

## POLYMERISATION REACTION INHIBITION : AN ALTERNATIVE BASIS OF SAFETY

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**SUMMARY** : Experimental data, obtained in the adiabatic pressure Dewar calorimeter, on the peroxide initiated polymerisation of styrene have been used in calculations to compare a number of bases of safety available for the protection of a large scale reactor against overpressure generated by runaway reaction. *p-tert*-Butyl catechol (ptbc) has been found to be a retarder of the polymerisation reaction when injected to the runaway at elevated temperature (up to 150°C) and at concentrations up to 0.015 mol (ptbc) per mol (initial styrene present). A semi-quantitative comparison of the merits of reaction inhibition has been made with other potential bases of safety. Results indicate that, with systems capable of high rate delivery and rapid uniform intermixing, reaction inhibition (potentially in conjunction with another basis of safety) is a viable alternative to emergency relief venting. The reduction in reaction rate afforded by the inhibitor reduces the requirements for supplementary safety measures (eg. emergency relief diameter or secondary cooling demand). Consideration has been given to inhibitor injection control system design, reliability and maintenance as well as methods for ensuring rapid injection and intermixing.

(**KEYWORDS** : Inhibition, runaway, polymerisation, venting, styrene)

### 1. INTRODUCTION

A number of practical solutions are available for the protection of reactors against exothermic runaway reactions. These include physical containment, secondary (emergency) cooling, quenching (ie. addition of a cold, inert diluent), emergency relief venting and reaction inhibition. Currently, emergency relief venting is the preferred basis of safety of most major industrial companies. However, the climate of increasing concern regarding environmental protection has placed severe restrictions on the release of materials direct to atmosphere. This is particularly true of the polymerisation industry where many of the process materials are toxic, harmful and flammable. A survey of industrial runaway reactions reported to HSE<sup>1</sup> between 1962 and 1985 indicated that this industry is particularly susceptible to such incidents (due to the inherent exothermicity of many polymerisation processes).

The problems associated with emergency relief venting for the protection of such reactors are :

- Treatment of vented streams is problematic. Papers by McIntosh<sup>2</sup>, Singh<sup>3</sup> and Grossel<sup>4</sup> indicate that the dumptank size required to achieve liquid / vapour disengagement (and minimise environmental losses) is typically 2 to 3 times the initial reactor volume.

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- For rapid runaway polymerisation reactions, emergency relief orifices can be particularly large (> 0.5 m diameter) and hence, often impractical. This is particularly true for older, low pressure reactors.
- The methodology for emergency relief vent sizing for two-phase liquid / vapour material is highly dependent on viscosity. The very large changes in viscosity that often accompany polymerisation reactions give rise to equally significant uncertainty in the sizing methodology (in the worst case, solidification in the vent line may lead to vessel rupture by continued, unabated pressure increase).

Research<sup>5</sup> has recently been completed into the use of reaction inhibition as an alternative method for the control of such polymerisation runaways. Recent incidents and subsequent discussion into the efficacy of inhibition systems have stimulated research in this area. Other workers are also currently investigating reaction inhibition including Kammel<sup>6</sup> (using isothermal calorimetric techniques), and van der Linden<sup>7</sup> (concentrating on mixing issues and large scale studies). A review of the topic of polymerisation reaction inhibition is provided (along with experimental data on inhibitor selection procedures) in a previous paper<sup>8</sup>. Further studies, under adiabatic conditions, have been conducted to determine the effect of addition temperature and concentration on the inhibition of the benzoyl peroxide (0.5% w/w) initiated bulk polymerisation of styrene (from 70°C). The polymerisation reaction has previously been studied on many other adiabatic calorimetry instruments as part of the DIERS bench scale apparatus Round-Robin series<sup>9</sup>. Data from the inhibited reaction have subsequently been used to assess the efficacy of a number of potential bases of safety for a typical, large scale, bulk polymerisation unit.

