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Branched polymers: Synthetic subtlety

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The degree of branching in a hyperbranched polymer can be controlled by changing the reaction conditions

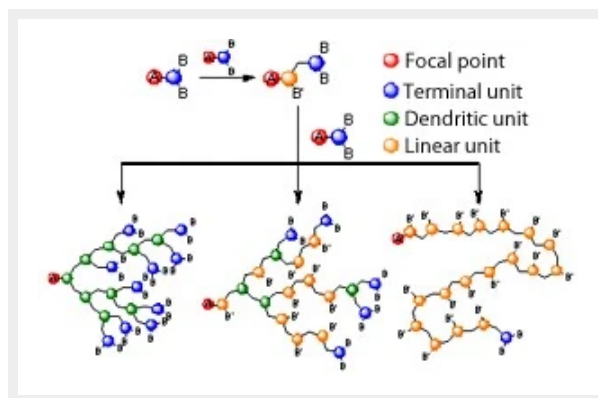


Fig. 1: Varying the relative reactivity of functional groups in the growing polymer chain and monomer by adjusting the reaction conditions (top) provides complete control over the degree of branching in a polymer, from 100% branching (left) to 0% branching (right). © 2010 ACS

The formation of branched products during polymer synthesis was historically viewed as an unwanted but unavoidable side reaction. More recently, highly branched molecules have been found to exhibit unique properties, such as low viscosity and high solubility, that make them attractive for use in coating and resin applications. Dendrimers can be regarded as the ultimate branched molecules — they have well-defined discrete structures with every molecule in the sample being the same, as opposed to polymers, which have variable chain lengths. Furthermore, every possible branching point in a dendrimer is populated. They are, however, difficult to synthesize and thus not suitable for large-scale applications. Hyperbranched polymers, typically made in a one-pot process, are more attractive for such applications, but their structure is more difficult to control. Mitsuru Ueda and co-workers from the Tokyo Institute of Technology in Japan¹ have now reported a polymerization reaction in which the degree of branching in the formation of a hyperbranched polymer can be controlled simply by adjusting the reaction conditions. “The degree of branching is the key parameter in characterizing a hyperbranched polymer,” explains Ueda. A 0% degree of branching (DB) represents a linear polymer, whereas a DB of 100% would mean that all branching points are populated. Hyperbranched polymers with DB of 100% differ from dendrimers only in that a range of molecular weights may be present in a sample. The reaction reported by Ueda’s team is the polymerization of an aryl ketone in the presence of a superacid. The results of a series of model reactions suggested that changing the ratio of the superacid to monomer in the reaction could provide control over the DB of the resultant polymer (Fig. 1). In this polymer system, they found that a 1:1 ratio of acid to monomer gave 100% branching, whereas using neat superacid solvent gave a linear polymer (0% branching). In between, at ratios corresponding to 2–6 equivalents of acid, the DB varied linearly between the two extremes. “These findings will allow us to synthesize other series of hyperbranched polymers with controlled DB and investigate their use as functional materials,” said Ueda.

References

- 1 Segawa, Y., Higashihara, T. & Ueda, M. Hyperbranched polymers with controlled degree of branching from 0 to 100%. *J. Am. Chem. Soc.* **132**, 11000 (2010).
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Additional information

This research highlight has been approved by the author of the original article and all empirical data contained within has been provided by said author.

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