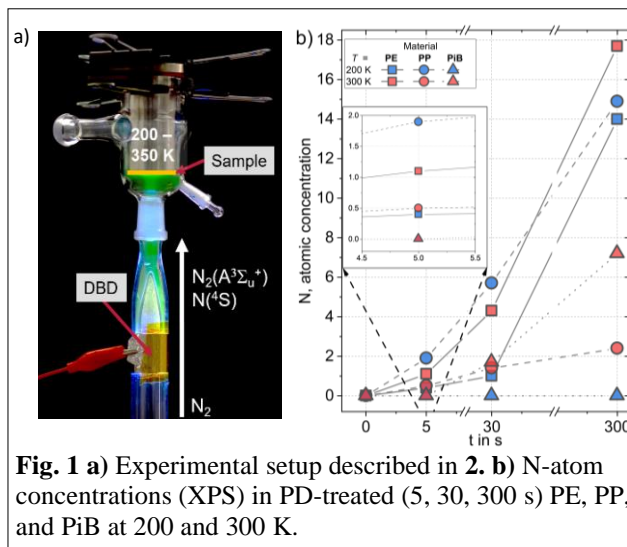


Fig. 1 a) Experimental setup described in 2. **b)** N-atom concentrations (XPS) in PD-treated (5, 30, 300 s) PE, PP, and PiB at 200 and 300 K.

of the fragments is more likely than cage escape, thus less reaction products with $N(^4S)$ are formed.

The present work focusses on a weakness of this model: While $\nu_{C=N}$ peaks and, with TFBA derivatization, ν_{CF_3} peaks are seen in IR spectra of nitrogenated samples, their intensities are at least an order of magnitude too small to account for N percentages measured by XPS. GC-MS analyses of nitrogenated squalane, too, reveal the formation of a large variety of alkanes, formed by bond scissions, rearrangements and even complete demethylation. N-containing species such as squalyl amines, however, have very small fractions at best, if they are present at all. So far it is postulated that thermolabile azoalkanes (dialkyldiazenes) are formed by nitrene dimerization, escaping the detection by MS due to decomposition on the hot GC column.

4. Conclusion

The proposed mechanistic model of plasma nitrogenation explains the formation of $C=N$ moieties, derivatizable by aldehydes such as TFBA, but a major fraction of incorporated N has still to be assigned to functional groups.

Acknowledgement

Project "NitroPol" is funded by the Deutsche Forschungsgemeinschaft (DFG) (No. 469852941).

References

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