## 2. EXPERIMENTAL RESULTS

The Adiabatic Pressure Dewar Calorimeter (ADC II) was used for the collection of experimental data. Details of the apparatus, test technique and results from a variety of inhibition reaction conditions are provided in the literature<sup>5</sup>. Data obtained using the equipment for the runaway polymerisation of styrene from 70°C initiated with benzoyl peroxide (0.5 %w/w) are provided in Figure 1. The comparison of Dewar data with the smoothed data set from Round-Robin DIERS testing is provided in Figure 2. The three distinct peaks in the rate of temperature rise versus temperature trace are explained by :

Peak 1 : Primary initiator radical polymerisation.

Peak 2 : Secondary initiator radicals (formed by either decomposition of primary radicals within the polymer chain or stabilised primary radicals). Benzoyl peroxide is known to decompose via intermediate species which have varying activity<sup>10</sup>.

Peak 3 : Thermally initiated polymerisation (which proceeds via second order kinetics (with respect to monomer concentration) according to Flory<sup>11</sup>).

- 2.1 Apparatus Modification : The Dewar apparatus was modified to allow rapid injection of inhibitor solutions during a thermal runaway. Injection was achieved using a pressurised cylinder and temperature-activated valve arrangement. Typical addition times were measured (during a runaway) to be of the order of 0.5 seconds. The inhibitor selected for study (p-*tert*-butyl catechol (ptbc)) is a well known inhibitor of the polymerisation of styrene. The prerequisites for a suitable

inhibitor include high solubility in a sufficiently high boiling, compatible solvent and known activity in the monomer system in question. For the current studies, styrene itself was found to be an acceptable solvent (with solubilities in excess of 40% being achievable at ambient temperature). The injection was conducted from a 90 cm<sup>3</sup> cylinder pressurised (initially) with air at 7 barg.

- 2.2 **Effect of Temperature** : When injection of 0.01 mol/mol of ptbc was conducted at 110, 130 and 150°C, a marked difference in the inhibition period was observed (Figure 3 illustrates results for injection at 110°C while Figures 4 and 5 illustrate results at 130°C and 150°C, respectively). The importance of runaway detection at as low a temperature as possible is thus illustrated. However, even at an injection temperature of 150°C, the rate of reaction is substantially reduced.
- 2.3 **Effect of Inhibitor Concentration** : The inhibition period obtained with differing inhibitor concentrations was not observed to vary in a linear fashion at 110°C or 130°C, although at 150°C, a near linear relationship was observed. A limiting concentration is obtained at lower injection temperatures above which a minimal increase in inhibition characteristics are observed. Further kinetic investigations indicated that the rate of continued reaction varies according to the relationship [styrene].[ptbc]<sup>-0.25</sup>. Figures 3, 4 and 5 illustrate the results for ptbc injection at 110°C, 130°C and 150°C, respectively.
- 2.4 **Effect of Inert Atmospheres (ie. the effect of the absence of oxygen)** : Styrene (like most other monomers) can form flammable atmospheres during processing. For this reason, the injection of air into the reactor is not regarded as safe practice. However, literature suggests that oxygen is required to maintain activity for certain types of inhibitor. An experiment conducted with a nitrogen purged Dewar vessel and nitrogen pressurised injection cylinder indicated that this does not significantly affect the activity of the inhibitor (in fact, the presence of oxygen appears to catalyse the polymerisation process by intermediate peroxide formation<sup>12</sup> and subsequent decomposition). Figure 6 illustrates the experimental results obtained under air and nitrogen atmospheres.

The tests conducted indicate that ptbc is a retarder of the polymerisation of styrene even at elevated temperatures at which the rate of thermally initiated polymerisation is substantial. Although the reaction is not completely halted, the reduction in rate provides additional time for corrective action. The inhibitor examined is observed to be active even in the absence of oxygen.

### 3. **LARGE SCALE POLYSTYRENE REACTOR : CONSIDERATION OF VARIOUS BASES OF SAFETY**

The efficacy of all bases of safety were assessed with respect to a typical, industrial bulk polystyrene reactor operated by a multinational producer (some process details have been changed to protect manufacturing confidentiality).

