

A Calorimetric Study of the Self-polymerization of a Commercial Monomer: an Incident Investigation

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In this work the analysis of an incident in transport of dangerous goods is proposed. The objective of this study is to contribute to the determination of the causes that brought about the self-polymerization of commercial divinylbenzene (DVB 63%) contained in an isothermal container, in order to prevent this incident from happening in the future.

Time and conditions during transport/storage of monomers (in particular storage temperature) are very important factors that affect their aptitude of self-polymerization. In particular one hypothesis has been investigated: that the quantity of oxygen in the tanker was insufficient to activate properly the inhibition mechanism. Consequently, the self-polymerization of DVB and the inhibition mechanism of 4-tert-Butylcatechol (TBC) have been studied as a function of temperature and monomer exposure to air with Differential Scanning Calorimetry and Adiabatic Calorimetry techniques.

The incident

Divinylbenzene is an aromatic monomer used principally for cross-linking styrene in the production of ion exchange resins. Much of this production is located in Europe. In 2006, in Grangemouth docks (Scotland), 24000 litres of DVB 63% contained in a tanker exposed to sunlight self-polymerized. A fracture cause by the movement of the tank, led to the loss of very big amount of monomer, as a dense, white plume of vapours. The firemen sealed off the zone for a range of 500 metres. The residents were not evacuated but were forced to stay at home for 24 hours as a preventive measure, because of the irritating characteristics of the substance for the skin and eyes. The seaport was idle for 36 hours, until the wind had completely dispersed the vapour cloud. No injuries were reported.

From available data, it is known that oxygen considerably influences the inhibition properties of TBC, the inhibitor usually added at a level of 900-1200 ppm by weight to commercial DVB to prevent the self-polymerization of the material.

The self-polymerization generate a runaway reaction (Burton & Nolan 1987 and Maschio et al. 1992).

For this reason, attention has been paid in this study to the effect of atmospheric oxygen exposure and of the storage temperature on the DVB/TBC system.

Oxygen role in inhibition mechanism

DVB polymerizes by a self-initiated radical chain mechanism. Termination can be either by the reaction of two polymer radicals (by combination or by disproportion, Bowden 1969) or by the action of the inhibitor. Self-heating will be due to the exothermic polymer radical propagation.

The inhibition mechanism of TBC toward DVB is highly influenced by oxygen. It has been reported by Morrison et. al. in 1997 that the TBC radical can also react with oxygen, probably with the formation of a TBC peroxy radical $TBC-O_2\cdot$, which could itself form a peroxide either by reaction with a polymer radical or with a TBC radical:



The new radical, depending on its reactivity may either terminate another radical or initiate polymerization either by addition of a monomer or by chain transfer to a monomer. There may also be homolysis of the peroxide O-O bond with the production of two radicals. These radicals may then react by terminating radicals or by acting as initiators for polymerization. At lower temperatures the peroxides would be expected to react more by chain transfer and the radical produced to terminate another radical. At higher temperatures homolysis of the O-O bond would be expected to predominate and the radicals formed to initiate polymerization. The peroxides may therefore pass from having an inhibiting effect at lower temperatures to acting as initiators at higher temperatures.

Because of the possible reaction of the TBC radical with oxygen, there may not be an exact stoichiometric ratio between oxygen and TBC consumed.

Oxygen is present dissolved in the DVB and in the air in the container head space. The molar ratio (R) of available oxygen to TBC is an important factor in the TBC inhibition mechanism. A concentration of 15 mg/l has been reported for oxygen dissolved in DVB at 25°C. For a TBC concentration of 1200 ppm R is ≈ 0.06 .

So the inhibition mechanism discussed requires the formation of radicals.

A simplified kinetic mechanism for TBC inhibition in DVB is



with reaction rate constants k_f for the forward reaction and k_r for the reverse reaction in the first step and with a reaction rate constant k for the second.

Considering just these first two steps of inhibition mechanism, as inhibition takes place during the early part of the reaction, the contribution from the termination may be neglected. The two important differential equations then become

$$\frac{d[P\cdot]}{dt} = v_1 - k_f[P\cdot][O_2] + k_r[PO_2\cdot] \quad (4)$$

where v_1 is the rate of initiation, and

$$\frac{d[\text{PO}_2\cdot]}{dt} = k_f[\text{P}\cdot][\text{O}_2] - (k_r + k[\text{TBC}])[\text{PO}_2\cdot] \quad (5)$$

Application of the steady state approximation to $\text{PO}_2\cdot$ gives

$$[\text{PO}_2\cdot] = \frac{k_f[\text{P}\cdot][\text{O}_2]}{(k_r + k[\text{TBC}])} \quad (6)$$

