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The Effect of the Chain Length on MMA Free Radicl Polymerization

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Abstract: In the polymerization process of methyl methacrylate (MMA), the Arrhenius parameters (activation energy and frequency factor) of propagating reaction monotonically decrease with increasing monomer conversion. At the beginning and middle stage of the propagating reaction, the increase of radical chain length is the main reason of above mentioned change. And at the end stage, the sharp decrease of k_p indicates that the activation energy is approximately incline to zero and the propagating reaction is controlled by molecular diffusion motion.

Keywords: MMA, Arrhenius parameters, propagating reaction, radical chain length.

It has been known that the propagation rate coefficient (k_p) will change with monomer conversion, Friss, Hamielec *et al.*[1-5] have proposed many formulas about k_p to fit this change. In order to obtain the relation between Arrhenius parameters and monomer conversion, a group of k_p values at the same monomer conversion must be measured. We adopted a new method through analysis of k_p values measured by usual experimental techniques for this purpose. Firstly, we chose a value of monomer conversion, such as 0.1. Then a group of k_p values at different temperatures corresponding this conversion could be obtained from the average linking line of experimental k_p values. The Arrhenius parameters could be calculated with k_p values according to Arrhenius equation. If monomer conversion was changed, a series of activation energy and frequency factor values at different conversion were available. To our knowledge, such method has not been reported so far.

Results and Discussion

1. The linear relation of k_p *vs.* 1/T is quite well (**Figure 1**). It shows that at the same monomer conversion, the propagating reaction has the same Arrhenius parameters. Since the chain length of radical will change (or increase) with increasing monomer conversion in the same experimental conditions, activation energy and frequency factor are also determined by the chain length.
2. Both activation energy and frequency factor decrease with increasing monomer conversion (the change of activation energy with conversion as shown in **Figure 2**). The variations of activation energy can be explained by the increase of interaction energy between the radical and monomer. When the medium changes from liquid to solid, the

conversion increased. The energy difference between initial and transient state of propagating reaction (activation energy) will decrease due to the energy of initial state increases more rapidly than that of transient. The change of frequency factor can be ascribed to the decrease of the mobility (or the collision frequency) of radicals in the process of the reaction, as the length of radical chain increased.

3. Since k_p is correlated with Arrhenius parameters, whether it apparently changes or not, k_p can be expressed as the function of the chain length of radical (or the average polymerization degree of radical).

Figure 1 The Arrhenius plots of MMA monomer conversion

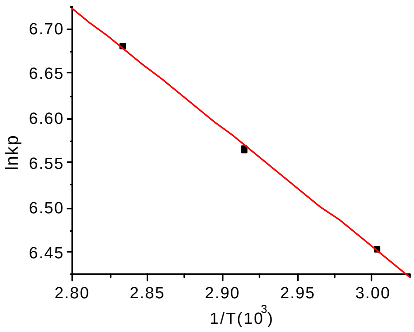
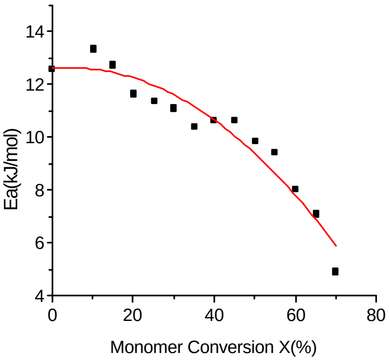


Figure 2 The change of activation at of 0.3 energy of propagation with conversion



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