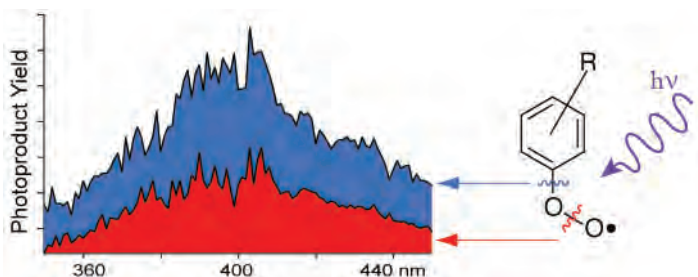


## Lights, peroxy radicals, action spectroscopy!

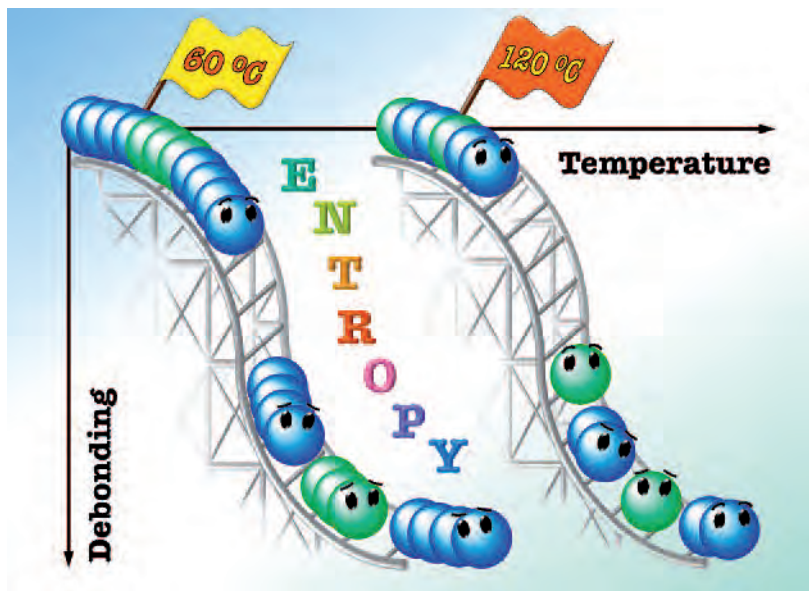
Peroxy radicals have a key role in the degradation of volatile organics in the atmosphere, as well as the oxidation of cellular lipids and other integral biomolecules. The excited electronic (B) state of alkylperoxy radicals is dissociative and lies reliably in the ultraviolet region. Arylperoxy radicals, on the other hand, are predicted to have a dissociative state accessible

within the visible spectrum. To date, however, there have been no resolved room-temperature spectra of these species or any characterisation of the photoproducts of the B state of an arylperoxy. The research groups led by Dr Adam Trevitt and Professor Stephen Blanksby at the University of Wollongong have now reported the controlled synthesis and isolation in vacuo of charge-tagged phenylperoxy radicals that were then subjected to photodissociation action spectroscopy (Maccarone A.T., Kirk B.B., Hansen C.S., Griffiths T.M., Olsen S., Trevitt A.J., Blanksby S.J. *J. Am. Chem. Soc.* 2013, **135**, 9010–14). Using their approach, the authors observed a broad absorbance feature centred firmly in the visible spectrum with the photoproducts clearly identified as resulting from losses of molecular and atomic oxygen. These findings suggest that the photo-activation of arylperoxy radicals in the troposphere, which yields atomic oxygen, could feed into the production of tropospheric ozone independently of the well-known  $\text{NO}_x$  cycle.



## Harnessing entropy to heal polymers

Self-healing polymers are based on dynamically bonding functional groups that allow the material to undergo reversible de-bonding in response to a pre-selected trigger such as heat, light or pH. Currently, the method for tuning the de-bonding point of such materials is to design the reversibly bonding functional groups (i.e. the chemistry), which essentially requires new monomers to be synthesised each time an adjustment of the de-bonding point is desired. However, scientists from the Australian National University, the Karlsruhe Institute of Technology, the University of Dresden and Evonik Industries report that the de-bonding temperature of a polymer can also be tuned by changing the chain length of the polymer building blocks, thus altering the entropy released on de-bonding (Guimard N.K., Ho J., Brandt J., Lin C.Y., Namazian M., Mueller J.O., Oehlschlager K.K., Hilf S., Lederer A., Schmidt F.G., Coote M.L., Barner-Kowollik C. *Chem. Sci.* 2013, **4**, 2752–59). In this



work, entropy-driven de-bonding is predicted theoretically and demonstrated experimentally for two Diels–Alder polymer systems, each based on a different difunctional diene and a common difunctional dienophile. This

finding has the potential to fundamentally transform the approach polymer and materials chemists take to designing dynamically bonding materials.