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Understanding Vinyl Acetate Polymerization Accidents

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Abstract:

Vinyl acetate is processed to produce polymers and copolymers used in water based paints, adhesives, paper coatings or nonwoven binders and various applications at moderate temperatures. The polymerization processes used include solution, suspension and emulsion processes. Many incidents involving the runaway polymerization of vinyl acetate monomers (VAM) are known. In processes where the polymerization initiator was dissolved in the monomer, the initiator premix polymerized violently in the premix vessel. In polymerization processes where vinyl acetate monomer conversion ratio was not 100%, storages of recycled monomers containing no polymerization inhibitor and possibly some traces of polymerization initiator exploded due to VAM violent bulk polymerization. Incidents happened either in batch or semi-batch polymerization processes in connection with wrong catalyst introduction. In this paper, a review of polymerization incidents is given. Radical chain polymerization kinetics are used to explain some accident features such as polymerization isothermal induction periods. Experimental results on bulk VAM polymerization obtained in DSC, Dewar flask, and VSP are given. The accidental polymerization of VAM in a vessel is simulated using the WIN SIM software. The simulation is based on radical chain polymerization kinetics and thermochemical data on VAM and polymers and on specified initial and boundary conditions. Simulation of accidental polymerizations is useful to validate accident scenarios and evaluate various cause hypotheses.

Introduction: Overview of Incidents

The production of vinyl acetate monomers (VAM) was 4.5 million metric tons worldwide in 2003, increasing by 100,000 tons/year. Vinyl acetate is processed to produce polymers and copolymers used in water-based paints, adhesives, paper coatings, or nonwoven binders and various applications at moderate temperatures. The global use includes the manufacture of polyvinyl acetate (40%), poly(vinyl alcohol) (37%) and vinyl acetate copolymers (23%).The polymerization processes used include batch, semi-batch or continuous, solution, suspension, and emulsion processes.

The bulk polymerization of vinyl acetate is not used in industrial operations due to the violent reaction obtained. However, the unwanted bulk polymerization of vinyl acetate is involved in many industrial accidents where the polymerization occurred in storage vessels containing fresh or recycled monomers or in premix vessels where a polymerization initiator was dissolved in vinyl acetate monomer, previous to its use in the polymerization process. Therefore, the study of vinyl acetate bulk polymerization is of great interest from a process safety point of view, even if it is not a commercial widespread process. The bulk polymerization of vinyl acetate in storage vessels occurred spontaneously under constant temperature conditions, due to a chemical acceleration phenomenon related to the free radical nature of vinyl acetate chain polymerization. The bulk polymerization of vinyl acetate in initiator premix vessels is related to the same phenomenon, but the reaction is even more violent due to the high initiator concentration in initiator premix vessels.

The incidents in polymerization processes happen either in semi-batch or continuous polymerization processes due to wrong initiator introduction, absence of agitation, or inadequate priming operation. The consequences of the unwanted or uncontrolled vinyl acetate polymerization depend on the various process conditions.

The bulk polymerization of vinyl acetate is extremely violent and may generate a pressure surge to above 40 bar due to the monomer vapor pressure, a pressure exceeding the pressure resistance of most storage vessels. The uncontrolled polymerization of vinyl acetate in the presence of light solvents in polymerization reactors may also result in a high-pressure surge due to the high vapor pressure of the solvent under the runaway reaction final temperature.

If the runaway polymerization causes the vessel to rupture, this may occur with severe mechanical and blast effects. In case of the loss of containment, the vessel inventory consisting of polymers would be released into the neighborhood. In most incidents involving the bulk polymerization of vinyl acetate, the release did not ignite. This is probably due to the high monomer conversion ratio reached as vinyl acetate is a highly flammable liquid due to its low flash point. The presence of a flammable solvent or a lower conversion ratio of the monomer may allow the release ignition. Therefore, vinyl acetate runaway polymerization incidents are very serious and occur with a high frequency.

Thermal Stability of Vinyl Acetate Monomer

Thermal Stability of Commercial Monomers. Vinyl acetate is a reactive monomer which may undergo a free radical chain polymerization phenomenon under constant temperature conditions. The chain polymerization of the monomer may be initiated by radical initiators including inorganic or organic peroxides. In addition, vinyl acetate is a peroxide-forming chemical in the presence of oxygen or air, as are many vinyl derivatives. Therefore, vinyl acetate is a monomer which may autopolymerize as a result of peroxide formation under an oxygen-containing atmosphere. Vinyl acetate is a "Class C" peroxide former in the classification presented in ref 1.

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In commercial monomer storage vessels, there is no such radical initiator in normal process conditions. However, there is a slow thermal production of free radicals in the bulk liquid monomer, even under ambient temperature. The thermally produced radicals may accumulate and further initiate the free radical chain polymerization of the monomer in the storage vessel. To provide enough thermal stability, some polymerization inhibitor is added to the commercial product, which is a radical scavenger. The polymerization inhibitor used for the stabilization of vinyl acetate monomer is hydroquinone (HQ). Diphenylamine as well as polyhydroxyl phenols and amino phenols are also possible inhibitors. Diphenylamine is recommended for prolonged storage.

Two grades of vinyl acetate monomer are currently supplied:

- the low hydroquinone grade containing 3−7 ppm HQ to be used within 2 months of delivery
- the high hydroquinone grade containing 12−17 ppm HQ for storage up to 4 months before use.

Influence of Oxygen. Many questions arise concerning the recommended storage conditions of vinyl acetate.

It is sometimes recommended to store VAM under ambient air atmosphere to enhance the polymerization inhibitor efficiency as it is known that phenolic inhibitors need oxygen to be active. For example, air is bubbled in acrylic acid storage vessels to allow the polymerization inhibitor, hydroquinone monomethyl ether (MeHQ), to be active.[2] Therefore, the presence of oxygen in the storage vessel atmosphere is favorable for the polymerization inhibitor activation and detrimental to the monomer thermal stability by the formation of peroxides which could initiate the monomer polymerization and accelerate the inhibitor consumption.

Contrary to acrylic acid which is stored at a temperature below 25 °C and has a flash point of 49 °C,[3] above the storage temperature, VAM is a highly flammable liquid with a flash point of −7 °C.[3] Under ambient temperature conditions, the storage vessel gas phase under air atmosphere would be flammable for VAM. Therefore, storage of VAM under air atmosphere should be avoided.

It was further pointed out by A. Nicholson[4] that the optimum stability of methacrylic acid in the presence of HQ or MeHQ as polymerization inhibitor was obtained at a much lower equilibrium oxygen concentration than that provided by an air atmosphere.

