Radical predictions in polymer chemistry

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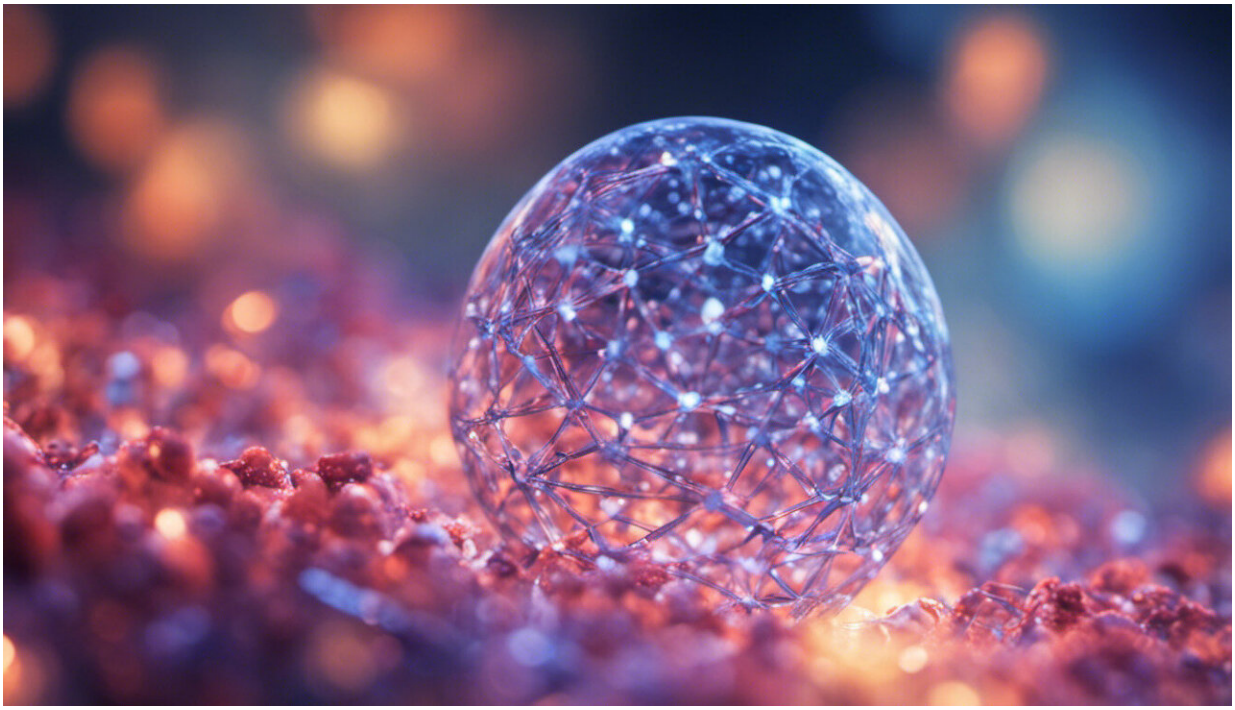

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Free radicals may have a bad reputation for causing ozone depletion and premature aging, but they are in fact extremely useful for making novel materials, particularly polymers. Skilled chemists can link up a wide range of free radicals into long-chain polymers using a technique called atom transfer radical polymerization (ATRP). Using different metal catalysts, one can precisely control the rates of polymerization and termination and therefore the architecture and functionality of the

polymer.

Fabio di Lena and Christina Chai at the A*STAR Institute of Chemical and Engineering Sciences have now performed the first-ever theoretical modeling of copper-catalyzed ATRP to explain quantitatively how radical polymerization rates are influenced by molecular structures and properties—laying out a critical roadmap for the production of next-generation polymer materials.

The success of an ATRP reaction depends on how well the metal catalyst generates and deactivates organic radicals by intermittently stealing or giving up electrons. If radical production is too fast, the polymerization stops, while sluggish activation or deactivation makes it hard to produce high-quality polymers. Unfortunately, fine-tuning ATRP rates is tricky because researchers must simultaneously optimize many diverse factors such as catalyst and radical geometries, solvents and reaction conditions.

To solve this problem, di Lena and Chai turned to computer-aided molecular design, a technique widely employed in the pharmaceutical drug discovery. They first performed theoretical calculations to extract hundreds of numerical parameters or 'molecular descriptors' corresponding to specific structural and chemical properties for a series of ATRP copper catalysts and organic radicals. They then conducted sophisticated statistical analyses on the data to reveal subsets of principal descriptors that had the most influence over polymerization rates.

Next, the team combined their chemical intuition with stringent testing to further narrow the list of descriptors. Finally, biology-inspired artificial intelligence techniques called genetic function algorithms were used to produce mathematical models that relate ATRP rates to algebraic combinations of descriptors like energy levels, molecular volumes and bond lengths. According to di Lena, these models are striking because they agree with the generally accepted mechanistic picture of ATRP and

can provide unprecedented predictive insights.

“This method should facilitate the design of new ATRP catalysts by screening, in a virtual way, hundreds of metal complexes at time,” says di Lena. “Labs will only need to prepare the most promising candidates, saving time and money.” Di Lena is also confident that the method will become a powerful tool for developing polymers with tailored properties and functions.

More information: Di Lena, F. & Chai, C.L.L. Quantitative structure–reactivity modeling of copper-catalyzed atom transfer radical polymerization. *Polymer Chemistry* 1, 922–930 (2010).

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