Contribution of the Differential Scanning Calorimetry to the investigation of complex polymerization kinetics

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Abstract

Radical polymerization usually involves vinyl monomers with at least one double bond in their structure. Polymerization of these monomers is usually accompanied by a significant heat release. The polymerization enthalpy can be recorded by thermal analysis techniques, such as Differential Scanning Calorimetry (DSC) and converted to polymerization rate after some appropriate mathematical transformations. DSC has long been proven a powerful technique for measuring the variation of polymerization rate as a function of time (isothermal mode) or temperature (nonisothermal mode). It offers the advantage of continuous recording of the variation of the reaction rate, which permits the identification of specific phenomena taking place during polymerization (such as diffusion controlled, besides chemical reactions). This is very significant, since in other techniques of measuring the polymerization conversion (e.g. gravimetry, FTIR, etc.) only discrete experimental data are collected. DSC measurements can be easily carried out in a variety of experimental conditions and monomer(s) chemical structure. The latter is very important especially when polymerization leading to crosslinked structures is investigated, where other techniques, requiring the dissolution of the polymer formed, significantly fail.

In this research, the polymerization kinetics of two oligomers, namely the poly(ethylene glycol) methacrylate and poly(ethylene glycol) methyl ether methacrylate, in the presence of benzoyl peroxide initiator, is investigated. These oligomers include two parts in their molecular structure: a polymerizable methacrylate and a PEG side chain with a few number of repeated poly(ethylene oxide) units. Besides depending on their structure may or may not have terminal hydroxyl groups. Polymerizations were carried out at several constant heating rates (non-isothermal conditions) and reaction temperatures (isothermal conditions). Differential and integral isoconversional methods were employed and compared. Differences in the reaction kinetics were attributed to the chemical structure of the oligomers used and possible side chemical bonds formed. In addition, nanocomposites of these monomers with silver nanoparticles (AgNPs) were formed and the effect on the polymerization kinetics was investigated. Isoconversional methods were employed to estimate the variation of the overall polymerization activation energy as a function of the degree of double bond conversion.