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Mechanistic Understanding of Nitroxide Mediated Free Radical Polymerization Processes

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Living-radical polymerizations continue to interest the polymer community because of the relative simplicity in how they are performed. Underlying that simplicity is the complexity in understanding what is actually going on in these polymerizations. In the case of the nitroxide-mediated polymerization process the two most popular areas of research are (i) the design of new nitroxides to perform acrylate polymerization and (ii) the development of an emulsion polymerization process. In the former case there is a widely held belief that new nitroxides are required to polymerize acrylates.^{1,2} However, there is ample evidence to suggest that acrylates can be polymerized in the presence of nitroxides such as TEMPO and 4-oxo-TEMPO. For example, it is known that random copolymers of styrene and acrylate can be made with acrylate concentrations of up to 50% acrylate (Figure 1, Table 1).

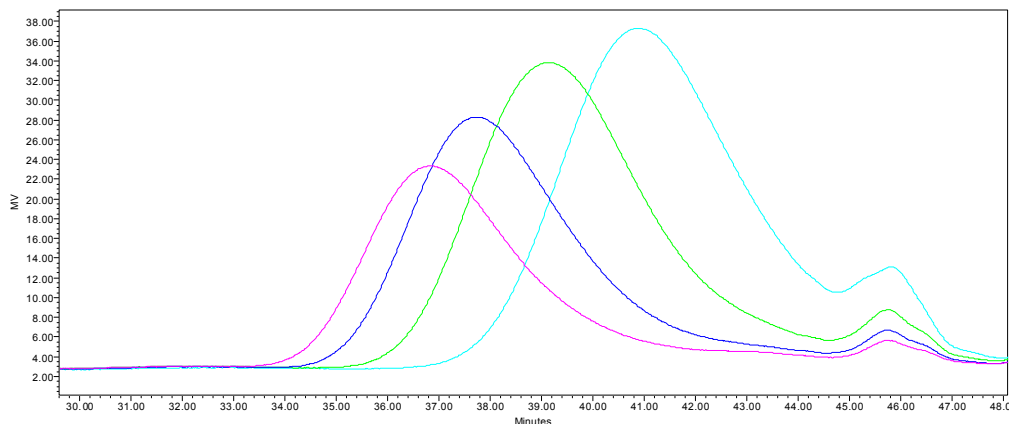


Figure 1. GPC of a random copolymer of styrene and n-butyl acrylate copolymer prepared over 4 hours with TEMPO.

Sample	M_n	PD
i. 1 hour	1400	1.25
ii. 2 hours	2200	1.27
iii. 3 hours	3300	1.24
iv. 4 hours	4000	1.25

Table 1. Reaction times, number average molecular weights (M_n 's), and polydispersities (PD) for the samples in Figure 1.

It would seem reasonable to assume that at any give time a significant number of chains are terminated with nitroxide attached to an acrylate moiety yet the polymerization continues at a good rate, while narrow polydispersities are maintained. Furthermore, homopolymers of acrylates have been prepared with TEMPO in the presence of acetol, an additive that reduces the amount of free nitroxide in the reaction mixture.³ ESR studies have demonstrated that the rate of polymerization of *n*-butyl acrylate tracks with the concentration of free nitroxide. In this presentation we add further experimental proof that under the appropriate conditions homopolymers of acrylates, such as *n*-butyl acrylate, can be polymerized in the presence of 4-oxo-TEMPO while maintaining a narrow polydispersity (Figure 2).

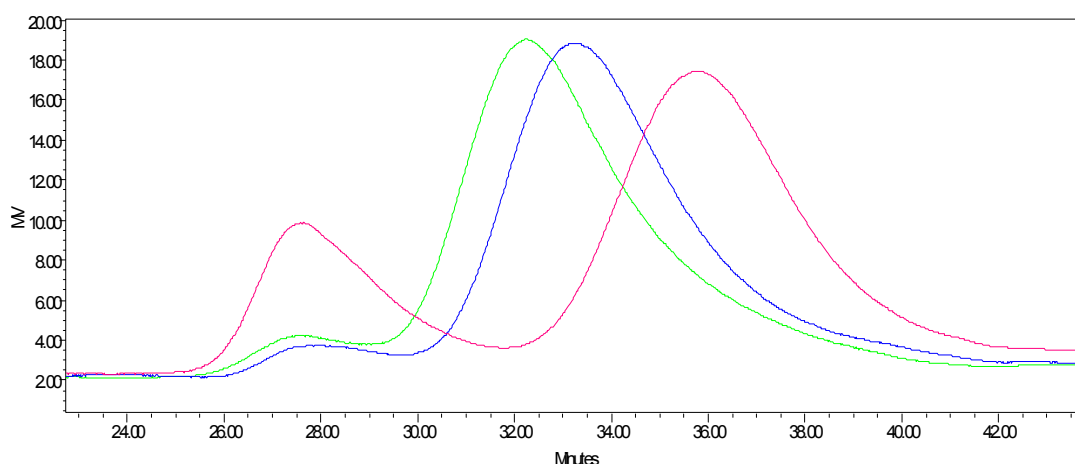


Figure 2. GPC of *n*-butyl acrylate homopolymer prepared in the presence of 4-oxo-TEMPO at 130°C.

Under the reaction conditions of the example presented in Figure 2, a small number of the acrylate chains have grown during initiation in an uncontrolled manner and terminated, accounting for the high molecular weight peak in the first sample. However, the remaining living-chains grow in a predictable fashion as evidenced by the subsequent distributions. Details of the reaction conditions will be given in the presentation since they continue to evolve.

References:

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