Oxygen Inhibition in Radical Polymerization: Investigations by CIDNP Spectroscopy and Visualization with a Thermal Camera

Roman Geier, Dmytro Neshchadin, Georg Gescheidt
Graz University of Technology, NAWI Graz, Institute of Physical and Theoretical Chemistry, Stremayrgasse 9, 8010 Graz
geier@tugraz.at

Introduction

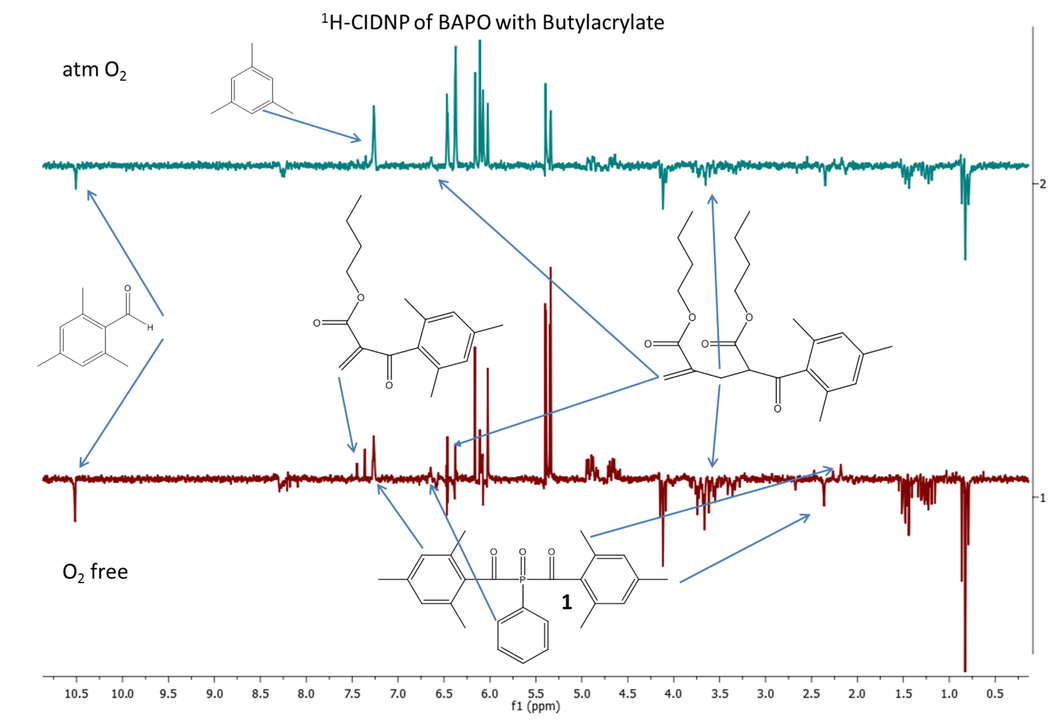
Photo-induced radical polymerization is a valuable technique for the fabrication of coatings comprising car manufacturing, electronics and dentistry. Here, photoinitiators have to be used which allow an efficient and spatially well-defined curing. Bisacylphosphine oxides (BAPOs) are often utilized photoinitiators for such processes.

Although radical polymerization is highly efficient, it suffers from substantial inhibition by oxygen. Therefore, it is crucial to obtain an accurate insight of the molecular background of the inhibition processes.

To this end, we have investigated the curing of formulations consisting of butyl acrylate and BAPO, by magnetic-resonance experiments (NMR, CIDNP) and measurements with a high-resolution thermal camera.

