TRANSESTERIFICATION OR POLYMERIZATION? MECHANISM AND KINETICS OF 2-(DIETHYLAMINO)ETHYL METHACRYLATE WITH METHANOL AND ITS COMPETITIVE EFFECT ON FREE-RADICAL POLYMERIZATION

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A wide range of stimuli-response materials have emerged over the past few decades, and ternary amino containing methacrylates (TAMAs) form an integral part of their synthesis. In this work the transesterification of 2-(diethylamino)ethyl methacrylate (DEAEMA) with methanol to give rise to methyl methacrylate (MMA) and 2-(diethylamino)alcohol, is studied by Density Functional Theory (DFT) calculations and in-situ ^{1}H-NMR measurements. A transesterification mechanism is proposed, involving the protonation of amino group by the H atom of methanol and the subsequent formation of an intermediate. Additionally, the cooperative effect of the methanol molecules in the transesterification process is plausible to explain the low energy barriers found experimentally. A second-order reaction was used to study the transesterification kinetic, and the Arrhenius parameters (A and E_A) are reported as function of the percent of DEAEMA in methanol (wM0, wt%). The competition between the transesterification and the (co)polymerization between DEAEMA and the MMA transesterification product, using a 2,2´-azobis(2-methylpropionitrile) (AIBN) as initiator at 70 °C, has been analyzed. When polymerizations are conducted in a low DEAEMA proportion with the molar ratio DEAEMA: methanol = 1: 46, a high MMA copolymer composition, as high as 60 mol% in 17 hr, is estimated in the mixture of copolymers and homopolymers. However, when polymerizations are conducted in high DEAEMA proportion with an equimolar ratio DEAEMA: methanol = 1: 1, the transesterification is mostly avoided and the poly(DEAEMA-co-MMA) only presents 2 mol% of MMA copolymer composition, being principally poly(DEAEMA) and preserving its amino functionality. The copolymer composition can also be tuned by the modification of the molar ratio of DEAEMA: AIBN, which directly incises on the polymerization rate. Therefore, this work provides guidelines for synthesis of well-defined DEAEMA copolymers in alcoholic media, in which the DEAEMA transesterification should be discussed.

Keywords: DEAEMA, Copolymerization, Smart materials

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