The most favorable oxygen concentration was shown to depend on the inhibitor considered and on its concentration in the monomer. A higher oxygen concentration than the optimum value was shown to decrease the monomer thermal stability due to unstable peroxide formation. Therefore, any monomer/inhibitor couple is specific and requires a special consideration for the choice of storage conditions. In the case of vinyl acetate containing hydroquinone as an inhibitor, it was later pointed out by Leon B. Levy[5,6] that the optimum thermal stability was obtained under dry nitrogen atmosphere without any oxygen present in the storage vessel gas phase. It was shown that between 30 and 120 °C, the length of vinyl acetate polymerization isothermal induction period is about −0.4 order in oxygen partial pressure. The detrimental effect of the presence of oxygen in the monomer gas phase on the thermal stability of vinyl acetate containing hydroquinone as an inhibitor is explained by the low thermal stability of the peroxides formed when VAM is stored in the presence of dissolved oxygen. The decomposition of accumulated peroxides near ambient temperature can induce an increased inhibitor consumption.

The fire and gas-phase explosion hazard should be emphasized concerning the transport, delivery, storage, and transfer of liquid vinyl acetate. Vinyl acetate is classified as a highly flammable liquid because its flash point is low, far under ambient temperature. The vapor density with respect to air is ∼3. The vapor may travel at long distance on the ground, allowing ignition by remote weak ignition sources.

The fire and gas-phase explosion accidents are frequent during transfer or injection of liquid vinyl acetate in vessels where the gas-phase was probably not carefully blanketed with nitrogen. One should note that the recommendation of keeping vinyl acetate under air atmosphere in a flask at laboratory scale to enhance the inhibitor activity and provide long shelf life is not suitable for industrial operations where nitrogen blanketing of gas-phases is most important. Therefore, for flammability and thermal stability reasons, it is recommended to store vinyl acetate under dry nitrogen blanket.

The above conclusion holds for high-temperature (100 °C) and ambient-temperature conditions. However, when stabilized with 3−5 ppm HQ, both air-saturated and oxygen-free VAM exhibit adequate thermal stability at normal transport and storage temperature (25−50 °C).

Influence of Impurities. It was shown by Leon B. Levy that acetaldehyde impurity does not cause oxygen-induced destabilization of vinyl acetate.[6] Acetaldehyde is a class B peroxide former. It is sometimes inferred that the peroxides formed by acetaldehyde in the presence of oxygen could behave as an initiator for the polymerization of VAM. As the concentration of acetaldehyde in VAM is limited, this should be a remote problem. The presence of humidity in vinyl acetate would produce some degree of hydrolysis and alter the monomer quality.

Influence of Light. Exposure to light induces the polymerization of VAM to colorless transparent polymers. The light-induced polymerization is faster with increasing temperature. This phenomenon may be observed in glass distillation columns where uninhibited monomers are present.

Influence of the Storage Vessel Wall Material. As for other reactive monomers and especially in the case of

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(1) Kelly, Richard J. Review of Safety Guidelines for Peroxidizable Organic Chemicals. *Chem. Health Saf.* **1996**, September/October, 28−36.

(2) Levy, Leon B. Inhibitor-Oxygen Interactions in Acrylic Acid Stabilization. *Plant/Oper. Prog.* **1987**, *6*, 188−189.

(3) *Les mélanges explosifs*; INRS, 1980.

(4) Nicholson, A. The Effect of O_2 Concentration on Methacrylic Acid Stability. *Plant/Oper. Prog.* **1991**, *10*, 171−183.

(5) Levy, Leon B. The Effect of Oxygen on Vinyl Acetate and Acrylic Monomer Stabilization. *Process Saf. Prog.* **1993**, *12*, 47−48.

(6) Levy, Leon B.; Hinojosa, L. Effect of Oxygen on Vinyl Acetate Polymerization. *J. Appl. Polym. Sci.* **1992**, *45*, 1537−1544.

Table 1. **Vinyl acetate in 2-L colored glass vessel**

time (days)	HQ concentration (mg/kg)
0	20.1
5	19
18	18.4
41	17.8
55	18
67	17.6

Table 2. **Vinyl acetate in 2-L oxidized carbon steel vessel**

time (days)	HQ concentration (mg/kg)
0	21.7
1	20.8
7	19.2
12	19.1
22	17.6
48	16.5
61	16.5
76	15.9

polymerization accident inquiries[7] the influence of the wall material of storage vessels and transport containers was investigated. The influence of carbon steel on the thermal stability of VAM containing 5 ppm HQ at 48.9 °C and blanketed with 10% oxygen was investigated by Leon B. Levy.[6] It was found that untreated carbon steel covered with rust had a strong destabilizing influence on VAM compared to a glass vessel, whereas clean carbon steel would increase thermal stability.

The influence of carbon steel on vinyl acetate thermal stability could also be measured by monitoring the inhibitor concentration as a function of time.

Two 2-L samples of vinyl acetate containing approximately 20 ppm HQ were submitted to aging at 20 °C, one in a colored glass vessel, the other in a 2-L oxidized carbon steel vessel. Both vessels were closed under air atmosphere. The ensuing depletion of HQ concentration was observed by UV spectrometric determinations (see Tables 1 and 2, respectively).

In these experiments the HQ consumption in carbon steel vessel was twice the HQ consumption in colored glass vessel. Also, enough inhibitor concentration would be present under ambient temperature to prevent polymerization over a very long period of time in both containers. However, considering the lower thermal stability of VAM in oxidized carbon steel vessels, it is recommended to design stainless steel storage vessels for VAM and to prevent existing carbon steel storage vessels from rust. This should be easier under dry nitrogen blanket.

Accidents and Incidents in Storage Vessels

Bulk Polymerization of Recovered Vinyl Acetate. The data found in the literature and additional data provided show that commercial vinyl acetate should never polymerize in normal storage conditions. However, polymerization accidents in storage vessels are known concerning VAM which is not exactly the commercial product. This was the case for vinyl acetate recovered from polymerization processes where the monomer conversion ratio is not 100%. An example of such a process was the manufacture of poly(vinyl alcohol) by polymerization of vinyl acetate in the presence of methanol initiated by azo-bis-isobutyronitrile (AIBN), followed by alkaline hydrolysis of the polyvinyl ester. The unreacted vinyl acetate was separated from the polymer and recycled to the polymerization step. The recovered vinyl acetate was free of polymerization inhibitor and possibly contained some traces of polymerization initiator. A 35 m^3 storage of recovered VAM happened to polymerize during the summer vacations in a southern country. The long residence time and the warm temperature, possibly one month and 50 °C, respectively, allowed the polymerization to occur. The polymerization was violent. The storage vessel roof was ejected to a distance of 100 m, and polymers were spread in the neighborhood.