Substitution into Eqn, (4) gives

$$\frac{d[\text{P}\cdot]}{dt} = v_1 - \frac{k_f k [\text{P}\cdot][\text{O}_2][\text{TBC}]}{(k_r + k[\text{TBC}])} \quad (7)$$

Two situations may be considered:

a) If $[\text{TBC}] \gg k_r$, then

$$\frac{d[\text{P}\cdot]}{dt} = v_1 - k_f[\text{P}\cdot][\text{O}_2] \quad (8)$$

b) If $k_r \gg k[\text{TBC}]$, then

$$\frac{d[\text{P}\cdot]}{dt} = v_1 - \frac{k_f k [\text{P}\cdot][\text{O}_2][\text{TBC}]}{k_r} \quad (9)$$

Remembering that the equilibrium constant for the formation of $[\text{PO}_2\cdot]$ is

$$K = \frac{k_f}{k_r} \quad (10)$$

$$\frac{d[\text{P}\cdot]}{dt} = v_1 - kK[\text{P}\cdot][\text{O}_2][\text{TBC}] \quad (11)$$

In (a), soon after a $\text{PO}_2\cdot$ radical is formed it is removed by reaction with TBC. This would correspond closely to the usual view of an inhibitor if oxygen was regarded as the inhibitor. In (b) there is the possibility of some build up of $\text{PO}_2\cdot$ radicals.

Both Eqns (8) and (11) show that the rate of inhibition depends on the concentration of oxygen dissolved in the DVB. In a container with no head space, inhibition will cease shortly before all the oxygen is consumed, meaning that only a fraction of ≈ 0.06 of the TBC has reacted. In a container with air in the head space a situation may be reached where the rate of inhibition becomes controlled by the rate at which oxygen is dissolving in DVB. After the reaction has started the inhibition reaction may go on but at an ever decreasing rate, and this would be manifested as an apparent self-acceleration of the reaction.

Experimental results

The aims of the laboratory tests are to better understand the role of the storage temperature in the self-polymerization of DVB and the role of the oxygen in the TBC inhibition mechanism, in order to validate the original hypothesis.

The experimental runs described here have been carried out in a Differential Scanning Calorimeter (DSC): both isothermal (in order to evaluate the heat produced by the polymerization, the conversion and the induction period as a function of the set temperature) and scanning tests (5°C/min from 30°C to 250°C, whose objective is to determine the onset temperature of the reaction) have been run. In every DSC test a mass of 20 µg of DVB at room temperature was processed in aluminium pressured pan. The result of the first scanning test on fresh DVB was a detected onset temperature of 162°C and maximum temperature of 173.7°C.

In figure 1 the heat of reaction is reported for each of the isothermal tests done. It is possible to observe, when the set temperature changes from 110°C to 140 °C, that the reaction rate increases and the induction period decreases: in the first experiment the maximum temperature is reached after 3 hours, decreasing to 10 minutes in the last isothermal run. When the set temperature increases, the height and shape of the temperature peaks also change: they become higher and sharper, indicating a more hazardous behaviour of the monomer. In addition the heat evolved by the polymerization increases with temperature. This could be due to the following factors:

- At lower temperatures the viscosity of the reacting mass increases, so the final conversion decreases (due to the reduced mobility of the propagating chains) leading to a reduction of the total heat evolved.
- During the induction period, for tests run at temperatures below 140 °C, in the presence of air and peroxides, DVB can be oxidized to form epoxides (Morrison et. al., 1997), which are less reactive toward polymerization.

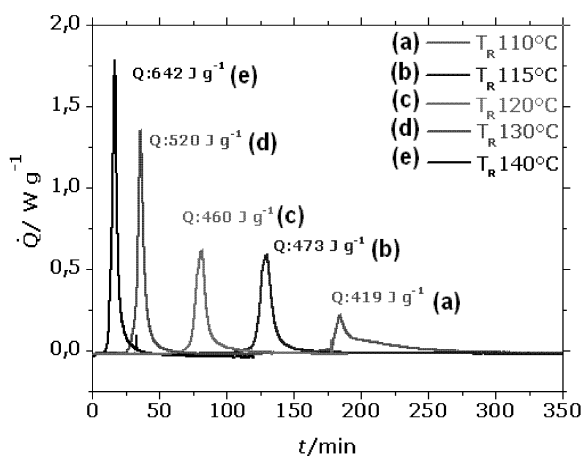


Fig. 1. DSC isothermal tests: the effect of temperature on self-polymerization of DVB.