- 3.1 **Details of Reactor and Process** : The continuous polymerisation of styrene is conducted via a two reactor system. The primary reactor (36 m<sup>3</sup> in volume) is run under slight vacuum at 140°C. The feed consists of styrene monomer with 0.05 %

benzoyl peroxide initiator. The reactor has a design pressure of 7.0 barg and is normally filled to 17300 kg. The agitation system comprises of three, pitched blade turbines (run at 25 rpm). The reactor temperature is controlled by reflux facilities with a maximum capability of 1 MW. A jacket filled with hot oil (at 130°C) is used to heat the reactor contents for start-up. The primary reactor produces a continuous out-feed at a conversion of ca. 40 % (the secondary reactor operates at higher temperature to complete the conversion and de-volatilise residual monomer).

- 3.2 Assessment of Worst Case Scenario for Protection System Design** : The reactor is currently installed with a 60 cm diameter bursting disc arrangement (set at 3.5 barg) for emergency relief (sized for runaway reaction and subsequent two-phase vent flow). A formal HAZOP of the plant has been conducted by the operating company although, for this work, a derived worst case scenario has been considered. That is, isolation of reflux facilities (during, for example, routine maintenance) and normal start-up (with the normal loading of pure styrene) with a ten-fold increase in initiator concentration. As with all process safety testing, the safety measures specified for the plant must be adequate to contend with the worst-case process deviation(s). The assessment of potential failures is thus one of the most important aspects of such studies (although this aspect is not within the scope of the current paper). The reaction was simulated in the modified adiabatic pressure Dewar calorimeter with injection of 0.015 mol/mol ptbc (in styrene) at 150°C. A comparison between the inhibited and uninhibited reactions is provided in Figure 5.
- 3.3 Consideration of Bases of Safety** : A number of bases of safety were assessed which may typically be considered as part of the plant safety system. The aim of the comparison is to determine (in a semi-quantitative fashion) whether reaction inhibition is a viable method for reactor protection.
- 3.3.1 Process Control** : This (most desirable) basis of safety relies on the identification of potential deviation conditions and subsequent provision of engineering control measures to prevent such deviations giving rise to overpressurisation. For the polymerisation of styrene, there are a number of potential deviation scenarios which could give rise to an overpressurisation hazard. This method of reactor protection is usually employed to eliminate certain potential failure scenarios but is not commonly used (in isolation) in the polymer industry. Process control can be employed to eliminate particularly hazardous scenarios for which protective measures are unfeasible. Other bases of safety are generally employed (in conjunction with process control) to protect the reactor from scenarios which cannot otherwise be avoided (at reasonable cost) by preventative, engineered solutions.
- 3.3.2 Process Control plus Physical Containment** : Design of a reactor to withstand the maximum possible runaway reaction pressure is a feasible and desirable basis of safety which prevents a loss of containment (and associated requirement of an adequate downstream treatment facility). However, in the case of the current reactor, the design pressure (7.0 barg) is considerably below the peak reaction pressure (12.5 barg). Although strengthening of the vessel (or construction of a new vessel) are options, the economic implications outweigh the potential benefits.

The design and installation of a secondary vessel into which the initial reactor vents, but does not allow escape of vented materials, could be considered although this is likely to involve high costs.