The conditions where this accident occurred are fairly compatible with the stability data of Leon B. Levy for VAM with no HQ, 10−20% vol O_2, and the presence of carbon steel wire.

It was also shown that oxidized iron lowered the product thermal stability measured in DTA stainless steel closed cell under 5 °C/min temperature scan. The polymerization exotherm onset temperature was shifted from 300 to 230 °C in the presence of oxidized carbon steel. The product polymerization exotherm was 1221 j/g close to the literature data of 1036 j/g.[8]

A sample of recovered VAM showed polymerization isothermal induction periods at high temperature in DTA (see Figure 1) but such data cannot be extrapolated to ambient temperature where induction periods are too long to be measured using DTA machines. Our comment on this incident is that one should take care of the thermal stability of noncommercial or recovered vinyl acetate in particular if high storage temperature and long residence time are possible. The storage of uninhibited monomer should be avoided.

Polymerization Incidents in Premix Vessels. It is an unexpected practice, from a process safety point of view, that concentrated solutions of polymerization initiators in the monomers are used in a premix to be injected in a continuous or semi-batch polymerization process. Premix vessel polymerization accidents are known for many reactive monomers. This type of incident occurred also in vinyl acetate polymerization processes. Dilauroylperoxide (1.8 wt %) was dissolved in vinyl acetate in a premix to be injected in a VAM polymerization process. The premix was prepared in advance, to be used 8 h later. Due to the hot summer temperature, the premix happened to polymerize. The reaction was extremely violent. A two-phase flow of polymer and vapor was ejected in the vessel vent header. The release did not ignite.

This incident was investigated on an experimental and theoretical point of view to assess the conditions of occur-

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(7) Kurland, J. J.; Bryant, D. R. Shipboard Polymerization of Acrylic Acid. *Plant/Oper. Prog.* **1987**, *6*, 203−207.

(8) *Encyclopedia of Polymer Science and Engineering,* 2nd ed.; Kroschwitz, J. L., Ed.; John Wiley: New York, 1989; Vol. 17, p 504.

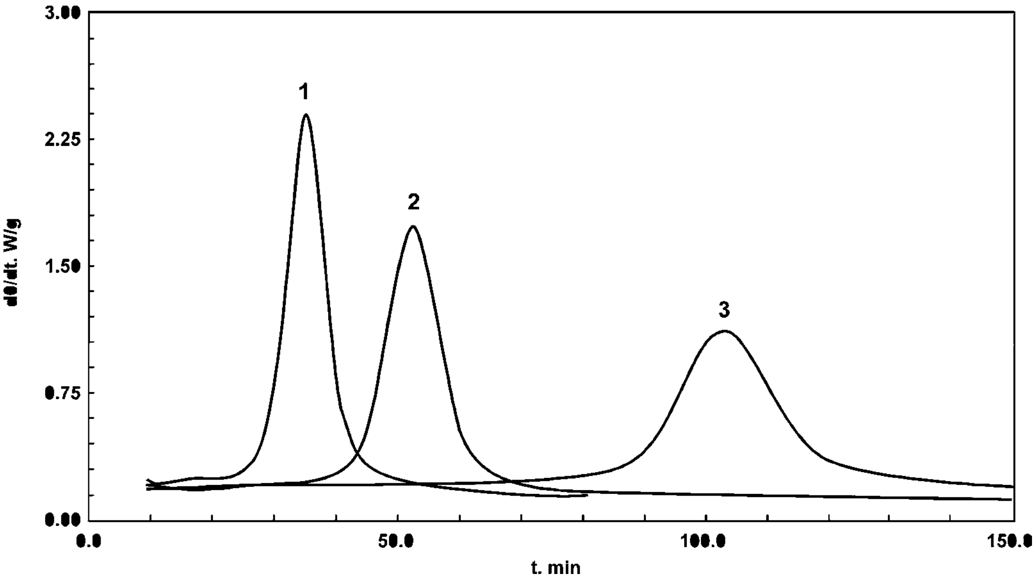

Figure 1. **Recovered VAM. Polymerization isothermal induction period measured in DTA stainless steel closed cell. Curve 1 = 300 °C, curve 2 = 290 °C, curve 3 = 280 °C.**

rence and to evaluate the venting requirement of this scenario. The relevant experimental study, vent-size calculations, and simulation using Win Sim are given in the Experimental Section and Simulation sections of this paper.

Our conclusion on this issue is that the practice of dissolving the polymerization initiator in the reactive monomer in a premix should be eliminated from polymerization processes for process safety reasons.

Incidents, Accidents in Polymerization Processes. Runaway reaction incidents in polymerization processes are related to the reactive monomer accumulation in the polymerization reactor and the subsequent runaway polymerization of the accumulated quantity of unreacted monomer. The monomer accumulation may have several causes.

- The polymerization initiator was not injected and could later reach the reaction vessel.

In a semi-batch solution polymerization process where VAM was polymerized in acetone as a solvent, a valve was closed on the polymerization initiator feed pipe. A large quantity of vinyl acetate was charged to the reactor when the polymerization catalyst could reach the reaction vessel through the vent line. A runaway polymerization occurred with a severe pressure surge which may have been caused by the use of a light solvent.

Other frequent causes of monomer accumulation are:

- A too-low process temperature which does not allow the charged monomer to react.
- No agitation. This process deviation allows the monomer and the polymerization initiator to be in two separate liquid phases. The accumulated monomer may react violently if the agitation is restarted.
- The process is a batch process with respect to the reactive monomer and the polymerization initiator.

In a series of incidents in various VAM polymerization processes, the common factor seemed to be the fact that the processes were batch processes with respect to the reactive monomer and the polymerization initiator. This made the reaction mixture temperature control more difficult and the process sensitive to loss of cooling. In a batch process the heat of reaction is released over a short period of time, producing a high heat flux and making the reaction mixture temperature control critical. Batch processes are better replaced by semi-batch operations where the controlling reactant and the initiator are introduced over a period of time long enough to adjust the heat flux produced to the reactor available cooling capacity. This advantage is well explained for vinyl acetate polymerization by H. U. Moritz.[9]

Incidents in Priming Procedures. The initiation of polymerization in semi-batch or continuous processes is frequently made using a priming procedure where a limited charge of controlling reactant is introduced in the reaction vessel to check the reaction initiation through the detection of the reaction exotherm.

On detection of the reaction exotherm, a continuous feed of controlling reactant to the reaction vessel is established. If the continuous feed of reactant is established too early or too late with respect to the priming charge reaction, an “unexpected” faster reaction is obtained (1) due to a larger amount of unreacted monomer in the reaction mixture if the continuous feed is established too early or (2) due to the priming reaction extinction and monomer accumulation if the continuous feed is established too late. See also ref 9.

