

Heat-responsive polymers that do not breakdown in water may lead to new antifouling coatings and enhanced oil recovery

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Credit: AI-generated image (disclaimer)

Thanks to the positively and negatively charged units in their monomers, zwitterionic polymers have a high affinity for water—a property known



as hydrophilicity. This property helps prevent fouling, namely the buildup of contaminants. Current zwitterionic polymers are not effective in water as they use monomers such as commercially available acrylamide and methacrylates that tend to decompose and lose their electrostatic characteristics when wet.

To solve this issue, a team led by Vivek Vasantha from the A*STAR Institute of Chemical and Engineering Sciences in Singapore has now developed zwitterionic polymers based on water-stable monomers that incorporate nitrogen-containing derivatives known as imidazoles. The team introduced the zwitterions to readily accessible, hydrophobic polystyrene to boost its hydrophilicity in water by forming a hydration layer through electrostatic interactions and hydrogen bonding.

To synthesize the monomers, Vasantha's team reacted styrene precursors with positively charged imidazoles before attaching the negatively charged sulfonate functional groups. The <u>monomers</u> produced polymers with intact zwitterionic properties, meaning that they retained their positive and negative charges.

These new imidazole-based polymers exhibited some novel solubility characteristics: unlike their conventional water-soluble counterparts, they swelled in water and dissolved only in highly concentrated brine. These differences stem from dipole–dipole interactions and the more hydrophobic nature of the new polymers compared to acrylamide and methacrylate.

With high tolerances to salt, pH and temperature, these polymers became increasingly viscous when subjected to higher shear forces in brine. This characteristic—similar to 'silly putty', which is malleable in one's hands but is unchanged when hit with a hammer—makes the polymers attractive for <u>enhanced oil recovery</u> and marine antifouling coatings.



Another advantage of the new polymers is their reversible phase change: between 5 °C and 95 °C, the polymers formed gels that become clear fluids when heated above the so-called <u>critical temperature</u> in brine and that revert to their stable cloudy state on cooling.

"This phase transition results from the disruption of the equilibrium between salt, water and zwitterionic species," says Vasantha. The polymer chains expand on heating and collapse below the critical temperature. The researchers can control the critical temperature by simply varying either the brine or polymer concentration. For example, the transition occurred at 20 °C at a low polymer concentration but at 40 °C at a higher polymer concentration.

"We are currently designing new zwitterionic polymers and copolymers with salt- and heat-responsive behavior for a wide range of applications, such as enhanced oil recovery, low-temperature protein separation and antifouling," says Vasantha.

More information: Vasantha, V. A., Jana, S., Parthiban, A. & Vancso, J. G. Water swelling, brine soluble imidazole-based zwitterionic polymers – synthesis and study of reversible UCST behavior and gel–sol transitions. Chemical Communications 50, 46–48 (2014). DOI: 10.1039/c3cc44407d

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