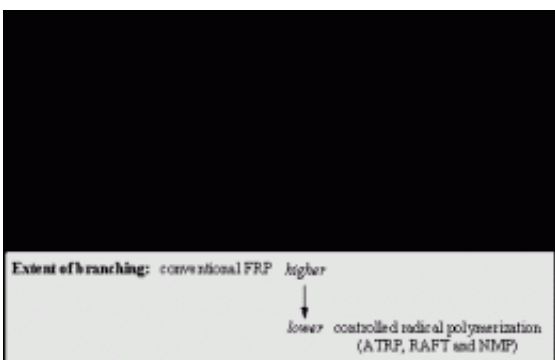


# The Long and the Short of Acrylate Polymerization

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(PhysOrg.com) -- Used in such diverse applications as adhesives, detergents, and super-absorbent disposable diapers, polyacrylates are key polymers, but the mechanisms of their formation are complex and have long been incompletely understood. Understanding how polyacrylates form brings opportunities to better control their molecular structure and hence their properties and recent research has been enlightening. Leading the field is an international group coordinated by Pete Lovell from the University of Manchester, UK.

In a new paper to appear in a *Macromolecular Rapid Communications* special issue devoted to highlights of the recent revolution in acrylate research, this group explains the relationship between the type of reaction used to polymerize the acrylate monomers and the resultant

polymer structure.

There are two broad approaches used in the polymerization of acrylate monomers: the traditional free-radical polymerizations and the more recently developed controlled radical polymerizations (CRPs). The traditional approach allows for little control of skeletal architecture, while the array of newer “controlled” techniques (also called living free-radical polymerizations) facilitates architectural control. What happens at the active end of the growing [polymer chain](#) is the main differentiating factor. In the traditional approach when one active chain end encounters another, both are likely to die, killing chain growth. In the controlled techniques, the chain ends are repeatedly activated and deactivated through the growth cycle, resulting in continuous growth with fewer dead chains, a more uniform product, and an ability to extend chains using different monomers.

Pete Lovell and Frank Heatley in Manchester have developed in recent years a very thorough understanding of the free-radical polymerization of n-butyl acrylate (which produces soft, rubbery poly(n-butyl acrylate), known as PBA). They revealed PBA has a significantly branched structure, which influences its end-use properties significantly, and were able to explain the chemistry behind this. When they analyzed PBA prepared using a CRP technique called atom-transfer radical polymerization by Kris Matyjaszewski’s group at Carnegie Mellon University, USA, they discovered it was much less branched. Curious, they then analyzed PBA prepared using other CRP techniques by other specialist groups led by Bert Klumperman (South Africa), Bernadette Charleux (France), and Brian Hawke (Australia), and found branching to be reduced, no matter which CRP technique was used. A generic result - what a boon for scientists!

As Pete Lovell explains, “the challenge then was to find a common explanation, which took considerable time through discussions when

opportunities arose, mainly at conferences. Many possibilities were considered and eliminated until the effect of differences in the distribution of active chain lengths was seeded by Dominik Konkolewicz in the Australian group.” The key was the role that highly reactive short chains play in CRPs; their presence increases the amount of branching in the final polymer, but in CPRs they are only present early in the reaction.

The special issue of *Macromolecular Rapid Communications* featuring acrylate free-radical polymerization in which this paper will appear is edited by Christopher Barner-Kowollik of Karlsruhe Institute of Technology, Germany. He explains that “the paper by Lovell fits perfectly into the special issue as it addresses a fundamental mechanistic issue in free-radical polymerization, i.e., how do living/controlled polymerization processes influence the microstructure of a polymer. In addition the findings of the paper are highly relevant for materials scientists who wish to employ polyacrylates generally via living/controlled polymerization methods, as the exact structure of the polymer needs to be known for many applications. This contribution is a brilliant example of a group of highly distinguished scientists working together in an exciting field. The contribution is my favourite paper from the special issue and I expect it to be highly cited.”

More information: “Chain Transfer to Polymer and Branching in Controlled Radical Polymerizations of n-Butyl Acrylate” N. A. Ahmad, B. Charleux, C. Farcet, C. J. Ferguson, S. G. Gaynor, B. S. Hawkett, F. Heatley, B. Klumperman, D. Konkolewicz, P. A. Lovell, K. Matyjaszewski, R. Venkatesh, *Macromolecular Rapid Communications*, 2009. [DOI: 10.1002/marc.200900450](https://doi.org/10.1002/marc.200900450)

Special Issue *Macromolecular Rapid Communications*, with guest editor C. Barner-Kowollik, “Acrylate Free Radical Polymerization: From Mechanism to [Polymer](#) Design” to be published in November 2009 .

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