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Critically evaluated termination rate coefficients for free-radical polymerization: Experimental methods

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Abstract

The knowledge of accurate rate coefficients for individual steps of free-radical polymerization (FRP) is of scientific interest and of application-oriented importance. For a wide variety of homopolymerizations and for many copolymerizations, reliable propagation rate coefficients, k_p, are accessible via the IUPAC-recommended method of PLP-SEC (pulsed laser polymerization—size-exclusion chromatography). For termination rate coefficients, k_t, the situation is less favorable. Even for very common monomers, no k_t benchmark data sets are available. Moreover, instead of having one recommended technique for measuring k_t, there are a plethora of such methods. Seventeen of the most prominent approaches for measuring k_t are here reviewed, including innovative ones that have emerged over the last decade. The methods have been subdivided into two categories: (i) 'Kinetic methods', in which analysis of the time dependence of concentrations is essential, and (ii) 'MWD methods', in which the analysis of the molecular weight distribution plays the dominant role. The methods are evaluated with respect to their potential for providing routine access to measuring k_t as a function of monomer conversion and of free-radical chain length. Moreover, it has been considered whether expensive instrumentation or highly demanding analysis is required for a particular method and whether a method is applicable to many types of monomers. A table summarizes all these evaluations in a readily accessible form. The use of kinetic methods appears to be generally preferable over MWD-based methods. The largest potential is currently seen for methods in which

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polymerization is induced by a single laser pulse and where the subsequent time evolution of either monomer concentration or free-radical concentration is measured.

Keywords: Free-radical polymerization; Kinetics; Termination rate coefficients; Pulsed-laser polymerization; Molecular weight distributions

Contents

1. Introduction

Methods abound for measuring termination rate coefficients, k_t, in free-radical polymerization (FRP). Fifteen years ago, it would have been impossible to outline such methods, as will be done in this review, without also discussing the measurement of propagation rate coefficients, k_p: the two issues seemed to be inextricably linked, in that essentially all methods yielded either k_p/k_t or k_p^2/k_t rather than either rate coefficient individually. However, this landscape has changed dramatically since it was pointed out in 1987 that k_p can be obtained in an essentially assumption-free manner from the chain-length distribution (CLD) resulting from pulsed-laser polymerization (PLP) in which pulses are periodically applied [1]. Although