Simple Theoretical Background

Why Is the Polymerization so Violent in Initiator Premix Vessels? As pointed out earlier, this bulk polymerization of VAM occurs during the storage of a premix where the polymerization initiator has been dissolved in the monomer. The very violent polymerization occurs after an isothermal induction period caused by the chemical acceleration of the radical chain polymerization. This phenomenon can be accounted for as follows. The kinetic behavior of radical chain polymerizations has been presented by Flory[10]

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(9) Moritz, H. U. Reaktionskalorimetrie und Sicherheitstechnische Aspekte von Polyreaktionen. In *Sichere Handhabung chemischer Reaktionen*. *Praxis Sicherheitstechnik* **1995**, *3*, 115−173.

and will be described in the Simulation sections of this paper. In this theory, the rate of monomer consumption is referred as the rate of polymerization.

$$R_P = -\frac{d[M]}{dt} = k_P[M][P]$$

where [M] is the monomer concentration, [P] is the polymer radical concentration, and k_P is the propagation rate constant.

According to the theory of Flory, the rate of polymerization is controlled by the initiator concentration.[10,11]

$$R_P = -\frac{d[M]}{dt} = k_P[M]\left(k_d \frac{f[I]}{k_t}\right)^{1/2}$$

where k_d is the initiator decomposition rate constant

$$I \xrightarrow{k_d} 2R\bullet$$

k_t is the termination rate constant, [I] ισ the initiator concentration, and f is the fraction of initiator radicals successfully reacting with the monomer.

Consequently, the rate of polymerization is an Arrhenius function with first order with respect to the monomer concentration and half order with respect to the initiator concentration which controls the population of polymer radicals. Considering the maximum rate of polymerization, the higher the initiator concentration, the faster is the maximum rate of polymerization. This explains the very violent polymerization observed in premix vessel polymerization accidents, where high initiator concentrations are dissolved in the monomers.

Cause of the Polymerization Isothermal Induction Period Phenomenon. In the monomer storage vessels where some polymerization inhibitor is present, the polymerization induction period is the time necessary for the thermally generated radicals R• or M• to consume the polymerization inhibitor and produce enough radical concentration to initiate the chain polymerization reaction. Radicals are produced by the polymerization initiator, if present, or by the monomers themselves. Consequently, the isothermal induction period is influenced by the inhibitor and polymerization catalyst concentrations in the monomer. In the case of commercial monomer storage, there should be no polymerization catalyst present, and the induction period is the time necessary for the thermally generated monomer radicals to consume the inhibitor concentration.[12]

$$\tau = \frac{[Z]}{k_0\, e^{-E/RT}\, [M]}$$

or

$$\tau = \frac{m[Z]}{k_0\, e^{-E/RT}\, [M]}$$

depending on whether one or more monomer radicals react with each molecule of inhibitor Z. Consequently, the induction period is an Arrhenius function of the inhibitor concentration with an activation energy characteristic of the monomers.

$$\tau = K[Z]\, e^{E/RT}$$

For storage vessels of commercial monomer, the slope of the Arrhenius plot of the isothermal induction period is a characteristic of the monomer. This may not be the case if a polymerization catalyst is present and if the inhibitor is eliminated first. Then the isothermal induction period is:

$$\tau = \frac{m[Z]}{k_0\, e^{-E/RT}\, [M] + k_{d_0}\, e^{-E_d/RT}\, [I]}$$

In this case, the polymerization inhibitor is consumed by the monomer thermal generation of radicals and by the decomposition of the polymerization initiator.

Under moderate temperature where the polymerization initiator is active and the thermal generation of monomer radicals is negligible compared to that of the initiator, the above equation reduces to:

$$\tau = \frac{m[Z]}{k_{d_0}\, e^{-E_d/RT}\, [I]}$$

In this case, the polymerization isothermal induction period is an Arrhenius function of the inhibitor and polymerization initiator concentrations with an activation energy E_d characteristic of the polymerization initiator

$$\tau = K[Z][I]^{-1}\, e^{E_d/RT}$$

The higher the initiator concentration, the shorter the polymerization isothermal induction period. The slope of the Arrhenius plot of the induction period is a characteristic of the polymerization radical initiator. The Arrhenius plot of the polymerization induction period is a key piece of information to prevent runaway polymerization accidents. Also interesting is the experimental data on the polymerization exotherm, rate of reaction, pressure effect.

This experimental information is presented in the following for the bulk polymerization of VAM containing 1.8 wt % dilauroylperoxide, concerning a premix vessel polymerization accident.

Experimental Section

Experimental Results Obtained Using Differential Thermal Analysis (DTA). VAM samples containing 1.4, 1.8, 2.2 wt % dilauroylperoxide were submitted to DTA tests under 5 °C/min temperature scan conditions in stainless steel closed cells. (Figures 2 and 3).

The samples exhibited two separate exotherms:

- the first asymmetric exotherm, $\Delta Q1 = 639-676$ J/g was attributed to the monomer-initiated radical polymerization,

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[10] Ham, G. E. *Kinetics and Mechanisms of Polymerizations*; Marcel Dekker, Inc.: New York, 1967.

[11] Gustin, J. L. Thermal Stability Screening and Reaction Calorimetry. Application to Runaway Reaction Hazard Assessment and Process Safety Management. *J. Loss Prev. Process Ind.* **1993**, *6*, 275−291.

[12] Brandrupt, J., Immergut, E. H., Eds. *Polymer Handbook*, 3rd ed.; John Wiley: New York, 1999; Vol. II, p 371.

