

Electron paramagnetic resonance as a tool for mechanistic and structural investigation of depolymerization processes

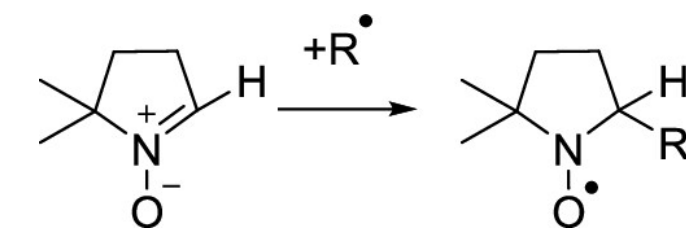
Mikhail Agrachev,¹ Gunnar Jeschke.¹

¹ Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland.

1. EPR spectroscopy for polymers science and spin trapping

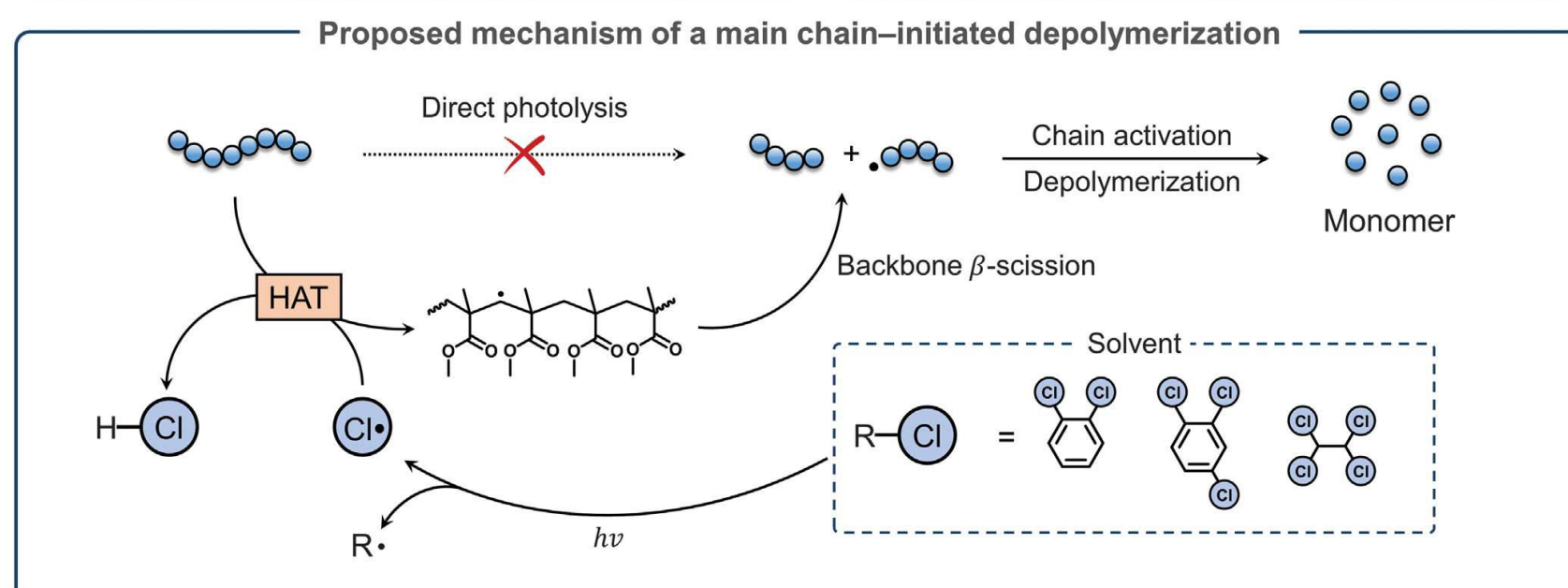
Electron Paramagnetic Resonance (EPR) is a spectroscopic technique sensitive and selective towards compounds with non-zero spin. It is therefore the ideal method for the investigation of free radicals that are commonly formed during depolymerization processes. If the radicals are stable enough, their signals can be directly recorded and they can be identified from two spin Hamiltonian parameters: the **g** tensor, related to electron spin-spin dipolar coupling for organic radicals, and the hyperfine tensor **A**, related to the electron-nuclei hyperfine interactions. In fluid solutions, the anisotropic contributions are averaged and we are left with isotropic parameters B_{iso} and a_{iso} ; the former determines the position of the center of the spectrum, while the second induces a line splitting into $[I(2n_iI_i+1)]$ (n_i =number of equivalent magnetic nuclei i , I_i =its nuclear spin).

