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Summer 2021 Newsletter

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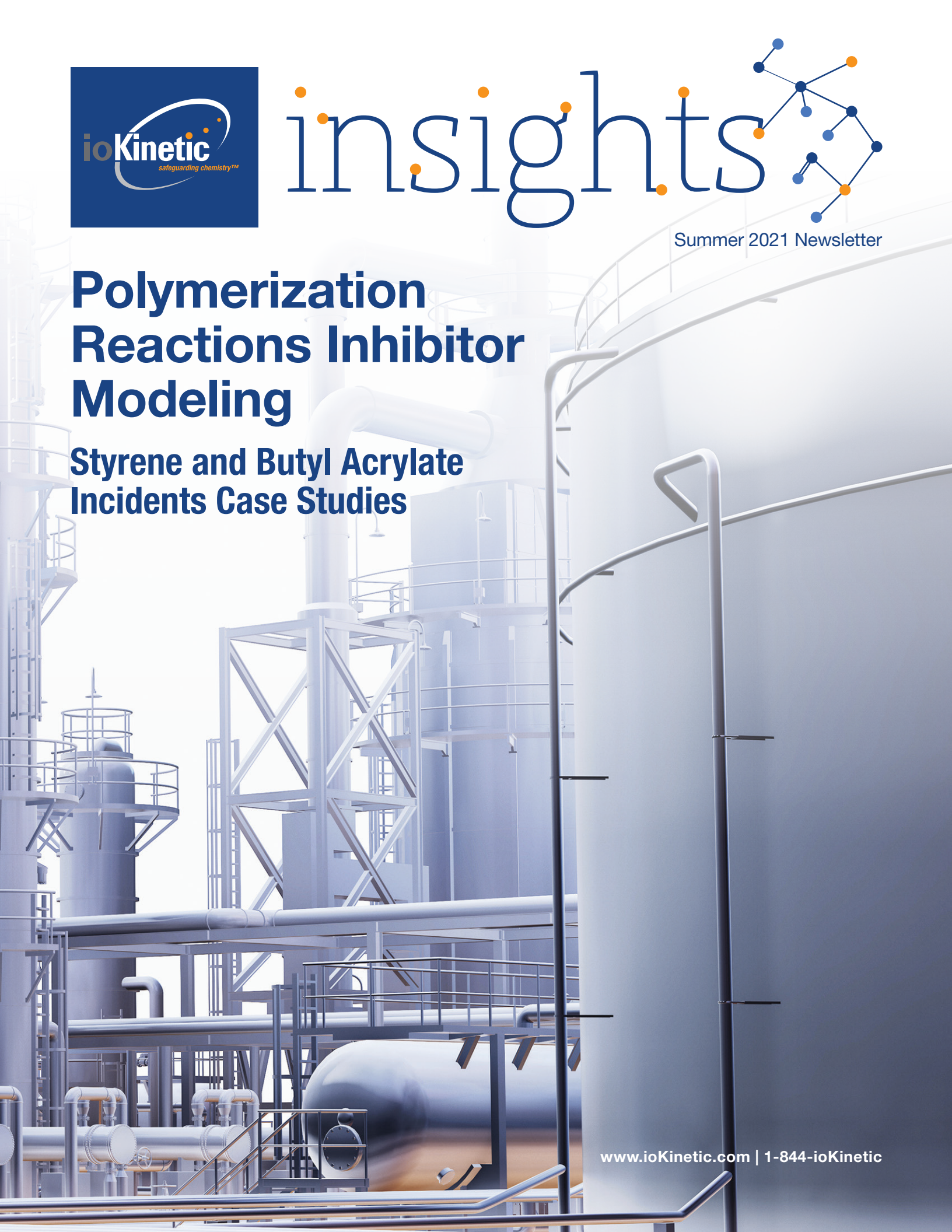
Styrene and Butyl Acrylate Incidents Case Studies



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Polymerization Reactions Inhibitor Modeling - Styrene and Butyl Acrylate Incidents Case Studies

An ioKinetic White Paper by Georges A. Melhem, Ph.D., FAIChE, James Close, and Ying Zhang

Introduction

Inhibitors are chemical substances that are used in small amounts to suppress the polymerization reaction of a monomer. An inhibitor has to be completely consumed before a polymerization reaction can proceed at normal rates. The time required to completely consume the inhibitor is often referred to as an "induction" time. Inhibitors react with polymerization initiation radicals to produce products that cannot induce further reaction. Inhibitors are different from reaction "retarders". A retarder does not suppress the reaction but merely slows it down, i.e. the reaction continues to increase at a slower rate until the retarder is consumed. Some impurities in monomers can act as retarders.

