Perturbation of the oscillatory BZ reaction with non-ionic polymers: experiments and model calculations


*Center for Complex and Nonlinear Systems and the Department of Chemical Physics - Budapest University of Technology and Economics

Introduction

Macromolecules play a more and more important role in investigations of various phenomena in nonlinear chemistry like oscillations, chaos, waves and pattern formation. Polymers are widely used in continuously fed unstirred reactors (CFURs) to establish a convection free inert medium like oscillations, chaos, waves and pattern formation. Other examples of the application of polymeric reagents in nonlinear chemistry is the creation of a self-oscillating gel by coupling chemical oscillations with osmotic swelling. The synthesis of a polymer itself can be conducted in an oscillatory chemical medium with interesting results. The above examples demonstrate that perturbation of nonlinear chemical systems with polymeric reagents can lead to various new dynamic phenomena thus it is worth to study the chemical mechanism of these perturbations. When investigating the chemical mechanism of a perturbation with a polymer it is an important question whether it affects the reaction system by its reactive side groups only or the polymeric nature of the reagent also matters. In order to answer this question we have conducted parallel experiments with the polymer polyethylene glycol and with low molecular weight reagents containing the same reactive side group, methanol and ethylene glycol. The dynamics of BZ reaction was investigated in a stirred batch reactor by measuring CO2 evolution rate and CrI absorbance changes. The experimental results have been compared with model calculations applying a latest model of the BZ reaction, the Marburg-Budapest-Missoula (MBM) mechanism (1).

Model calculations

To simulate the response of the oscillatory reaction to polymer perturbations qualitatively we applied the latest model of the BZ reaction the MBM mechanism (1) and added the perturbation reactions of the polymer backbone (P2)-(P4)

- the perturbation reactions of the alcoholic endgroup (P5)
- estimated rate constants were used for the polymeric reactions (P2)-(P5)
- semi-quantitative calculations prove that the assumed mechanism of the polymeric perturbations is realistic
- qualitative prediction of the observed perturbation effects due to the polymers
- polymer backbone reaction (Figure 4B) causes a shortening of the induction period in accordance with the experiments
- perturbation due to the alcoholic endgroups (Figure 4C) lengthens the induction period and shortens the time period of the oscillations
- Finally a perturbation by the polymer backbone and alcoholic endgroup (Figure 4D) reactions causes some shortening of the induction period (this is a result of the two opposite perturbation effects) and a shortening of the time period (again a result of opposite effects but now it is the effect of the alcoholic endgroup, which dominates)

Experimental conditions

- [MA] = 0.1 mol dm
- [BrC] = 0.03 mol dm
- [CrI] = 4·10-4 mol dm
- 1.87·10 mol dm [additive ± 7.35·10 mol dm
- t = 20 ± 0.5 °C

Perturbation effect of the polymer backbone can be studied separately using metoxylated PEGs (MPEGs)

Experimental results

- The effects of the perturbation at low concentration can be explained by means of the following reactions (2,3):
- \[ \text{Cr}^{II} + \text{PEG} \rightarrow \text{Poly-I} + \text{Cr}^{III} + \text{H} \]
- \[ \text{Poly-I} + \text{HBrO} \rightarrow \text{Poly} + \text{HBr} + \text{HOBr} \]
- \[ \text{BrC} + \text{HBrO} \rightarrow \text{BrMA} + \text{HOBr} \]
- \[ \text{BrMA} \rightarrow \text{Br}^+ + \text{H} \]
- \[ \text{HBrO} \rightarrow \text{Br}^- + \text{H} \]

- The effect of the perturbation at high concentration can be explained by means of the following reactions (4):
- \[ \text{BrC} + \text{HOBr} \rightarrow \text{BrMA} + \text{H} \]
- \[ \text{BrMA} \rightarrow \text{Br}^- + \text{H} \]

References