- 3.3.3 Process Control plus Secondary Cooling** : The rate of power output from the reaction at 150°C is calculated, from the experimental data, to be 1122 W.kg<sup>-1</sup> (using an assumed heat capacity for styrene (at 150°C) of 2535 J.kg<sup>-1</sup>.K<sup>-1</sup>). Calculations based on a heat exchange system with an overall heat transfer coefficient of 400 W.m<sup>-2</sup>.K<sup>-1</sup> and a jacket to reaction mixture temperature differential of 150 K indicate the need for a heat transfer area of at least 324 m<sup>2</sup>. Additional problems are presented by the extreme viscosity gradients that would exist if the material were pumped through an external heat exchanger (with resulting mal-distribution). The reliability of such a device is unlikely to be acceptable. Provision of facilities capable of removing this heat load are likely, at best, to be very expensive and, to all intents and purposes, not a viable economic alternative. The currently installed reflux facilities are undersized for the required duty. For the inhibited process, the rate of power output at 150°C reduces dramatically to 15 W.kg<sup>-1</sup>. For the 43.16 m<sup>2</sup> available heat transfer area of the reactor jacket, this requires a minimal temperature differential of only 15 K (ie. a more realistic requirement).
- 3.3.4 Process Control plus Passive Quenching** : Provision of a cold, soluble and compatible diluent (either added to the runaway reaction mixture or vice versa) could be considered to protect the vessel against the runaway reaction. Calculations indicate that 14140 kg of ethylene glycol at 0°C added to the mixture at 150°C would be capable of reducing the reactor temperature to 70°C. However, the reduction in batch size required to accommodate this mass would significantly affect the economics of the process. Provision of a secondary vessel (containing the cold diluent) into which the batch could be discharged is a possible alternative although, again, the design and construction of this vessel would impact on the process economics.
- 3.3.5 Process Control plus Emergency Relief Venting** : Calculations using DIERS methodology<sup>13</sup> for two-phase flow indicate that the required relief diameter to prevent overpressurisation would be 0.59 m for the uninhibited process. Full details of the calculation are provided elsewhere<sup>9</sup>. After injection of 0.015 mol/mol ptbc at 150°C, the required relief diameter reduces dramatically to 0.19 m (ie. a 10-fold reduction in vent area requirement is achieved). Both calculations include safety factors of 2.0 to reflect reproducibility in the experimental data, uncertainties in vent line flow and the down rating effect of the vent line and bursting disc assembly. The currently installed relief device is thus adequate in preventing overpressurisation. However, the main current area of concern relating to emergency relief venting is prevention of atmospheric discharge of the two-phase material to minimise environmental damage due to the venting of harmful monomers. In order to prevent such discharges, horizontal, vertical, cyclonic or quenching dumptanks can be designed (when adequately sized) to separate the liquid / vapour discharge<sup>3,4</sup>. Using equations for a horizontal knock-out tank derived by McIntosh<sup>2</sup>, the size of the required dumptank to effect this separation is immense (110 m<sup>3</sup>). This large size is attributable to many factors including the

large reactor size, large mass flow rate and vent area, and the high vent opening pressure. The dumptank (as recommended by the American Petroleum Institute<sup>14</sup>) should be rated and certified to withstand 3.5 barg. Provision of such a facility (particularly on high density chemical plants where available space is minimal) provides a serious economic and engineering challenge. Additional problems are also involved in the dispersion of the vented vapour phase (which is harmful, flammable and has a characteristic odour even at low concentrations). The polystyrene reactor on which the calculations are based has been equipped with a knock-out drum of the required capacity. The cost involved in providing this separation capability was £500,000.

#### 4. DESIGN OF LARGE SCALE INHIBITION SYSTEMS

The indications, from the calculations provided in Section 3, are that reaction inhibition can be considered as a basis of safety either alone, or in conjunction with another basis of safety (eg. emergency relief venting or secondary cooling). There are however several engineering issues (predominantly related to scale-up of the inhibition system) that must be considered. These are :