Small amounts of inhibitors can substantially prolong the shelf life of a reactive monomer. Common polymerization inhibitors, typically antioxidants, include MEHQ (monomethyl ether hydro quinone), TBC (4-t-butylcatechol), HQ (hydro-quinone), PTZ (phenothiazine), etc. The effectiveness of most commonly used inhibitors depends on the presence of dissolved oxygen to convert free radicals to peroxy radicals that in turn react with the inhibitor to stabilize the monomer. Both inhibitors and oxygen deplete over time. Understanding inhibitor requirements is essential for polymerization reactions safety.

High levels of inhibitor can improve long term storage stability but may be detrimental to operational safety in the case of a fire, loss of cooling, or an external heating induced runaway reaction.

Inhibitor Modeling & Induction Time, L_{ip}

An inhibitor effectiveness model is usually coupled with polymerization kinetic model(s) in order to properly develop relief requirements and also for accurate hazard assessment. In general, inhibitor effectiveness models correlate the induction time with temperature and initial concentration of

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inhibitor [1] where L_{ip} is the polymerization induction time, $A^{\bullet}$ is the pre-exponential factor, E is the activation energy, C_i is the initial inhibitor concentration, and m is the concentration exponent.

$$(1) \quad {}_{ip} = \frac{1}{A^{\bullet}\exp\left[-\frac{E}{T}\right]}C_i^m = \frac{C_i^m}{k^{\bullet}}$$

$$(2) \quad \frac{{}'C}{lt} = -A\exp\left[-\frac{E}{T}\right]C^n = -kC^n$$

$$(3) \quad L_{ip} = t_f - t_i = -\frac{1}{k}\int_{C_i}^{C_f}\frac{dC}{C^n} \text{ where}$$

$$(4) \quad \int_{C_i}^{C_f}\frac{dC}{C^n} = \frac{C_f^{1-n} - C_i^{1-n}}{1-n} \text{ for } n \neq 1 \text{ and } \ln\left(\frac{C_f}{C_i}\right) \text{ for } n = 1$$

'or $n = 1$ and $t_i = 0$:

$$(5) \quad {}_{ip} = t_f = -\frac{1}{k}\ln\left(\frac{C_f}{C_i}\right) = \frac{\ln\left(C_i/C_f\right)}{k}$$

'or $n \neq 1$, $t_i = 0$, and $C_f = 0$:

$$(6) \quad {}_{ip} = t_f = -\frac{1}{k}\left(\frac{C_f^{1-n} - C_i^{1-n}}{1-n}\right) = \frac{C_i^{1-n}}{k\left(1-n\right)}$$

An inhibitor depletion model is more effective when coupled with polymerization kinetic model(s) for dynamic simulation of relief requirements and hazard assessment [2] where t is time and n is the reaction order. Inhibitor data is provided in the literature or measured as induction time as a function of storage temperature at a specific initial level of inhibitor concentration. If we assume the inhibitor is completely depleted when the concentration reaches a small value, typically 1 ppm, we can develop an expression for induction time and fit the rate parameters from published or measured induction time data [3, 4, 5, 6].

Table 1 summarizes inhibitor depletion and effectiveness models based on data reported in references [1, 3, 4, 5, 6, 7, 2, 8, 9, 10], and this work and model development.

Safety and Operational Considerations

Using the right inhibitor concentration is essential for safe operations. High levels of inhibitor can improve long term storage stability but may be detrimental to operational safety in the case of a fire, loss of cooling, or an external heating induced runaway reaction. The use of high levels of inhibitor can cause the monomer system temperature to far exceed the onset temperature of thermal polymerization under external heating. Once the inhibitor is exhausted, the thermal runaway reaction proceeds at an elevated temperature with a substantial reaction rate and very little reactant/monomer consumption.

