ABSTRACT

The aim of this work is the experimental optimization, the mathematical modeling and the simulation of the photochemically initiated pre-polymerization process of methyl methacrylate (MMA). According to the industrial interests a pre-polymer of narrow molecular weight distribution (MWD) and defined weight concentration was pointed as an optimum since it improves the production process and the characteristics of Plexiglas.

The experiments were carried out employing two experimental set-ups, which consist of an annular photochemical reactor connected to reservoir. In the first experimental set-up a medium pressure mercury lamp, Heraeus TQ 150 W was employed. In the second a xenon and chlorine (XeCl) source of radiation was employed. The electricity was supplied by a pulse generator, which operates within a wide frequency range (840Hz – 46,4kHz).

The experimental time-evolution of the initiator (benzoin) and the MMA concentration as well as the molecular weight distribution of the pre-polymer were evaluated for different pulse frequencies, initial initiator concentrations and recirculation flow rates conditions. Therefore, analytical techniques were employed as spectrophotometry, chemical actinometry, size exclusion chromatography and reverse phase chromatography.

The experimental optimizations were carried out according to two optimal experimental designs based on the classical Doehlert matrix. The chosen variables affect significantly the characteristics of the final product. Mainly due to the different conditions of initial radical production rates, which have shown to be the key on controlling the MWD and the MMA conversion.

The mathematical modeling was based on mass, momentum and photons balance equations. The kinetic mechanism of bi-radical and initial radical production from MMA and benzoin respectively, were included in the classical kinetic model of free radical polymerization. The reaction rate equations were developed according to method of the chain size distribution moment. The proposed mathematical model was validated comparing the simulation results obtained with a computational fluid dynamics program (PHOENICS) and the experimental results.