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Light does not have to be a (rapid) killer of chemical molecules

Chemical molecules strongly interacting with light generally disintegrate very rapidly. At the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw, the main mechanism conducive to this destruction has been determined. This knowledge makes it possible to enhance the photostability of molecules several times over, which is of significance not only for the measurement methods used in laboratory studies, but also for manufacturers of everyday objects, especially those made of coloured polymers.

Vivid colours of recently-painted walls fade in a flash. The plastic grass sprinkler is useless after only a few months of operation. And in the lab it's another bad day: measurements fail, because the laser-illuminated chemical molecules are disintegrating too quickly. In all these cases, the factor responsible for the molecular disintegration is light. Now, the time of disintegration can be extended significantly – thanks to the research of a group of scientists from the Institute of Physical Chemistry of the Polish Academy of Sciences (IPC PAS) in Warsaw, Poland, headed by Prof. Jacek Waluk. The researchers have managed to identify the main mechanism accelerating the photodestruction of chemical molecules.

“In our lab we observe single chemical molecules. We use a fluorescence microscope for this, examining the light they emit. The main problem here is the lifetime of the particles: even those considered to be permanent disintegrate after a few to a dozen-or-so seconds. So we decided to extend their lifespans. The first step towards this goal had to be, of course, understanding the main phenomenon responsible for the destruction of the molecules,” says Prof. Waluk, the coauthor of a paper published in the Journal of Physical Chemistry Letters.

For the measurements to be credible, it is necessary to observe several to tens of thousands of photons emitted by the molecule in the process of fluorescence. The molecule emits photons in all directions, but only those travelling towards the detectors are recorded. This means that in the time over which the apparatus records several dozen thousand photons, the molecule must have emitted roughly one million of them. In the case of the TDI (terrylene diimide) molecules, studied at the IPC PAS, the fluorescence quantum yield was approx. 70%. It follows that during measurement each molecule had to have absorbed nearly two million photons.

“Each photon absorption causes the molecule to enter an excited state, which generally increases its reactivity, i.e. its ability to enter into chemical reactions. Thus, each absorbed photon brings the

particle closer to its own death. It is generally accepted that a molecule is photostable if it has a 50% chance of survival after absorbing a million photons. In our conditions, this means that we can observe it for a few seconds," explains Prof. Waluk.

The key to enhancing the photostability of the molecules has proved to be analysis of the manner of their preparation for observation under the fluorescence microscope. The procedure starts with the preparation of a very dilute solution of the molecules in a dissolved polymer. A droplet of this solution is then placed on the microscope slide located on a spinning disc. Spinning spreads the droplet over the surface, and the solvent evaporates. A thin layer of polymer remains on the slide, with a thickness of only 30 nm, together with trapped single molecules of the test substance, which are about one nanometer in size. If the concentration of the molecules in the initial solution has been skillfully selected, the single test molecules will be positioned in the polymer film at relatively large distances from each other, in the order of microns (if people were distributed with a similar density, the distance between neighbours would be several kilometres). The prepared slide is then placed under the microscope, where the polymer layer is swept by a narrow laser beam with a light wave of an energy selected so as to excite the test molecules. Any fluorescence appearing in the area that is lit most probably comes from a single molecule of the test compound.

What can the excited molecule be reacting with? From the beginning, the primary suspect was oxygen which can be dissolved in polymer solutions. The researchers therefore examined the effect of seven polymers on the lifetime of the TDI molecules, but could not detect any link between the capacity for improved oxygen dissolution and accelerated photodestruction of TDI. The correlation only appeared when they examined the effect of the rate of oxygen permeation through the polymer layer on the test molecules. Here the differences were significant: polymers through which oxygen permeated slowly clearly enhanced the photostability of the molecules. The record polymer – which turned out to be the popular polyvinyl chloride – could increase the lifetime of the molecules even a hundredfold. This time was also seen to lengthen with the age of the polymer. This was another argument in favour of the crucial role of oxygen, since it is known that oxygen permeates more slowly through older polymers.

"We are convinced that it is not only the reaction of molecules with light that is responsible for the accelerated photodestruction of our molecules, but also their reaction with oxygen. The excited molecule passes into what is technically known as a triplet state. In this state triplet oxygen in the basic state can combine with it. The oxygen is activated and passes into singlet state, and singlet oxygen is an extremely voracious chemical individual, instantly forming reactions with anything that is within its reach," explains Prof. Waluk.

The results of the IPC PAS group, obtained with funding from a grant from the Polish National Science Centre, are of broad practical significance. Applied in laboratories, they will increase the possibilities for the investigation of single chemical molecules using fluorescent methods, which has been a major challenge for over 20 years. Understanding the mechanism of photodestruction of molecules will also prove useful wherever everyday objects are produced with the participation of polymers and dyes. The selection of suitable polymers, hindering the migration of oxygen, may significantly extend the lifespan of dyes and the lifetime of the object.

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SCIENTIFIC PAPERS:

"In Search for the Best Environment for Single Molecule Studies: Photostability of Single Terrylenediimide Molecules in Various Polymer Matrices"; H. Piwoński, A. Sokołowski, J. Waluk; Journal of Physical Chemistry Letters 2015, 6 (13), pp 2477–2482;
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LINKS:

http://www.ichf.edu.pl/
The website of the Institute of Physical Chemistry of the Polish Academy of Sciences.

http://www.ichf.edu.pl/press/
Press releases of the Institute of Physical Chemistry of the Polish Academy of Sciences.

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The photostability of chemical molecules suspended in a polymer can be enhanced by limiting their contact with oxygen, as found by researchers from the Institute of Physical Chemistry of the Polish Academy of Sciences (IPC PAS) in Warsaw, Poland. (Source: IPC PAS, Grzegorz Krzyżewski)