This can also occur in free-radical polymerization where a free-radical initiator is used. If the initiator is added and the

Inhibitor	Monomer	Depletion Model A	E, K	n	Effectiveness Model $A^{\bullet}$	E, K	m	Figure
PTZ	Acrylic Acid	3.284×10^{9}	11747	0.25	1.975×10^{9}	11680	0.73	11
TBC	Styrene	2.400×10^{12}	12615	0	3.644×10^{12}	12615	1.308	12
MEHQ	Acrylic Acid	1.527×10^{21}	19100	0	1.975×10^{21}	19100	1.19	13
MEHQ	Ethyl Acrylate	3.992×10^{11}	13419	0.45	2.116×10^{11}	13403	0.55	14
MEHQ	Butyl Acrylate	3.515×10^{13}	14912	0.55	1.479×10^{13}	14880	0.45	15
MEHQ	Methyl Methacrylate	1.085×10^{11}	12450	0.1	0.822×10^{11}	12399	0.884	16
HQ	Vinyl Acetate*	1.733×10^{8}	10620	0.5	9.341×10^{7}	10620	0.54	17
HQ	Vinyl Acetate**	3.869×10^{7}	10963	0.15	2.981×10^{7}	10963	0.777	18

Table 1: Best fit inhibitor depletion and effectiveness model parameters.

Recent Incident

Aghorn Operating Waterflood Station Hydrogen Sulfide Release

On October 26, 2019, an Aghorn Operating Inc. (Aghorn) employee, Pumper A, responded to a pump oil level alarm at Aghorn's Foster D waterflood station in Odessa, Texas. The pump (called Pump #1) was located in a building called a pump house. In response to the alarm, Pumper A worked to isolate the pump from the process by closing the pump's discharge valve and partially closing the pump's suction valve. Pumper A did not first perform Lockout / Tagout to isolate Pump #1 from energy sources before performing work on the pump. At some point on the night of the incident, the pump automatically turned on, and water containing hydrogen sulfide (H2S), a toxic gas, released

Source: CSB website.

from the pump. The CSB found post-incident that the pump had a broken plunger from which the water and H2S released. Due to the limitations of the available evidence, the CSB was unable to determine whether the pump failure and loss of containment of the produced water (1) occurred before Pumper A arrived at the facility, or (2) occurred when the pump energized while Pumper A was closing valves to

Download the Incident Report

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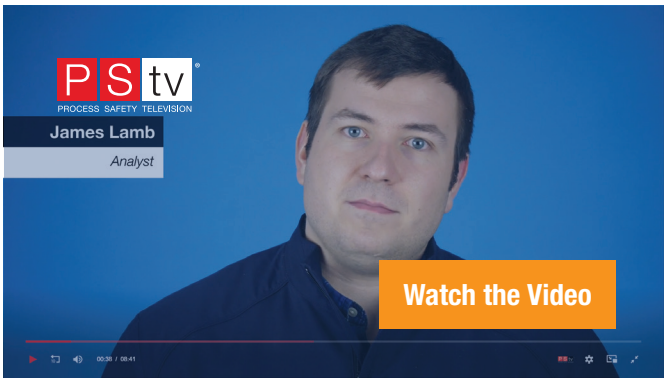
Process Safety Culture Safety Moment

This PStv® Safety Moment explores the role process safety culture plays to ensuring safer process operations. Communication and engagement are key to developing and sustaining a sound process safety culture. Learn what role they play in establishing solid safety procedures and what can occur if not adopted or fostered company wide.



PHA Basic Online Trainng

This course provides learners with a thorough understanding of the essentials of leading Process Hazards Analysis (PHAs) using the industry's most popular methodologies such as HAZOP, What-If, Checklist, FMEA, etc. This training is ideally suited for anyone working for the chemical or oil and gas industries, particularly those involved in project development, operations, and safety and risk management looking to become more knowledgeable about PHAs.