In many cases the lifetime of the formed radicals is too low compared to the EPR timescale and they cannot be directly detected. Therefore the **spin trapping** technique is used, where special compounds (e.g. N-tert-butyl-a-phenylnitron (DMPO), alpha-phenyl N-tertiary-butyl nitron (PBN) etc.) are used that quickly react with short-lived radicals and form stable paramagnetic adducts. The original radicals can be again identified from the hyperfine couplings (typically with ¹⁴N and ¹H, but also other nuclei in specific cases).



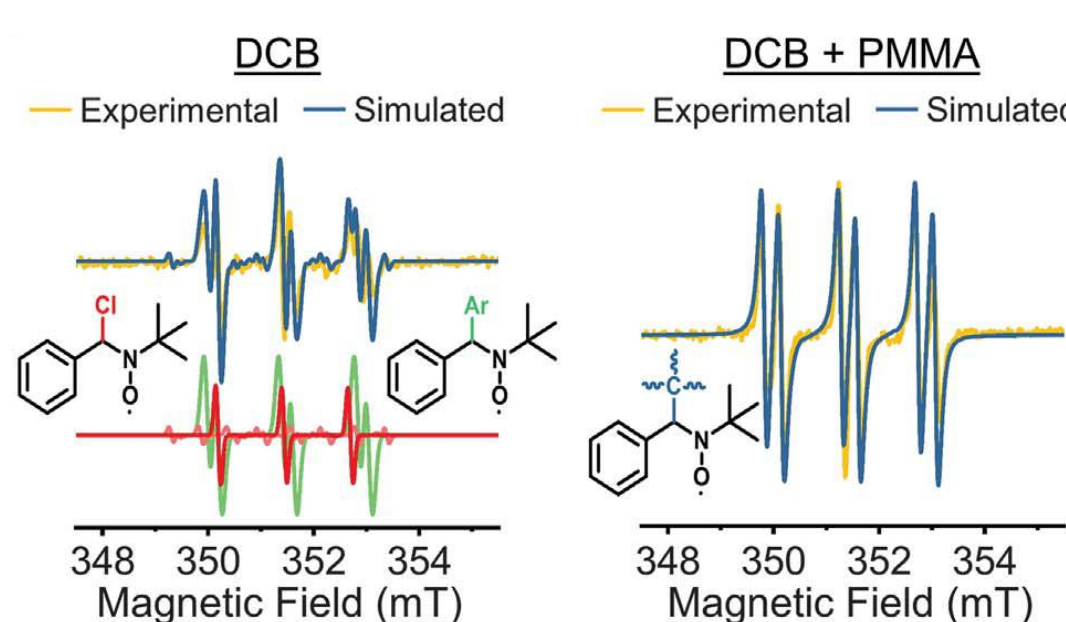
2. Optically induced depolymerization: plastics recycling

The reversion of vinyl polymers with carbon-carbon backbones to their monomers represents an ideal path to alleviate the growing plastic waste stream. We reported a main chain-initiated, visible light-triggered depolymerization directly applicable to commercial polymers. [1] By in situ generation of chlorine radicals directly from the solvent, near-quantitative (>98%) depolymerization of polymethacrylates could be achieved regardless of their synthetic route.



Photodissociation of dichlorobenzene (DCB) was demonstrated by EPR using DMPO as a spin trap to detect unstable radicals.

