THERMAL HAZARD TECHNOLOGY

µRC Technical Application Note

Monomer Polymerisation

Introduction

It is well documented that spontaneous polymerisation is a safety concern during transportation of polymerising materials. If left uncontrolled the reaction can generate considerable heat and pressure . Inhibitors are commonly used to prevent polymerisation from occurring during transportation and storage. Such inhibitors can stabilise the monomers for some period of time (polymerisation induction time, PIT) until either oxygen or inhibitor has been depleted.

In this study the Micro Reaction Calorimeter (µRC) from THT was used to evaluate PIT for the monomer: methyl methacrylate (MMA) with 4-methoxyphenol (MEHQ) inhibitor. MEHQ works by transferring a hydrogen atom to an active radical to form a less active, stabilised radical thereby reducing the activity. The effectiveness of inhibitors also depends on the temperature, the inhibitor concentration and availability of oxygen.

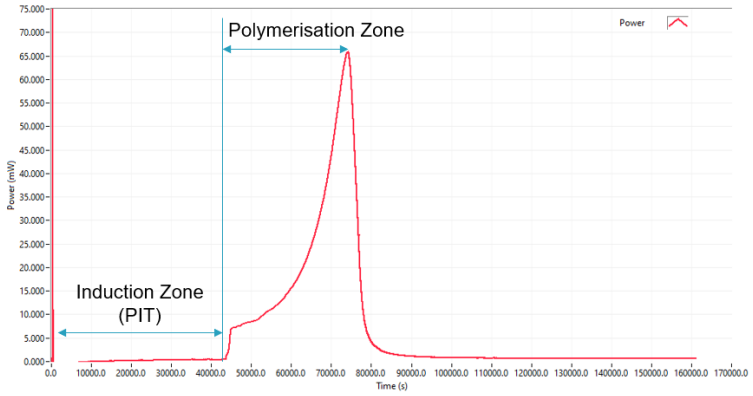
Experimental

In this experiment MAA (99% Sigma-Aldrich) containing ≤30 ppm MEHQ as inhibitor was studied. The µRC was set to equilibrate at 90°C for 30min before 1mL MAA. was loaded in to a glass sample vial and placed into the calorimeter. An empty vial was used in the reference position.

Using isothermal mode, the heat flow was recorded by the µRC. The 'start' of the test was considered to be from the point that the sample cell was placed into the calorimeter. The PIT is considered to be the time from the start of the test to the first indication of an increase in heat flow.

The sensitivity of the instrument is such that it can measure heat flow of both the induction period and the continuous heat flow from the bulk polymerisation reaction.

Results



Sample	Temp (°C)	PIT (min)	Total Heat (J/g)	Total Heat (kJ.mol)
1.4833g MAA ≤30ppm MEHQ	90	725.35	552.94	55.36

The shape of the thermogram is caused by the so called 'gel effect'. Polymerisation starts slowly, then accelerates due to localised increases in viscosity that cause rapid increase in the overall rate of reaction. The increase in rate of polymerisation is accompanied by a large rise in temperature. On a large scale if heat dissipation is not adequate, auto-acceleration of polymerisation systems could result in vessel failure, or even explosion.

Here we demonstrate how the µRC could be used as a tool to study the effectiveness of various inhibitors to control PIT.

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