Mechanistic consideration for the thermal degradation of polymers based on a continuous flow operation

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Abstract

In this paper the author pointed out some insufficiencies and inconsistencies in the radical transfer mechanism based on the macroscopic consideration and the experimental result observed by a continuous flow operation. Then a possible mechanism for the thermal degradation of polymers was proposed and discussed about its consistency with the observed fact. It is insufficient for the usual radical transfer mechanism to give a mechanism-based explanation for the existence of a gas-liquid interface (vaporization process) in the reaction system where the chemical reaction is the rate controlling step, the temperature drop from liquid to gas phase, the effect of pressure on the scission rate of C-C bonds and the temperature drop from the liquid to the gas phase in working reactor. And it is not possible to accomplish the consistency in the mechanistic consideration for the thermal degradation of polymers without any referring to non-monomeric constituents, because the thermal degradation product invariably consists of monomeric and non-monomeric constituents. Based on the experimental study of polystyrene, various inconsistencies in the usual radical transfer mechanism were illustrated for the formation of non-monomeric constituents.