On the Death of Polymers: Revisiting Termination Rate Coefficients in Radical Homopolymerization

February 19 2010

(PhysOrg.com) -- Although radical polymerization is used in the synthesis of about half the world's polymers, details of exactly what is going on in the reaction soup in complex industrial settings have been sketchy at best. As the materials enter our lives as, for example, drugs, coatings, fibers and solar cells, controlling their reactions and therefore their properties is extremely important.

Scientists in New Zealand have recently addressed a fundamental part of this story by considering termination rate coefficients for a couple of very common reactions, using results from new analytical techniques to revisit our old understanding. They found the way the small polymers (oligomers) in the system move and their speed, i.e., their diffusion behavior, to be the critical factor. This work is published in a special issue of *Macromolecular Chemistry and Physics*, devoted to radical polymerization.

The people responsible, Greg Russell and his colleagues at the University of Canterbury, are experts in polymer kinetics. Russell explains, “The majority of chemists simply try to bring about reactions by mixing different chemicals together under different conditions. However it is also important, especially for those who make chemical products on a large scale, to have precise quantitative descriptions of the speeds at which reactions occur. Chemical kinetics is the field of work that develops such descriptions. It is therefore an area where chemistry and

mathematics intersect."

He goes on to say, "Arguably the hardest nut to crack in the radical polymerization scheme has been the termination reaction. In layman's terms, termination is the fundamental reaction whereby a polymer molecule stops growing larger. A reasonable analogy is human death, the process which ceases human life and thus prevents a human's age from mounting and mounting. In radical polymerization this reaction is diffusion controlled in rate, which means that its speed is determined by how fast the molecules move." This speed of movement can depend on many factors such as how long the molecule is, the number of obstacles around the polymer, the temperature of the system, and so on. "This is the origin of the complexity of the termination reaction, and is the reason why, after over 60 years of intensive study, it is still not fully understood, not nearly."

In this work Russell revisited some of the earliest questions about termination. "Recent years have seen the development of highly specialized techniques for measuring termination rate coefficients under precisely controlled conditions. I have taken this information and attempted to see whether it is consistent with systems where many different termination reactions occur at once, as is the case in commercial processes. For the monomer styrene I find there is consistency, but for methyl methacrylate there is not."

In trying to explain this result, he eliminated most of the conventional views, and came to the conclusion that the answer lies with the oligomers in each system, which seem to have slightly different diffusional behavior.

Philipp Vana works at the University of Göttingen, where Greg Russell is currently on sabbatical. He specializes in radical polymerization and serves on the Advisory Board of Macromolecular Chemistry and

Physics. He is the Guest Editor of the special issue. In his view, "Russell's paper is especially exciting, as it demonstrates that the information gathered by modern and advanced methods is useful to reevaluate the results obtained by older methods. Completely new insights can be extracted by such an approach." He adds that Russell's work not only adds new information to the field, but also presents a nice view of the complete picture, "which helps us to understand the complete history of science instead of getting a short snapshot of the present."

This historical perspective of the field is especially pertinent as the special issue focused on the kinetics and mechanism of radical polymerization was prepared in order to honor Michael Buback, who turns 65 this year and who, according to the editor Vana, "undisputably is one of the doyens in this field." Recent years have seen the invention of new controlled polymerization methods and Vana says it is of "vital importance to fundamentally understand these new techniques in order to exploit their full potential for material design. The newly invented polymerization technologies also provided new avenues for unlocking the secrets of the conventional processes. Many important questions could be answered recently and it seems to be justified to resumé at this stage and to identify, which major questions need further attention."

More information: D. R. Tayler, K. Y. van Berkel, M. M. Alghamdi, G. T. Russell, "Termination Rate Coefficients for Radical Homopolymerization of Methyl Methacrylate and Styrene at Low Conversion," *Macromol. Chem. Phys.* 2010, DOI: 10:1002/macp.200900668

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