

## DECODING THE MECHANISM OF ENVIRONMENTAL POLYMER DEGRADATION: A MASS SPECTROMETRIC APPROACH

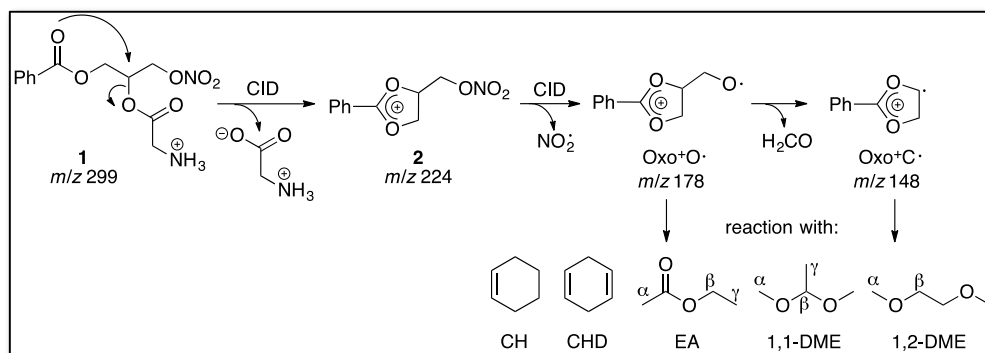
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Synthetic polymers are amongst the most widely used materials due to their extremely diverse properties. Unfortunately, exposure of polymers to environmental conditions, in particular UV radiation and humidity, leads to dramatic changes of their properties, resulting in decreased service life and limited usage. The most important degradation pathways in polymers proceed through radical steps. Key-intermediates are polymer-derived peroxy radicals,  $\text{ROO}^\bullet$ , which act as carrier in a radical chain process that propagates damage through hydrogen abstraction from a neighboring polymer strand.

We have recently demonstrated that  $\text{ROO}^\bullet$  reactions with polyester model systems can be explored on the millisecond time scale by mass spectrometry using the distonic radical ion approach.<sup>[1]</sup> This study revealed clear deficiencies in our understanding of  $\text{ROO}^\bullet$  chemistry and suggests that the current mechanistic model for radical polymer degradation is by far not complete. In particular, the role of C- and O-centred radicals (other than  $\text{ROO}^\bullet$ ) in the degradation process requires further investigation.<sup>[2]</sup> We have designed novel precursors of type **1** to generate distonic radical ions of type  $\text{Oxo}^+\text{O}^\bullet$  and  $\text{Oxo}^+\text{C}^\bullet$ , which were reacted with a series of small model systems featuring typical substructures in polyesters (alkenes, esters, acetals, amines, etc.). Product and kinetic studies, in combination with computational methods, were employed to elucidate the mechanism of these reactions.<sup>[3]</sup>



### REFERENCES

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