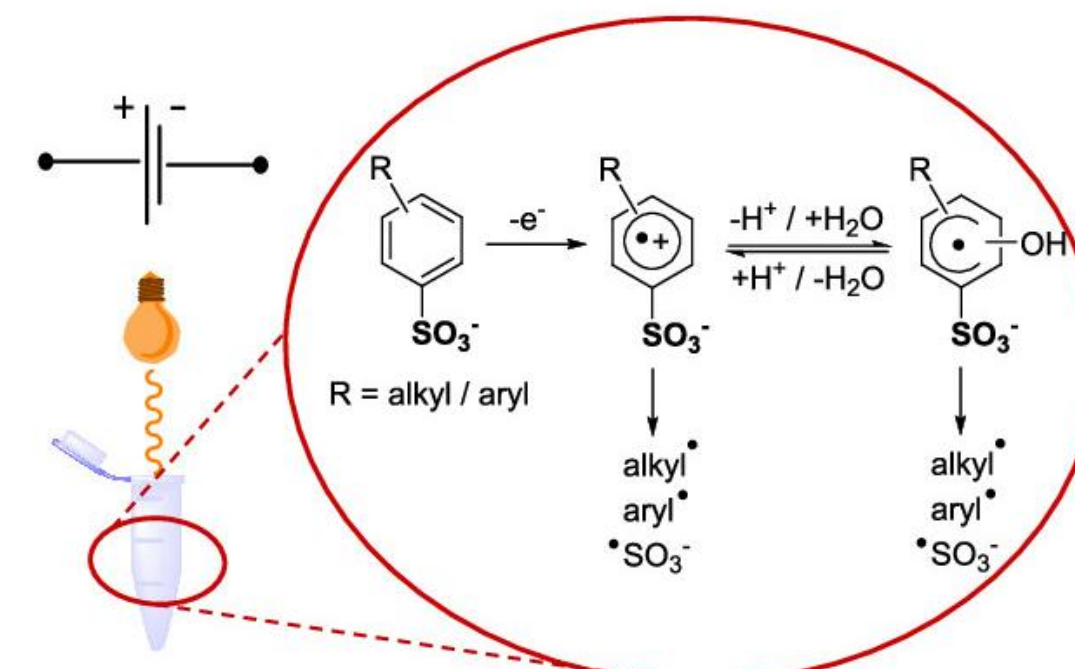
- The spectrum of irradiated pure DCB consisted of three components that exhibit hyperfine couplings with ¹H, ¹⁴N, and ^{35,37}Cl nuclei. From spectral simulations, these components were identified as aryl (green) and, most likely, Cl (red) radical adducts.
- In presence of PMMA, a single component has been detected, attributed to an alkyl radical adduct, due to polymer fragmentation.



We propose that the Cl radical generates a C-centered PMMA backbone radical through hydrogen atom transfer (HAT) of a backbone methyl or methylene unit, followed by β scission of the backbone and depolymerization under thermodynamically favorable conditions.

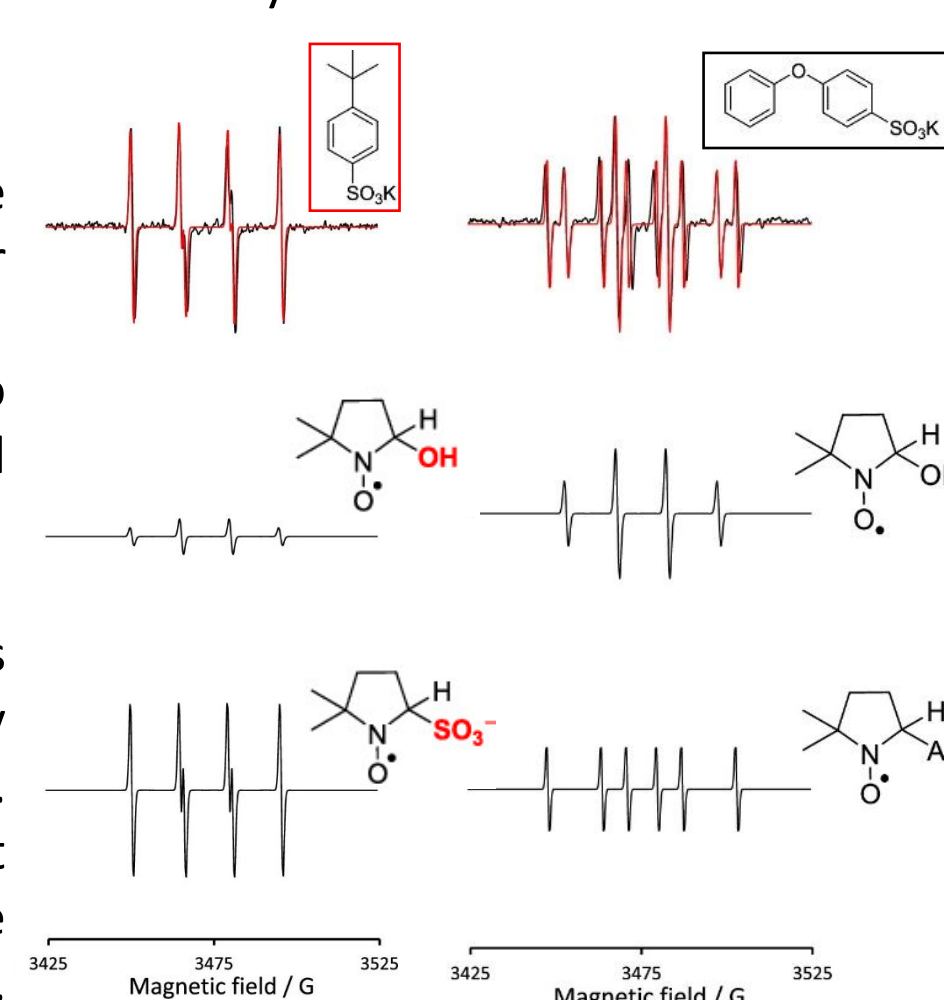
3. Optically induced depolymerization: membrane degradation in fuel cells

