Summer School on Polymeric Networks for Sustainable Development

July 6th – 12th, 2025

Self-rupturing polymer network as a source of reactive and persistent radicals

Kosei Oikawa[1], Masahiro Yoshida[2], Tasuku Nakajima[2,3], Jian. Ping. Gong*[2,3]

[1] Grad. Sch. of Life Sci., Hokkaido University, North 21 West 11, Kita-ku, Sapporo, Japan
[2] Fac. of Adv. Life Sci., Hokkaido University, North 21 West 11, Kita-ku, Sapporo, Japan
[3] WPI-ICReDD, Hokkaido University, North 21 West 11, Kita-ku, Sapporo, Japan
*E-mail: gong@sci.hokudai.ac.jp

[Introduction]

Polymer networks including elastomers and gels have been utilized in various applications such as tires due to their softness. This time we put a different spin on the applications of polymer networks and introduce an unprecedented concept: using polymer networks as radical sources.

When polymer chains break and their covalent bonds cleave homolytically, mechanoradicals are generated at both rupture ends.[1] Here, excess swelling beyond a gel's deformation limit is used as the driving force for polymer network rupture and mechanoradical generation. A high concentration of trapped polymer inside the network, termed a molecular stent[2], increases its osmotic pressure and leads to excess swelling, polymer chain rupture, and mechanoradical formation in good solvent.

Unlike conventional radical initiators, this method requires no external energy input such as heat or light. Furthermore, mechanoradicals at polymer ends cannot diffuse and are less likely to recombine, which leads to a prolonged radical lifetime. These features suggest a new direction for radical-based reactions.

[Experiment & Result]

An excessively swellable gel was prepared by incorporating high concentrations of poly(dimethylacrylamide) (PDMAAm) stent polymer into a PDMAAm gel. The gel was then dried and pulverized into microparticles, which were mixed with an aqueous precursor solution containing *N*,*N*-dimethylacrylamide and *N*,*N*′-methylenebisacrylamide under low-oxygen conditions. As a result, gelation of the solution occurred. This gelation was attributed to the microparticles undergoing excess swelling in the precursor solution, which generated mechanoradicals that triggered polymerization. Further analysis revealed that gelation occurred at lower radical concentrations than those required by conventional initiators, suggesting a prolonged radical lifetime. These results demonstrate that polymer networks can generate long-lived radicals without external energy input.

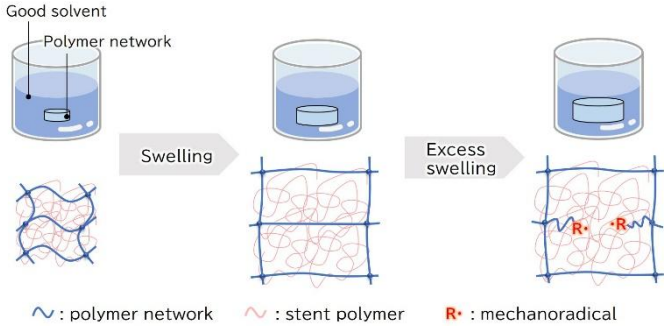

Fig. 1 Schematic illustration of mechanoradical generation by self-rupturing.

References:
[1] J. Sohma, et al., J. Soc. Chem. Ind. Jpn., 1965, 68, 1535-1538
[2] T. Nakajima, et al., Adv. Funct. Mater. 2012, 4426-4432