



## Review

## Radical polymerization of acrylic monomers: An overview



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## ABSTRACT

Since their discovery and development in the 20th century, acrylic polymers have become an integral part of numerous industries and are used in a myriad of applications. As is true for many polymers, the suitability of a particular polyacrylate for a given application comes from its structure, which is determined during its synthesis in the reactor, long before commercial use. Uniquely, the radical polymerization of acrylic monomers is strongly affected by radical transfer events which dictate reaction kinetics and lead to a range of distinct macromolecular structures, a fact that went unknown for many years and continues to generate unexpected results. In this review, we aim to present the current picture of the various competitive processes which occur during polymerization of acrylic monomers, as well as the ongoing issues that hinder our complete comprehension of this complicated monomer family.

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**Abbreviations:** ATRP, atom transfer radical polymerization; CTA, chain transfer agent; ESR, electron spin resonance; 2EHA, 2-ethyl hexyl acrylate; MMA, methyl methacrylate; NMP, nitroxide mediated polymerization; PLP, pulsed laser polymerization; RAFT, reversible addition-fragmentation chain transfer; S, styrene; SEC, size exclusion chromatography.

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## 1. Introduction

Acrylic (co)polymers encompass a wide range of polymeric materials which are applied in numerous applications including decorative and automotive coatings, adhesives, biomedical materials and textiles [1,2]. Like many polymers, polyacrylates are “products by process”, whose functionality is largely dictated by the conditions under which they are synthesized [3]. It is with this in mind that a substantial amount of work has been conducted into the macromolecular reaction engineering of acrylic polymerizations [4–7].

Whilst acrylic polymers have been produced commercially since the 1950s, it was not until much later that the complexity of acrylic polymerization was truly appreciated [8]. The main complication in the polymerization of acrylates centers around the fact that they readily undergo intramolecular transfer to polymer reactions that lead to production of a relatively unreactive radical in the polymer backbone [9]. The potential for intramolecular transfer to play a major role in the polymerization of acrylates was first proposed by Scott and Senogles based on a kinetic analysis of the polymerization of a number of acrylates [10–12], but it was only many years later that the direct observation of branching in acrylic polymers confirmed the occurrence of transfer to polymer reactions and their importance [9].

Although under most common synthetic conditions intramolecular transfer to polymer only occurs around once every 100 propagation events, it is arguably the most significant process in the polymerization of acrylic monomers. In some ways it is amazing that it went unknown for so many years, given that it is now accepted to be critical to understanding almost any aspect of the polymerization of acrylates. The intramolecular transfer reaction, also known as backbiting, leads to a midchain, tertiary radical in close proximity to the chain end. Due to the relatively high stability of the tertiary radical, it propagates at a very slow rate compared to the secondary radical and thus results in a decrease in the rate of polymerization and a large buildup of tertiary radicals in the system [13,14]. Upon propagation of the tertiary midchain radical, a branch point is introduced and thus the microstructure of the polymer is also influenced by intramolecular transfer to polymer. Transfer to polymer also occurs by an intermolecular pathway, generating a midchain radical, which upon propagation leads to a long chain branch. However, the rate of this reaction is considerably lower than the rate of intramolecular transfer, such that almost all transfer to polymer events are via the intramolecular pathway [15–18].

The huge difference in reactivity of the tertiary mid-chain radical compared to the secondary end-chain radical results in a number of complications, both in terms of kinetics and polymer microstructure, which continue to be the source of discussion in the literature. Scheme 1 presents an overview of all the kinetic processes occurring during the polymerization of acrylic monomers. These simultaneous competitive processes result in a number of potential polymer structures, which can be targeted by selecting appropriate reaction conditions, with reaction temperature and monomer concentration being particularly important parameters.

In this review article we aim to present a general guide to the polymerization of acrylic monomers. Our current understanding of the various competitive events that take place during the polymerization of acrylic monomers, as well as their relative rates, are described, including potential difficulties or ambiguities in the measurement of individual rate coefficients and mechanistic pathways. The review is divided into several parts to explain the significance and extent of each individual event shown in Scheme 1. Subsequently, we present a summary picture of the ability to con-

trol polymer structure through a mechanistic understanding of this challenging monomer family.

## 2. Secondary radicals

### 2.1. Propagation

The rate coefficient of propagation is of fundamental importance in order to gain a quantitative understanding of any given polymerization process, but for acrylates was consistently underestimated by at least an order of magnitude until the late 1990s. As an insight to how far our understanding has changed, a quick look at the *Polymer Handbook* published in 1998 reveals the measured propagation rate coefficient,  $k_p$ , at 30 °C for *n*-butyl acrylate to be scattered between 360 and 1360 M<sup>-1</sup> s<sup>-1</sup> as determined by analysis of polymerization kinetics [19]. In contrast, the current value, as determined by pulsed laser polymerization and subsequent polymer analysis by size exclusion chromatography (PLP-SEC) by the IUPAC working party for *Modelling of Polymerization Processes and Kinetics*, stands at 18,000 M<sup>-1</sup> s<sup>-1</sup> [20]. In order to understand how such a huge discrepancy can arise in such a fundamental constant, it is important to consider the unique reactivity of acrylic radicals.

As shown in Scheme 2, backbiting of the secondary radical leads to a tertiary radical which upon propagation reverts back to the secondary species, such that the two species are in equilibrium. On this basis, neglecting the occurrence of other reactions such as  $\beta$ -scission, termination etc., the fraction of secondary radicals,  $P_2$ , and tertiary radicals,  $P_3$ , in the system are given by [13]

$$P_2 = \frac{k_{p3} [M]}{k_{p3} [M] + k_{bb}} \quad P_3 = 1 - P_2 \quad (1)$$

where  $k_{p3}$  and  $k_{bb}$  are the rate coefficients for monomer propagation from the tertiary radical and backbiting of the secondary radical respectively. As such, any measured value of the rate coefficient of propagation from kinetic analysis,  $k_{p,eff}$ , is actually a composite of the rate coefficient of propagation from the secondary radical,  $k_{p2}$ , and tertiary radical,  $k_{p3}$ , such that

$$k_{p,eff} = k_{p2}P_2 + k_{p3}P_3 \quad (2)$$

The key point to understand is that even though backbiting occurs at a much reduced rate compared to propagation ( $k_{bb} \ll k_{p2}[M]$ ), the rate of propagation from the tertiary center is slow ( $k_{p3}[M] < k_{bb}$ ) which leads to a high fraction of tertiary radicals, such that the fraction of tertiary radicals is typically in excess of 0.7. Even in cases where the characteristic signs that backbiting has occurred, i.e. quaternary carbons arising from branching, are not easily visible, the fraction of tertiary radicals can still be in excess of 0.5 and can play a significant part in the kinetics of the reaction.

The presence of tertiary radicals leads to a measured value of  $k_{p,eff}$  which is significantly lower than the true value of the rate coefficient of propagation of the secondary species. This is particularly important to highlight since in the literature, when analyzing kinetic data it is often not appreciated that the value of  $k_{p2}$  as measured by PLP can only be used when the presence of tertiary radicals is correctly taken account and, critically, that except under very specific circumstances  $k_{p2} > k_{p,eff}$ .

Accurate values of  $k_{p2}$  by the now standard technique of PLP-SEC were elusive for a long time due to problems related to the backbiting reaction, which are not commonly observed for other monomer families [8,21–23]. Although it was not immediately obvious that these problems were directly related to backbiting, and various chain stopping reactions were proposed [23], the detection of branching in samples of poly(*n*-butyl acrylate) produced by PLP and molecular simulation have confirmed its effects [24–26].

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