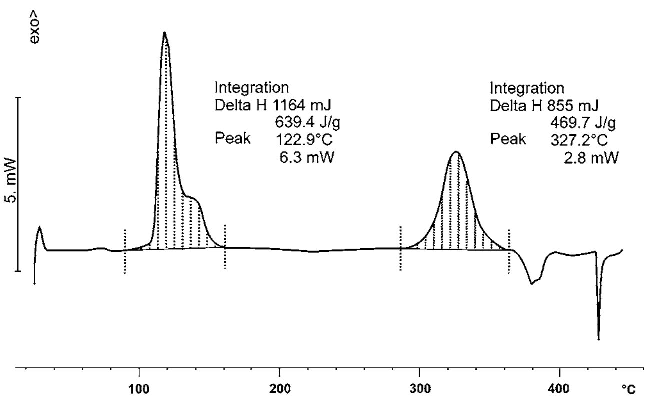

Figure 2. **Polymerization of VAMs containing 1.4% w/w dilauroyl peroxide. DTA determination: stainless steel closed cell; 5 °C/min temperature scan.**

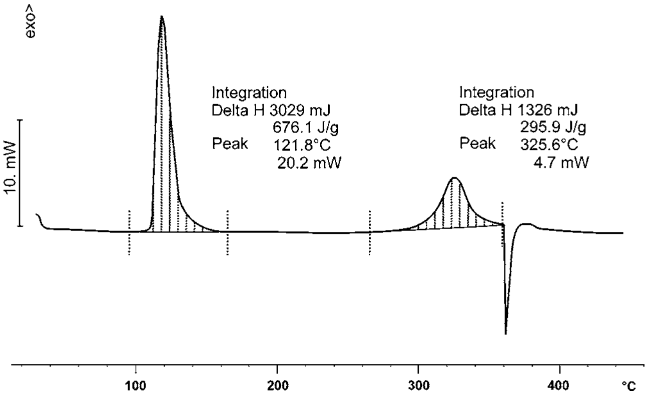

Figure 3. **Polymerization of VAMs containing 2.2% w/w dilauroyl peroxide. DTA determination: stainless steel closed cell; 5 °C/min temperature scan.**

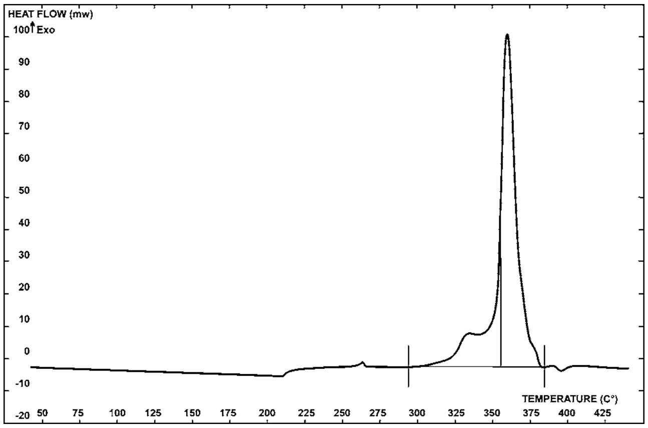

Figure 4. **Uncatalyzed polymerization of vinyl acetate: exotherm = 1221 J/g; DTA determination: stainless steel closed cell; 5 °C/min temperature scan.**

- the second exotherm of $\Delta Q = 296-469$ J/g was attributed to the monomer high-temperature thermal polymerization.

This was proved by the uncatalyzed thermal polymerization of VAM measured in DTA (Figure 4) giving up an exotherm of 1221 J/g above 290 °C.

The overall polymerization exotherm of 970−1221 J/g was of the order of magnitude of VAM heat of polymerization known in the literature:[8] $\Delta H = -1036$ J/g.

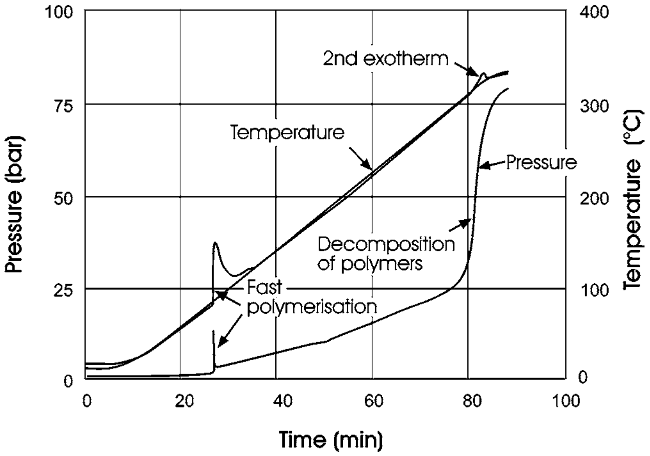

Figure 5. **Mini-autoclave experiment on VAM with 1.8% w/w dilauroyl peroxide. Temperature and pressure versus time curves.**

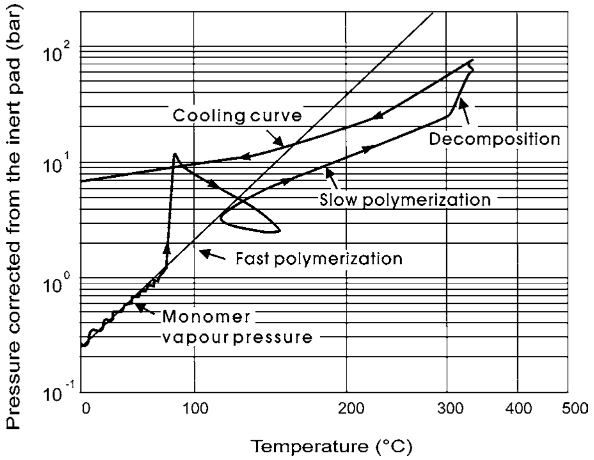

Figure 6. **Mini-autoclave experiment on VAM with 1.8% w/w dilauroyl peroxide. Pressure versus temperature curve.**

Kühner Mini-Autoclave Experiments. Kühner mini-autoclave experiments were carried out on 3-g samples of VAM containing 1.8 wt % peroxide in 7.4 cm^3 autoclave submitted to a 4 °C/min temperature scan. The temperature and pressure evolution obtained are presented in Figure 5. The initiated radical polymerization exotherm was obtained at 80 °C. The second high-temperature exotherm was related to decomposition gas production.

The autoclave pressure was corrected for the inert gas pad enclosed in the test vessel on isolation from ambient pressure:

$$P_{\text{pad}} = P_0 \frac{T}{T_0} = 1\ \text{bar}\ \frac{T}{T_0}$$

where T = current temperature (K) and T_0 = temperature of the vessel when it was isolated under ambient pressure P_0 = 1 bar.

The pressure corrected for the inert gas pad was then plotted on log scale as a function of the reciprocal temperature (Figure 6).

In this representation, the system pressure was a linear function of the reciprocal temperature, proving that the pressure was the monomer vapor pressure, even after the

Table 3. **Polymerization induction period of vinyl acetate containing 1.8 wt % dilauroylperoxide, measured under isothermal exposure conditions in stainless steel closed Dewar, Hastelloy C276 VSP closed cell, stainless steel DTA closed cell**

experimental method	temperature (°C)	polymerization induction period (min)
closed Dewar	37	1100
VSP closed cell	37	790
VSP closed cell	37	820
VSP closed cell	45	425
DTA	65	35
DTA	70	34
DTA	80	8
DTA	80	19
DTA	85	11
DTA	90	5

first polymerization exotherm. On increasing the temperature, a further polymerization was detected by the negative deviation of the pressure from the previously observed vapor pressure curve. This further polymerization appeared above 127 °C and did not produce a significant exotherm until 300 °C. However, above 280 °C, some decomposition gases were produced as shown by an increase in pressure and by the high residual pressure on cooling.