In order to determine the influence of oxygen on the TBC inhibition mechanism, a sample of DVB was stirred (500 rpm, 50°C) for different periods, ranging from 0 to 13

days, in order to allow thorough contact between the sample and the air. This modified sample was tested in both scanning and isothermal experiments. In figure 2 the results of the scanning tests are reported, where the 0d curve refers to fresh DVB. From this graph it is possible to see that when incrementally increasing the contact period between air (oxygen) and the DVB/TBC system, the polymerization starts at higher temperatures. A considerable difference can be observed after 1 week of air exposure: in particular the curve that refers to an air exposure of 13 days shows that the onset temperature changes from 162°C to 178 °C.

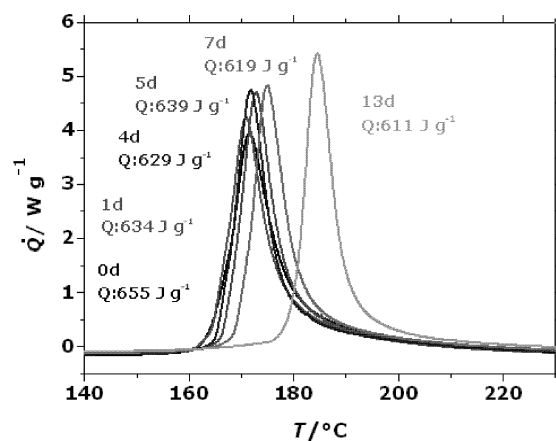


Fig. 2. DSC scanning tests ($5^\circ C/min$): the effect of air exposure on DVB polymerization.

Experimental profiles derived from isothermal tests (set temperature: $130^\circ C$) are shown in fig. 3. The 0d curve refers to fresh DVB, and the others to treated DVB (as explained before), for 1 to 7 days.

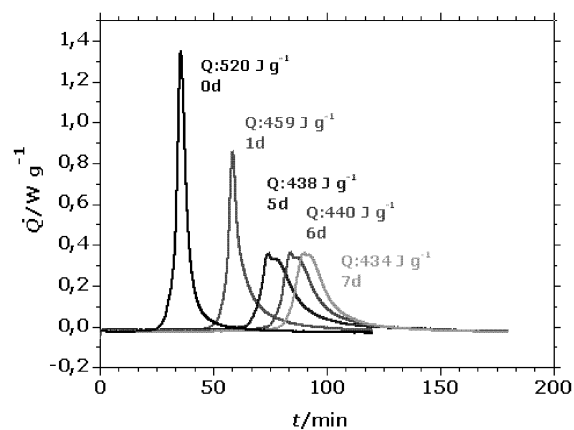


Fig. 3. DSC $130^\circ C$ isothermal tests: the effect air exposure on DVB polymerization.

These data show that the induction period increases for longer air exposures, confirming the role of the oxygen in the TBC inhibition mechanism. Upon passing from shorter to

longer air exposures, the shape of the peaks also changes, becoming lower and more rounded, and the heat of reaction also decreases. These facts sustain the hypothesis of the DVB oxidation to epoxide. So oxygen carries out two actions in this process: firstly it promotes the TBC inhibition mechanism thereby increasing the induction period. However it also oxidizes DVB, making the monomer inactive to polymerization (demonstrated by a lower heat of reaction and a lower reaction rate).

To validate the results just explained, additional tests have also been run in different chemical atmospheres (oxygen and nitrogen) using the PhiTecII adiabatic calorimeter operating in heat-wait-search conditions. Results are briefly shown in table 1.

Table 1: Adiabatic tests: comparison between air and nitrogen atmosphere.

DVB [g]	atmosphere	Tonset [°C]	Tmax [°C]	ΔT_{ad} [°C]	Pmax [bar]
50.38	air	103.5	397.9	294.4	8.8
50.35	N2	87.7	394.5	306.0	7.4

These experimental data confirm the importance of oxygen in the TBC inhibition mechanism: in fact the runaway behavior of the monomer is stronger in the presence of nitrogen than in air. The detected onset temperature shows a decrease of 16°C from the air to the nitrogen condition test, while ΔT_{ad} increases 11.6°C, proving the inadequacy TBC as an inhibitor toward DVB in oxygen poor conditions.

Conclusions

In conclusion, the aims of the laboratory tests are to better understand the role of the storage temperature in the self-polymerization of DVB and the role of the oxygen in the TBC inhibition mechanism, in order to validate the original hypothesis.

The shapes of the isothermal tests DSC curves on fresh DVB can be explained using the mechanism for radical polymerization, self-acceleration phenomena are accounted for by the gel effect. The final conversion decreases as the reaction temperature decreases.

The inhibiting effect of the oxygen on the self-polymerization reaction is evident by comparing the results with the ones of the adiabatic test carried out in a nitrogen atmosphere.

References

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