Sulfonated aromatic hydrocarbon-based ionomers are potential constituents of next-generation polymer electrolyte fuel cells (PEFCs). Widespread application is currently limited due to their susceptibility to radical-initiated oxidative degradation that, among other intermediates, involves the formation of highly reactive aromatic cation radicals. The intermediates undergo chain cleavage (dealkylation/dearylation) and the loss of protogenic sulfonate groups, all leading to performance loss and eventual membrane failure.

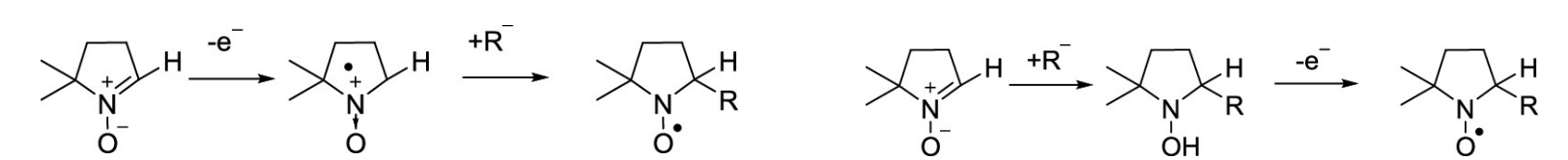


We aim to establish the major degradation pathway of proton-exchange membranes (PEMs). [2] To this end, we irradiated aqueous solutions of phenyl sulfonate-type model compounds with a Xe arc lamp, thus generating radicals. The radicals were trapped by DMPO, and the formed adducts were observed by EPR.

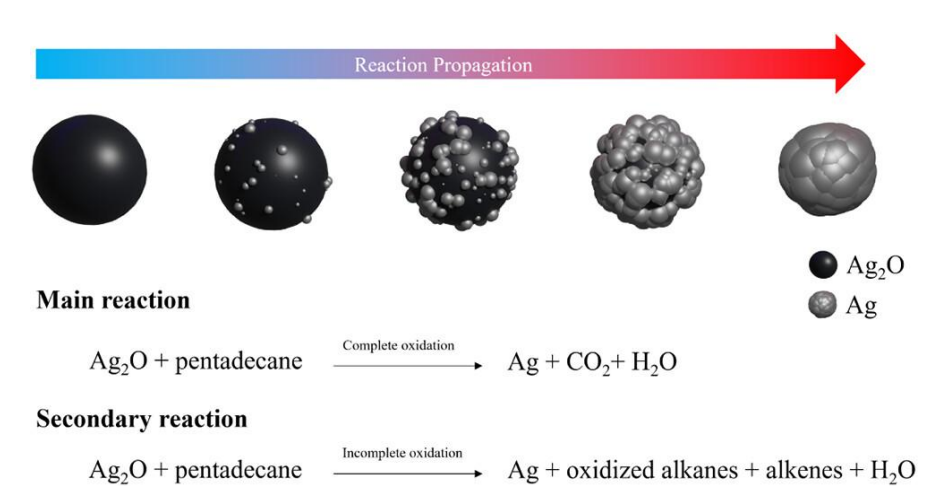
- Through the formation of the DMPO/•SO₃ - adduct, we established that desulfonation dominates for monoaromatic phenyl sulfonates.
- We observed that diaryl ether sulfonates readily undergo homolytic C-O scission that produces DMPO/•aryl adducts.