- 4.1 **Runaway Detection / System Activation** : The use of process signals to activate the inhibition system must be carefully considered. Normal process temperature and pressure variations should not be capable of spuriously activating the system. In most cases, it is envisaged that a number of process triggers would be required including temperature (possibly triggered on the  $d^2T/dt^2$  function rather than solely on temperature), pressure, agitation (measured by motion sensing or power draw) and / or reflux system temperatures.
- 4.2 **Reliable Intermixing** : Intermixing of the inhibitor, particularly in large process reactors, is crucial to successful inhibition. Laboratory scale simulations indicate that the viscosity increase due to polymerisation is off-set by the viscosity decrease due to advancing reaction temperature. In the event of agitation being present, intermixing durations should remain short. If it is considered that normal process agitation could be absent (eg. in the event of plant power failure), then more sophisticated methods of intermixing would be required. Jet mixing systems or multiple-point injection from pressurised gas cylinders may be considered to achieve concentration uniformity within reasonable timescales (this is a subject of continuing research). The addition of cold fluid will also induce thermal currents in the reactor. Clearly, areas of stagnant polymerising media must be avoided. For the industrial reactor under consideration, an inhibition cylinder of total volume 1.4 m<sup>3</sup> containing 414 kg of ptbc in 610 kg of styrene could be considered. The vessel should be pressurised with nitrogen to 50 barg. For a 6 inch delivery pipe and rapid acting valve, the addition time is very short (ca. 1.2 seconds). The final reactor pressure after injection (at 150°C, 1.14 barg) is calculated to be 2.64 barg (ie. below the bursting disc set pressure of 3.5 barg).
- 4.3 **Reaction Inhibition Control System and Reliability** : The reliability of the whole inhibition system, which is all (or part) of the ultimate basis of safety must be high. For such a Category 1 arrangement, all aspects of the control system must be

independent of the "normal" process control system. This requires the provision of separate (and duplicated) sensors, an independent (uninterruptable) power supply and high reliability engineering features (such as valves, interlocks and electronic control devices). The reliability of such systems is discussed further in an EEMUA publication<sup>15</sup>.

- 4.4 Maintenance** : A strategy for routine maintenance and testing of the system is required and should be integrated into the existing process documentation (maintenance should be treated as a safety critical operation). Additional procedures are required for recovery after injection, treatment of the inhibited reaction mass and vessel cleaning. The inhibited reaction mixture can be treated to remove inhibitor by use of a sodium hydroxide solution wash. Unreacted styrene could be recovered by distillation or the batch could continue to be processed by the addition of further initiator to consume the remaining inhibitor (clearly, the quality of the product should be confirmed in this case by small scale experimentation).

## 5. CONCLUSION

Increasing environmental awareness (coupled with increased regulation from the authorities) has led to a need for vessel protection systems which can provide minimal loss of containment. Emergency relief venting, currently the most widely used basis of safety, has problems associated with treatment of relieved fluids. Calculational techniques are available for the sizing of appropriate downstream equipment although the large size of horizontal (and vertical) dumptanks can provide a serious restriction to the application of such techniques.

Reaction inhibition provides a viable alternative (either alone or as part of a system with emergency relief venting or secondary cooling). The significant reduction in post-inhibition reaction rates makes the emergency relief vent requirement (or secondary cooling) requirement smaller and more feasible. The problems associated with runaway detection and successful intermixing can be overcome by the use of gas pressurised inhibition cylinders (a technique which also increases the turbulence within the reactor hence assisting the mixing process). For the styrene polymerisation system examined, viscosity increases due to polymerisation were not sufficient to prevent rapid intermixing of the inhibitor solution.

The principles of inhibition are equally applicable to monomer storage facilities and other forms of polymer manufacture (eg. emulsion, suspension or solution). Other mechanistic routes of polymer formation (ie. anionic or cationic initiated reactions) are also likely to be susceptible to inhibition by the addition of materials which deactivate the initiating species. An assessment of worst case scenario(s) for the process / storage facility in question followed by a structured laboratory assessment (under heat loss conditions that accurately simulate those observed on the large scale) is required to identify failure scenarios and conditions for the injection of suitable inhibitors. Engineering design is required to achieve rapid injection triggered by appropriate process signals. The use of pressurised cylinder injection systems is likely to be appropriate for introduction to agitated systems, as well as jet mixing or multiple entry inhibition systems which may be

appropriate for stagnant tanks (eg. storage tanks) or vessels in which agitation is not present or has stopped.