The production of noncondensable decomposition gases above 280 °C was a concern for process safety, because the vessel pressure became filling-ratio dependent and could reach high values at the runaway reaction final temperature.

The decomposition products causing this pressure rise were not those given in ref 12 which are compounds heavier than VAM. The nature of the light decomposition products of vinyl acetate polymers was not determined in this study.

Polymerization Induction Period of Vinyl Acetate in the Presence of 1.8 wt % Dilauroylperoxide. The bulk polymerization of vinyl acetate containing 1.8 wt % of radical initiator dilauroylperoxide could be initiated by constant temperature exposure under different temperatures.

The polymerization induction period was measured using various experimental techniques:

- DTA for high-temperature short induction periods
- closed Dewar experiments and VSP experiments for low-temperature long induction periods.

VSP is for vent sizing package, the DIERS bench-scale apparatus. DIERS is for Design Institute for Emergency Relief Systems, a working party of the AIChE.

A summary of results is given in Table 3. The isothermal induction periods are given for the exotherm onset detection since in some VSP experiments the test cell exploded due to the very fast pressure surge. Consequently, the maximum rate of reaction could not be observed.

The Arrhenius plot of the polymerization induction periods obtained is given in Figure 7.

A change in peroxide concentration between 1.4 and 2.2 wt % does not induce a significant change in the induction period. Induction periods in the range of 5−30 min obtained in DTA are not reproducible.

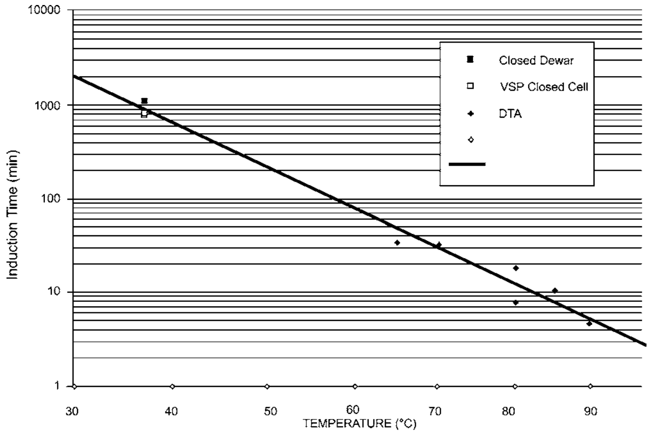

Figure 7. **Polymerization of VAMs containing 1.8% w/w dilauroyl peroxide. Induction time versus temperature.**

Runaway Polymerization Characteristics. The polymerization of vinyl acetate containing 1.8 wt % dilauroylperoxide was investigated using pseudo-adiabatic calorimetric techniques i.e., stainless steel closed Dewar experiments and VSP Hastelloy C276 closed cell experiments. The experimental techniques used are described in ref 13. The reaction was initiated by an isothermal exposure to obtain well-defined initial conditions representing the process conditions where the polymerization incidents occurred. Closed Dewar experiments were first carried out to study this very fast reaction. After improvement of the commercial VSP, this setup was also able to accommodate the fast pressure surge without cell rupture, allowing the reaction to be studied in conditions very close to adiabatic conditions.

Closed Dewar Experiments. A 100-g sample of vinyl acetate containing 1.8 wt % of dilauroylperoxide was submitted to a constant temperature exposure at 37 °C in a 1-L stainless steel closed Dewar. After an isothermal induction period of 1100 min, the reaction exotherm was initiated. The reaction heat rate increased by several orders of magnitude before a significant change in temperature was observed. After initiation, the reaction proceeded in at least two steps and became very violent. See Figure 8. The maximum heat rate measured was 2524 °C/min.

The pressure corrected for the nitrogen pad versus temperature curve (Figure 9) showed that when the polymerization was initiated the pressure presented a negative deviation with respect to the monomer vapor pressure. A reasonable explanation for this phenomenon is that the monomer vapor pressure was lowered by the formation of soluble polymers. Later on, long-chain polymers were obtained which were no longer soluble in monomers, allowing an increase of the monomer vapor pressure. The pressure overshot above the monomer vapor pressure was explained by the temperature measurement response time during the fast reaction. Above 170 °C, the reaction slowed, and the pressure appeared to be lower than the monomer vapor pressure.

A similar result was obtained for the polymerization reaction initiated by a constant temperature exposure at 50 °C. See Figure 10. In this case, the cooling curve was close to the monomer vapor pressure. There was no decomposition gas pressure.

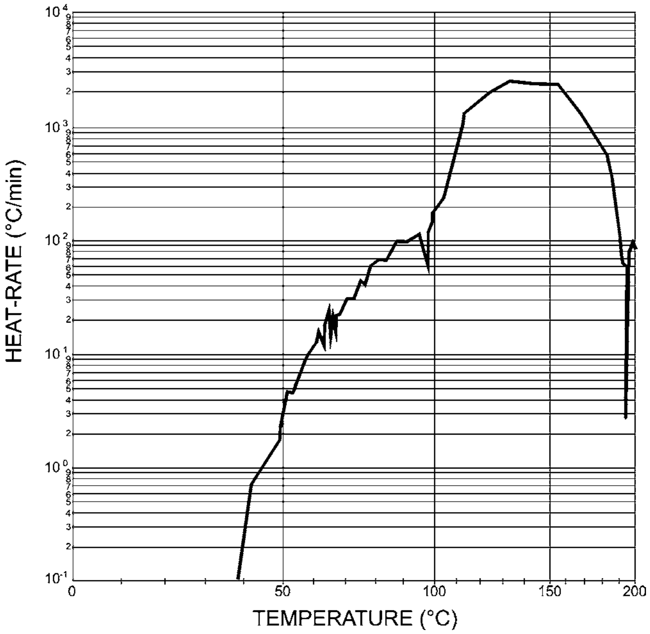

Figure 8. **Closed Dewar flask experiment. Polymerization of VAMs containing 1.8% w/w dilauroyl peroxide initiated by a constant temperature exposure at 37 °C. Heat rate curve.**