Our results support the notion that polyphenylene sulfonates are the most stable against oxidative attack and effectively transfer electrons from DMPO, forming DMPO/•OH. Our findings help to identify durable moieties that can be used as building blocks in the development of next-generation PEMs.

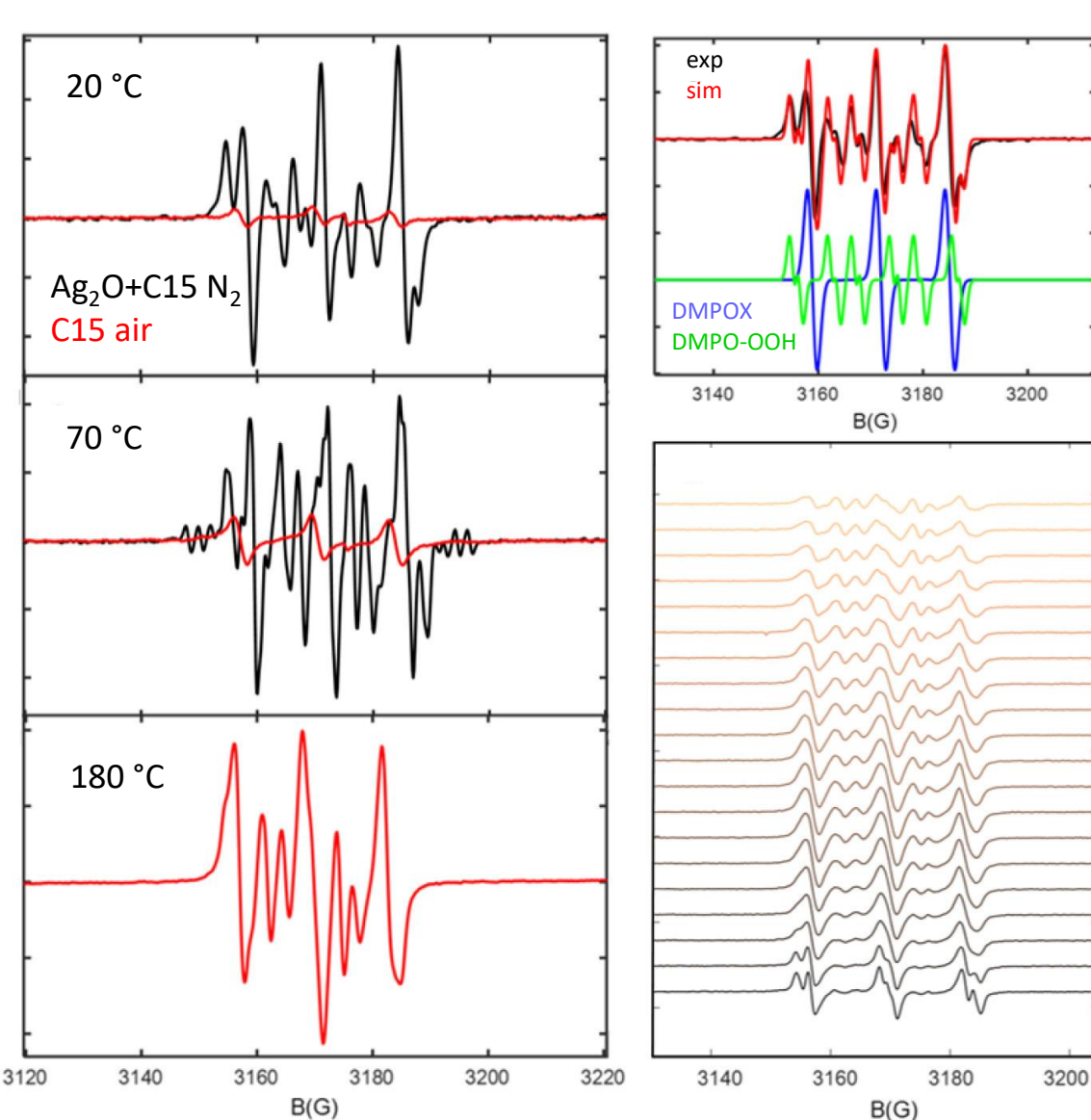
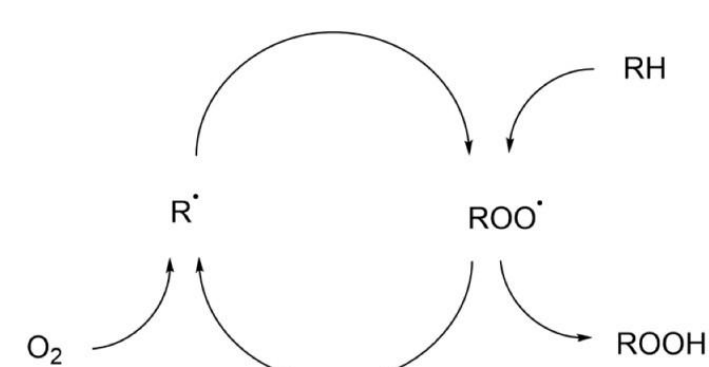
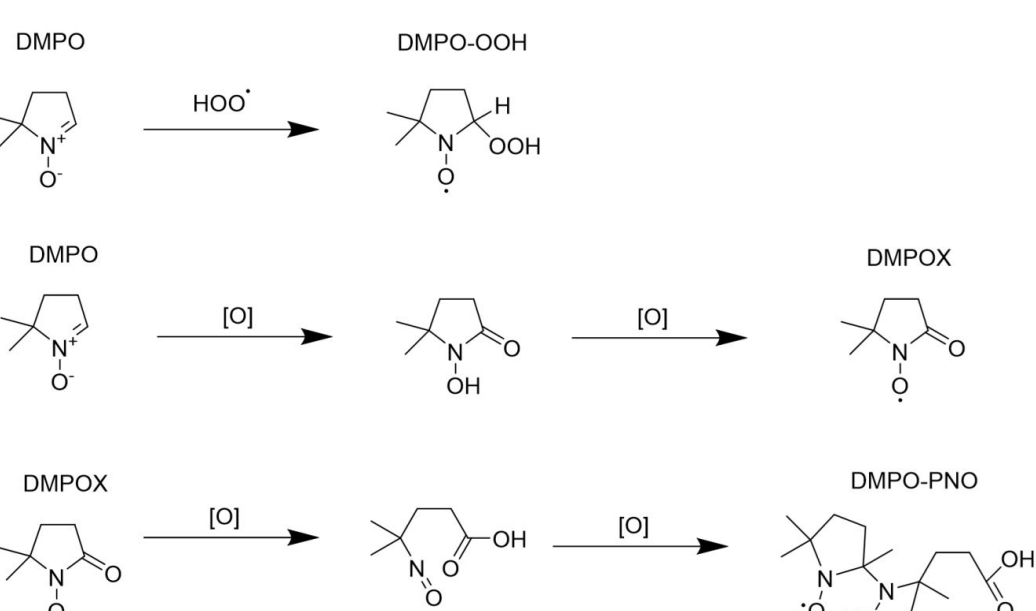


4. Thermally induced depolymerization: Ag particles formation



This study revisits the redox reaction mechanisms involved in forming metallic silver particles through the reduction of silver(I) oxide (Ag₂O) in an alkane and polymer melt environment and sheds light on the obtained particulate morphology. [3] Liquid pentadecane (C15) was selected as a model alkane. The reduction process was not linear, with Ag₂O acting both as a radical initiator and a source of oxygen. Gas chromatography detected CO₂ formation at a rather low temperature, as low as 70 °C during the reaction between Ag₂O and pentadecane, indicating a highly oxidative process resembling catalyzed combustion.