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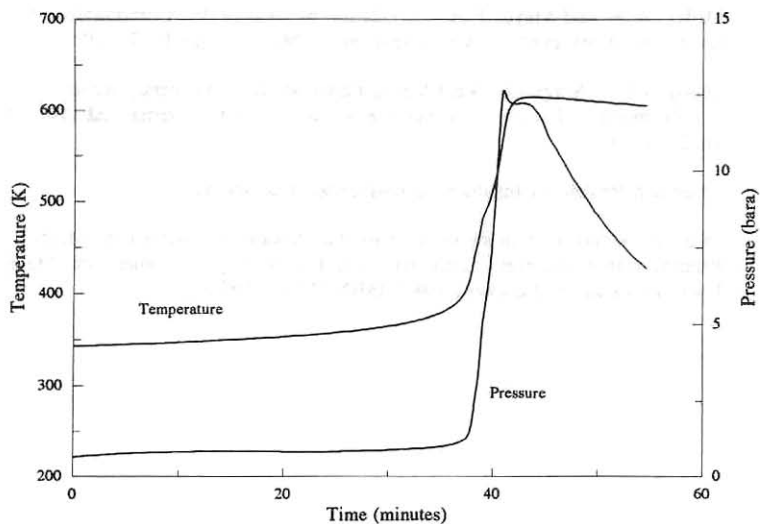
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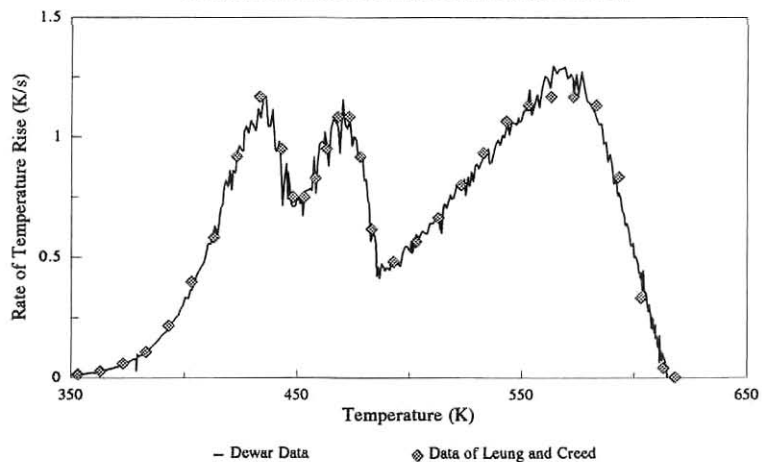


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**Figure 1 : Polymerisation of Styrene**  
Adiabatic Pressure Dewar Calorimeter Data