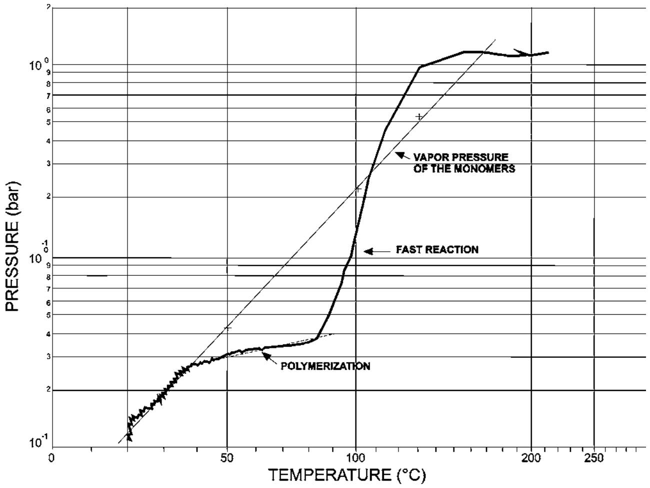

Figure 9. **Closed Dewar flask experiment. Polymerization of VAMs containing 1.8% w/w dilauroyl peroxide initiated by a constant temperature exposure at 37 °C. Pressure versus temperature curve.**

The Φ factor of these experiments[13] was close to 1.15, but the heat of vaporization corresponding to the gas-phase pressurization by the monomer vapor pressure ($V_{\text{gas}} = 0.9$ L $- P_{\max} = 12$ bar absolute $- \Delta H_{\text{v}} = 379$ J/g) induced a heat loss equivalent to an adiabatic temperature rise of 50 °C, based on a polymer specific heat of $C_{\text{P}} = 1.465$ J/g/°C.

The heat loss due to the vessel pressurization by vapor pressure and the Φ factor greatly influenced the reaction final pressure and temperature, even if the polymers decomposition was not initiated. For the polymerization shown in Figures 8 and 9, initiated at 37 °C, with an experimental final temperature of 210 °C, the experimental temperature rise was 173 °C, and the adiabatic temperature rise corrected for the Φ factor and vaporization was $\Delta T_{\text{ad}} = 1.15 \times 173$ °C $+ 50$ °C $= 249$ °C

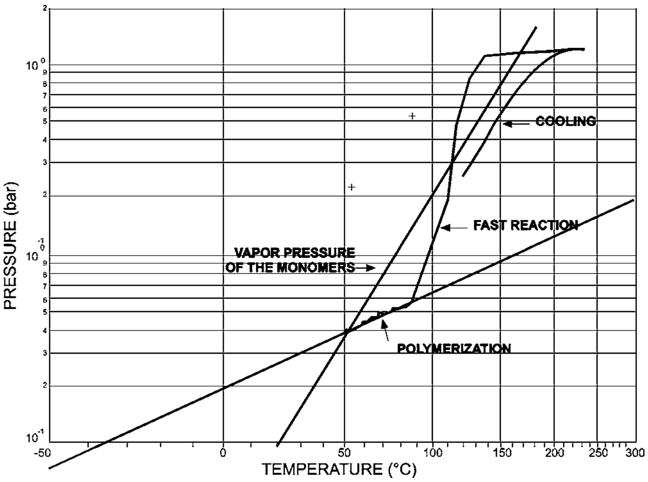

Figure 10. **Closed Dewar flask experiment. Polymerization of VAMs containing 1.8% w/w dilauroyl peroxide initiated by a constant temperature exposure at 50 °C. Pressure versus temperature curve.**

The adiabatic final temperature in the presence of negligible vaporization, with a high filling ratio would be: $T_{\text{F}} = T_0 + \Delta T_{\text{ad}} = 37$ °C $+ 249$ °C $= 286$ °C

As the final temperature was above the monomer critical temperature of 228 °C, the final pressure would be at least the critical pressure of 42 bar absolute. Note that a different monomer critical temperature of $T_{\text{C}} = 252$ °C is given in ref 14.

For a higher polymerization onset temperature, i.e., 50 °C as in Figure 10, the adiabatic final temperature

$$T_{\text{F}} \approx \phi \Delta T_{\exp} + \frac{Mh_{fg}}{m_0 C_{\text{p}}} \cdot \frac{\alpha_0 V P_{\max}}{R T_{\max}} + T_0$$

would be $T_{\text{F}} = 307$ °C, allowing the polymer decomposition and further vessel pressurization by decomposition gases.

The closed Dewar experiments allowed the runaway polymerization to be performed in closed vessels without cell rupture. However, the experimental conditions are far from adiabatic conditions and far from plant conditions due to the low filling ratio. Further to these experiments, VSP closed cell tests were performed after improving the commercial setup pressure compensation response time. The conditions of VSP experiments are close to full-scale adiabaticity conditions.

VSP Closed Cell Experiments. The runaway polymerization of vinyl acetate containing 1.8 wt % dilauroylperoxide was initiated on an 80-g sample under isothermal exposure conditions in a 116 cm^3 Hastelloy C VSP closed cell. The isothermal exposure temperatures were 37 and 45 °C. In one experiment at 37 °C the test cell did not rupture. The maximum heat rate was 4967 °C/min. The maximum rate of pressure rise was 2544 bar/min, i.e., 42.4 bar/s.

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(13) Gustin, J. L. Calorimetry for Emergency Relief System Design. Safety of Chemical Batch Reactors and Storage Tanks. In *Eurocourse on Reliability and Risk Analysis*; Kluwer Academic Publishers: Dordrecht, The Netherlands, for the Commission of the European Communities. 1991; Vol. 1, pp 311−354.

(14) *Encyclopedia of Polymer Science and Engineering,* 2nd ed.; Kroschwitz, J. L., Ed.; John Wiley: New York, 1989; Vol. 17, p 394.

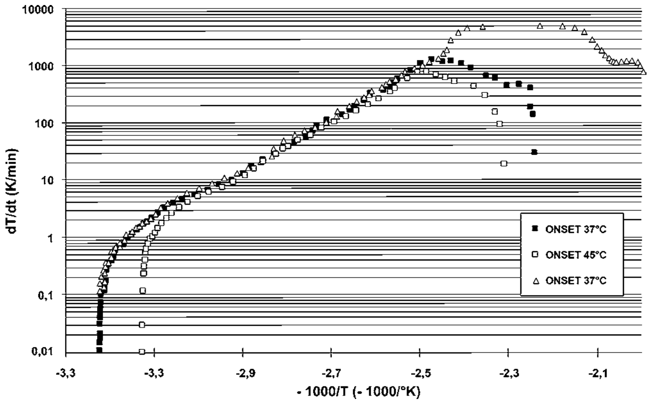

Figure 11. **VSP closed cell experiment. Polymerization of VAMs with 1.8% w/w dilauroyl peroxide initiated by constant temperature exposures at 37 and 45 °C. Heat rate curves.**

