

ARTICLES

**APPLICATION OF A MONTE CARLO METHOD FOR THE
EVALUATION OF REACTIVITY RATIOS IN THE
COPOLYMERIZATION OF FURFURYL METHACRYLATE WITH
N-VINYL-2-PYRROLIDONE**

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Abstract— Copolymers of furfuryl methacrylate (*M*) with N-vinyl-2-pyrrolidone (*P*) were prepared by free radical copolymerization in DMF solution at 50°C, using 2,2'-azobisisobutyronitrile (AIBN) as initiator. The reactivity ratios of both monomers were calculated according to the general copolymerization equation using the Fineman-Röss and Kelen-Tüdös linearization methods, as well as the Tidwell-Mortimer non linear least-squares treatment and the Monte Carlo random method. The values of the reactivity ratios calculated using the first methodology were $r_M = 3.92$ and $r_P = 0.004$. Similar results were obtained by both, the Monte Carlo and the non-linear least square techniques that certified the precision of the proposed method. The microstructure of copolymer chains based on the first order Markov statistics is described.

Keywords— Reactivity ratios, Copolymerization, Microstructure, Furfuryl methacrylate, N-vinyl-2-pyrrolidone.

I. INTRODUCTION

The classical copolymerization model describes the relative change in monomer concentrations ($d[M_1]/d[M_2]$) as a function of the instantaneous monomer concentrations, $[M_1]$ and $[M_2]$, and the monomer reactivity ratios, r_1 and r_2 , by means of the general copolymerization equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (1)$$

that can be written as

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (2)$$

in function of one of the monomers (f is feed com-

position and F is the copolymer composition) (Galego *et al.*, 1987).

The reactivity ratios are not just parameters suited for the estimation of relative reactivities of monomers, but their correct utilization provides valuable and precise information for the determination of micro-structural parameters such as distribution of units and sequence lengths along the macromolecular chains (Elias, 1977). Therefore, the calculation procedures employed for the determination of r_1 and r_2 must be adjusted as quantitatively as possible to the experimental behavior of the copolymerization system.

The different methods proposed for calculating the reactivity ratios can be classified as: approximation (Alfrey, 1952), curve fitting (San Román and Madruga, 1985), intersection (Mayo and Lewis, 1944), linearization (Fineman and Röss, 1950, Eqn. 2; Kelen and Tüdös, 1975, Eqn. 3) and non-linear least squares methods (Behnken, 1964; Tidwell and Mortimer, 1965). It has been pointed out by Tidwell and Mortimer that the first four methods are not entirely satisfactory, since they all rely on a subjective weighting of data in the evaluation of the reactivity ratios. Also they do not provide possible means of establishing the quantitative error limits for the computed values. On the other side, the non-linear least squares method derived by Tidwell and Mortimer gives the best pair of values of reactivity ratios, independently of any subjective judgement of the experimental data and allows to quantify the errors in meaningful terms. However, the majority of researchers report the reactivity ratios using one of the methods derived from the composition equation, possibly due to the mathematical complexity of the