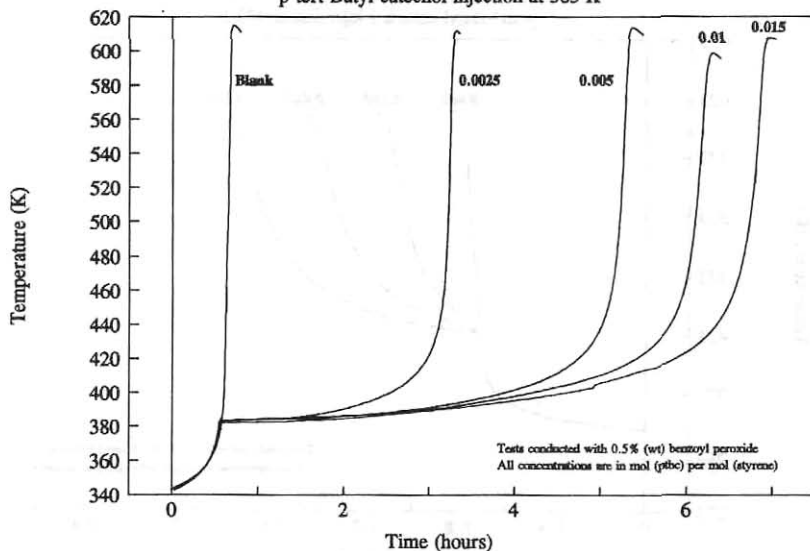


**Figure 2 : Polymerisation of Styrene**  
Comparison of Dewar Data with Round-Robin Test Data



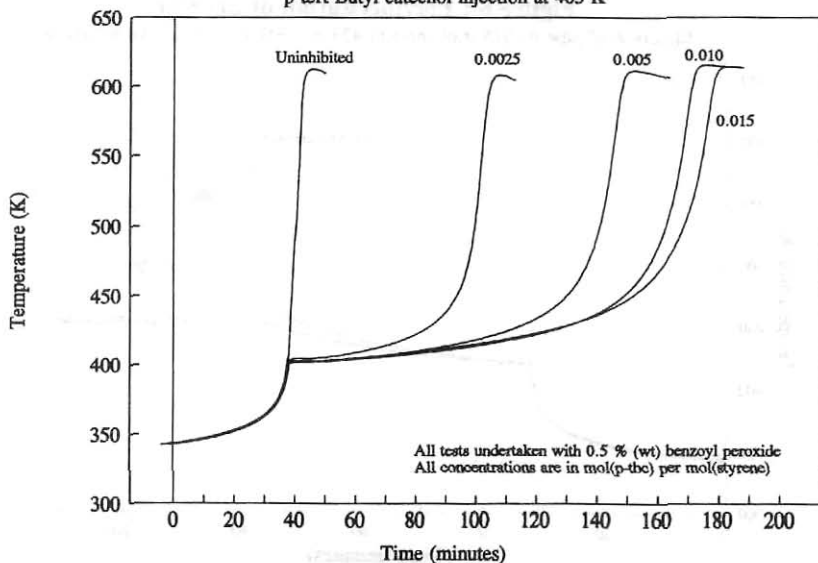
**Figure 3 : Polymerisation of Styrene**

p-tert-Butyl catechol injection at 383 K

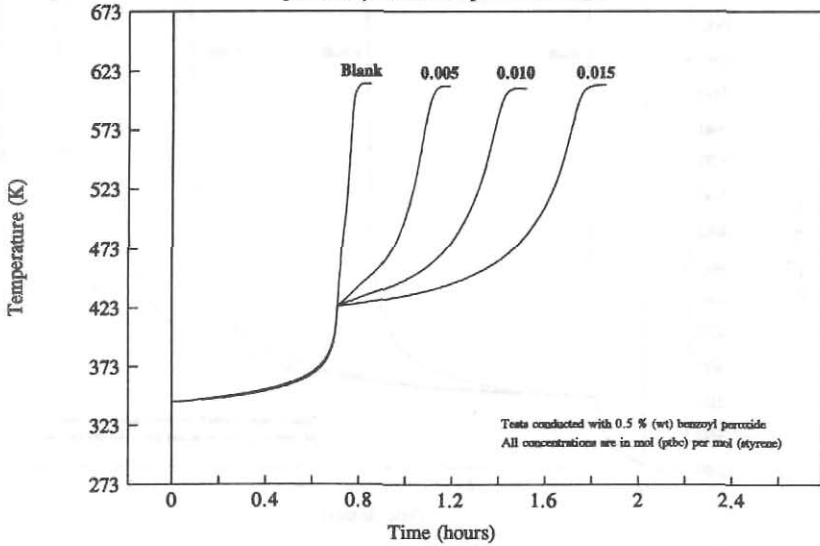


**Figure 4 : Polymerisation of Styrene**

p-tert-Butyl catechol injection at 403 K



**Figure 5 : Polymerisation of Styrene**  
*p*-tert-Butyl catechol injection at 423 K



**Figure 6 : Polymerisation of Styrene**  
 Injection of ptbc (0.015 mol/mol) at 423 K : Effect of Inert Atmospheres