^{1}H- and ^{31}P-CIDNP is used to observe the formation of short-lived products, while standard ^{1}H- and ^{31}P-NMR provides information about products formed after permanent UV exposure. [1] [2]

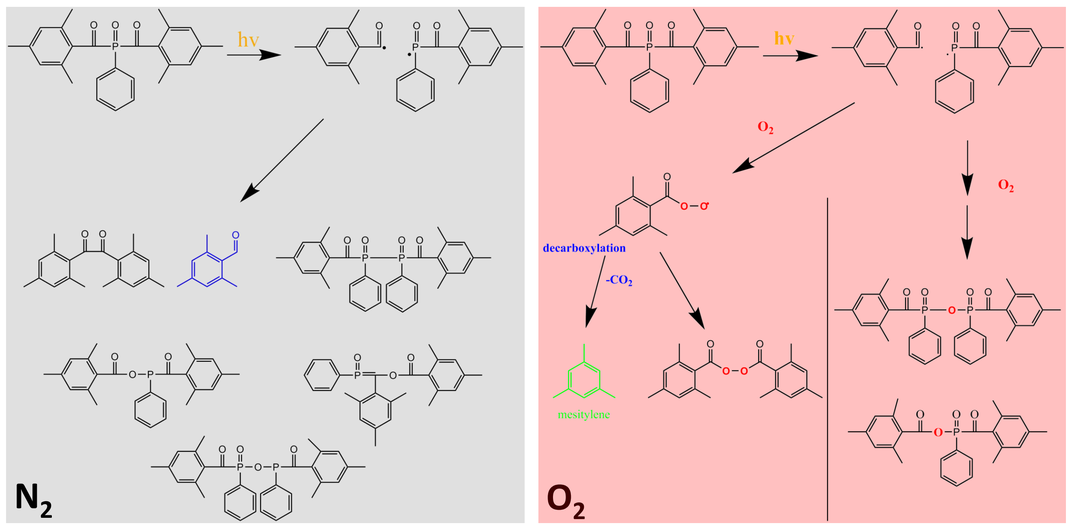
CIDNP Experiments



The ^{1}H-CIDNP spectra of BAPO in addition to butyl acrylate under atmospheric and oxygen-free conditions indicate different reaction pathways.

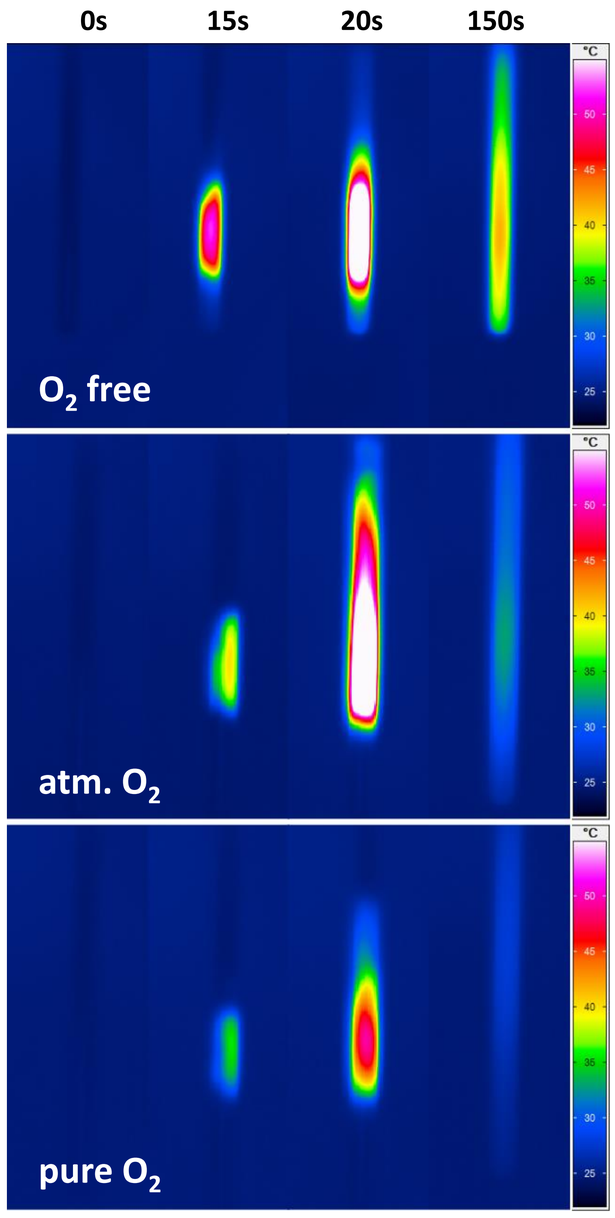
Reaction mechanisms

Further ^{1}H and ^{31}P CIDNP experiments revealed the differences in reaction mechanisms in absence and in presence of oxygen.