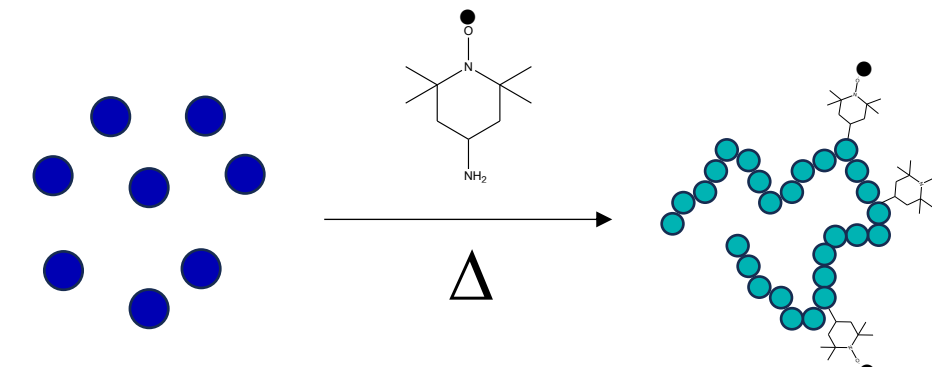
EPR spectroscopy, confirmed that radicals were involved in the redox process via ROO• and HOO• radical species typically found in hydrocarbon oxidation under oxygen conditions. We hypothesize that the reaction is predominantly a complete oxidation, with only a small fraction of incomplete oxidation.



5. In-situ viscosity evaluation during depolymerization

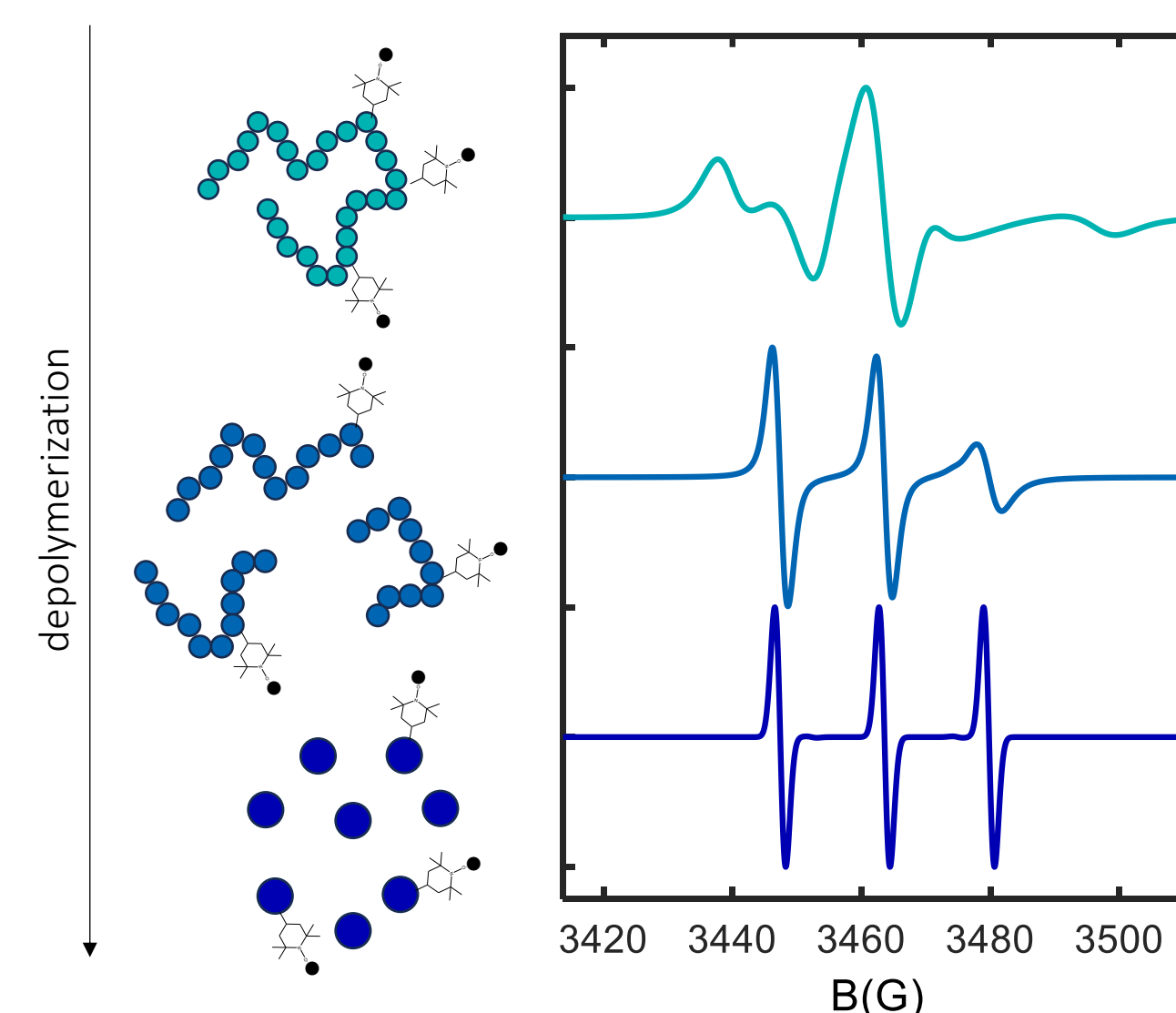
In addition to identifying the radical intermediates and thus elucidating the depolymerization mechanism, EPR can also provide information on polymer physical properties, such as viscosity. In-situ viscosity evaluation is a promising approach for the spectroscopic monitoring of the depolymerization process.

