NEW METHOD FOR THE ESTIMATION OF REACTIVITY RATIOS FOR FREE-RADICAL COPOLYMERIZATION THROUGH THE TRACKING OF MONOMER CONCENTRATIONS VIA IN-SITU 1H-NMR

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The reactivity ratios (r's) is a measure of the tendency for both comonomers in a copolymerization to show a preference for insertion into a propagating chain radical, in which the propagation rate constants are governed by the last unit of the propagating radical and monomer type. Mayo-Lewis equation (MLE) describes the instantaneous copolymer composition (Finst,i) for most of the copolymerization systems and it is a function of r's and the remaining monomer composition. The reactivity ratios have been estimated by using copolymer composition data at low or moderate/high conversion, being the nonlinear methods more proper to a good prediction of the r's. Recently, the integral or differential form of the MLE has been used to improve the estimation of r's, taking advantage of in-situ 1H-NMR spectroscopy, where the remaining monomer composition (fi) or the copolymer composition (Fcum,i) is the dependent variable to fit. However, either fi or Fcum,i is quantified in NMR spectroscopy by a ratio of integration of the signals, e.g. fA = I_HA /(I_HA + I_HB), this operation could contribute a higher experimental error on the dependent variable (fi o Fcum,i). However, a direct measurement of the monomer consumption (M1 and M2) can be tracked throughout the copolymerization process with in situ NMR, giving as result a decrease in the experimental error degree. We report a new methodology for the estimation of r's, in which the molar balance equations are used to fit the predicted values of r's with the corresponding observations by dynamic optimization in the copolymerization of vinyl acetate and methyl methacrylate. It is reported that MLE is valid for this binary system, so we perform five initial monomer compositions and follow the kinetics via in-situ 1H-NMR spectroscopy. The estimated values obtained for this method is compared with those reported in the literature. Finally, the joint confident regios are also analyzed.

Keywords: reactivity ratios, monomer balance equations, Join confident region

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