In the presence of oxygen additional radicals and follow up products can be observed as indicated above.

Thermal camera experiments

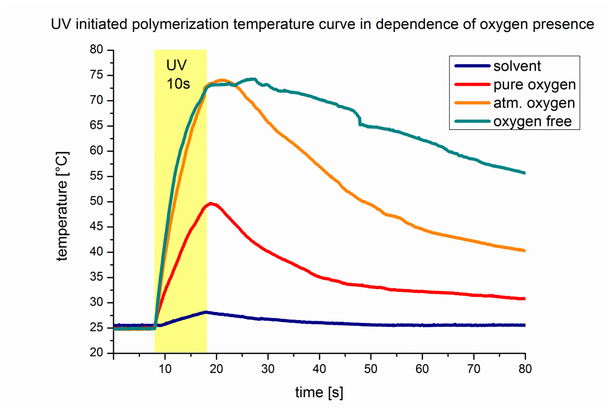


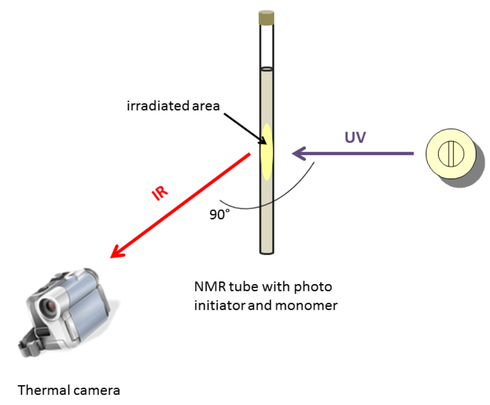
The thermal camera provides spatially resolved curing information. Here, the spatial extent of the polymerization can be observed through the accruing reaction heat.

Curing experiments of butyl acrylate with BAPO were conducted in 5mm NMR tubes at different oxygen concentrations.

After the initiation by 10s of UV irradiation by a dental lamp, temperatures started to rise. Differences in the maximum temperature and the spatial spread of the polymerization caused by the oxygen content were detected.

Under oxygen the polymerization starts (T_{max} 50°C), but when the UV exposure is stopped the reaction ends. Markedly the oxygen-free sample reaches a maximum temperature of ca. 75°C and descends slowly from this point.

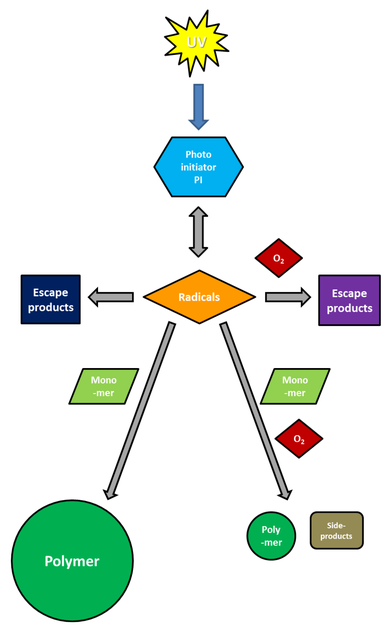




Conclusions

Different reaction mechanisms caused by the presence or absence of oxygen were investigated. Magnetic-resonance measurements indicate that the reaction of the initiating radicals with oxygen yields non-initiating products.
Imaging of the polymerization using a thermal camera shows the clearly differing extent of the polymerization depending on the oxygen.

Due to side reactions and quenching of radicals in the presence of oxygen, the polymerization efficiency is significantly reduced at the moment the UV source is turned off.



[1] J. Bargon, H. Fischer und U. Z. Johnsen, *Naturforsch.,* Bd. 22, pp. 1551-5, 1967
[2] H. R. Ward und R. G. Lawler, *J. Am. Chem. Soc.,* Nr. 89, pp. 5518-19, 1967

Acknowledgements. I thank Christina Wappl (TU Graz), for her help performing the measurements with the thermal camera.