- For this one can exploit the fact that the EPR signals is strongly influenced by molecular dynamics;
- broad and asymmetric signals for frozen and solid state samples, being determined by anisotropic **g** and hyperfine **A** tensors.
- narrow and isotropic signals in fast motion regime (e.g. fluid solution), where the tensors are averaged.
- specific shape in intermediate slow tumbling regime; from the simulations the rotational correlation time can be obtained, which is directly related to the viscosity.



Experimentally this can be done with EPR by means of the **spin probing** and **spin labelling** techniques.

- In **spin probing**, the polymer is mixed with a paramagnetic probe compound, typically a nitroxide, like (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO), but also transition metal complexes. In this way microviscosity is monitored from the lineshape analysis.
- In **spin labelling**, the paramagnetic site is chemically bond to the polymer in specific positions. A better measure of bulk viscosity can be obtained with this method, as well as a more detailed viscosity-related structural information.



6. Conclusions and outlook

EPR is a powerful method for in-situ monitoring of depolymerization processes. The following information can be obtained:

- Detection and identification of short-lived radicals, formed as polymer fragments or from other reaction intermediates, typically with **spin trapping** method.
- Evaluating and monitoring viscosity and its changes from the detailed lineshape analysis of the signals. **Spin probing** and **spin labelling** methods are used for this aim.

Case studies related to different applications are shown, such as optically-induced plastic recycling, membrane degradation in polymer electrolyte fuel cells and metallic Ag particles synthesis.

The present methodologies will be extended to in-situ structural and mechanistic investigations of depolymerization processes in the solid state.

Acknowledgements:

H. S. Wang (ETH Zurich) T. Nemeth (SINTEF Industry) A. Alfayez (Empa St. Gallen) M. P. Heuberger (ETH Zurich) A. J. Martín (ETH Zurich)
A. Anastasaki (ETH Zurich) T. Nauser (ETH Zurich) S. Gaan (Empa St. Gallen) L. Gubler (PSI Villigen) J. Pérez-Ramírez (ETH Zurich)

Contact:

Mikhail Agrachev
email: magrachev@ethz.ch

References:

- H. S. Wang et al., Science 387, 874.
- T. Nemeth et al., J. Phys. Chem. C 2022, 126, 37, 15606–15616.
- F. Alfayez et al., ACS Appl. Mater. Interfaces 2025, 17, 19, 28808–28821.