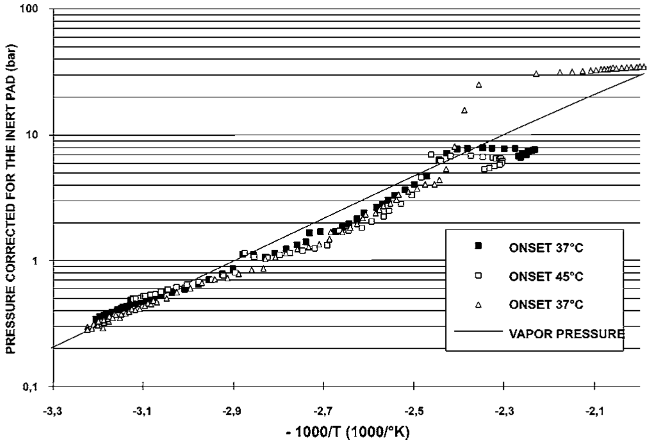

Figure 12. **VSP closed cell experiments. Polymerization of VAMs with 1.8% w/w dilauroyl peroxide initiated by constant temperature exposures at 37 and 45 °C. *P* versus *T* data. Curve represents vapor pressure of monomers.**

The maximum rates were obtained for a temperature range of 144−174 °C.

The experimental final temperature was 268 °C, and the final pressure, 44.5 bar.

The heat rates obtained are given in Figure 11.

The pressure corrected for the nitrogen pad as a function of the reciprocal temperature is given in Figure 12 for the three VSP experiments. The VAM vapor pressure is also represented.

After the polymerization initiation, the heat rate curve was the same for the three experiments because the heat rate was controlled by the test thermal inertia which was the same for the three experiments as long as the test cell did not rupture.

The pressure evolution was also the same for the three VSP experiments and similar to that observed in the Dewar experiments.

Let us consider the VSP test where the test cell did not rupture in Figures 13 and 14.

As the runaway polymerization proceeded, the pressure corrected for the nitrogen pad presented a negative deviation with respect to the monomer vapor pressure, showing the formation of soluble polymers. Above 135 °C, the reaction became very fast, and the temperature measurement was late with respect to the pressure because of the thermocouple measurement inertia causing a pressure overshoot above monomer vapor pressure. Above 175 °C the reaction slowed, and the pressure became lower than the extrapolated vapor pressure. There were no decomposition gases produced. The final temperature, 268 °C, was lower than the polymer decomposition onset temperature found in autoclave experiments above 280 °C.

A comparison of the Dewar and VSP experiments where the test vessel did not rupture is given in Table 4. This table shows that a pressure containment of the runaway polymerization is not acceptable due to the high final pressure obtained and the possibility of polymer decomposition under

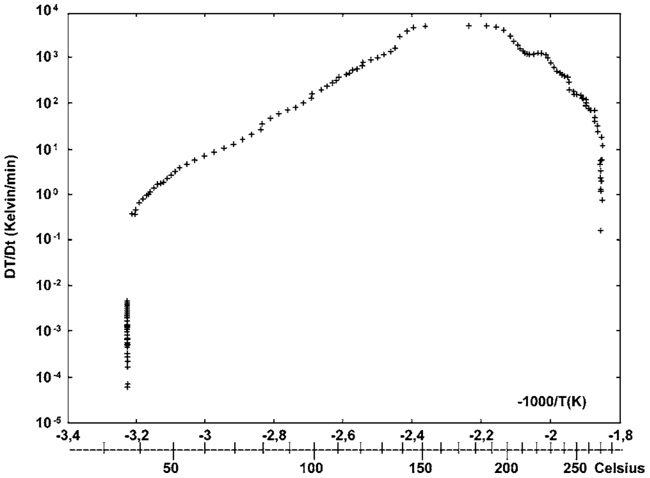

Figure 13. **VSP closed cell experiment. Polymerization of VAMs containing 1.8% w/w dilauroyl peroxide Heat rate curve.**

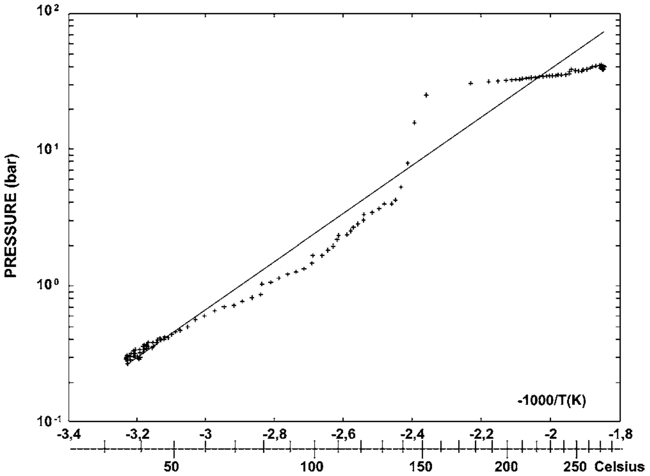

Figure 14. **VSP closed cell experiment. Polymerization of VAMs containing 1.8% w/w dilauroyl peroxide. *P* versus *T* curve.**

Table 4. **Comparison of closed Dewar and VSP experiments on vinyl acetate runaway polymerization in the presence of 1.8 wt % dilauroylperoxide**[a]

apparatus	T (°C)	T_{max} (°C)	ΔT_{exp} (°C)	$(dT/dt)_{max}$ (°C/min)	P_{max} (bar abs)	$(dP/dt)_{max}$ (bar/s)
Dewar	37	210	173	2524	11.8	7.2
VSP	37	268	231	4967	44.5	42.4

[a] Pressure is corrected for the nitrogen pad.

Table 5. **Vent size calculations**

P_S (bar abs)	T_S (°C)	$[dT/dt]_{T_S}$ (°C/min)	$\Phi[dT/dt]_{T_S}$ (°C/min)	Δt_{exp} (s)	$\Delta t_{exp}/\Phi$ (s)	ω	G^*	G_C (kg/m²/s)	A for 1000 kg (m²)
1.1	84	50	51.75	0	0	28.89	0.169	1457	
1.2	86	60	62.1	3.9	3.77	31.17	0.158	1413	
1.3	89	70	72.45	6.3	6.01	33.47	0.145	1349	0.119
1.5	95	100	103.5	9.78	9.44	37.97	0.124	1240	0.078
1.6	97	115	119	10.08	9.74	40.07	0.115	1187	0.078
1.7	100	163	168.7	11.58	11.19	42.43	0.107	1139	0.069

high filling ratio adiabatic conditions. Therefore, the protection of vessels by emergency relief vents was considered.

Protection of Premix Vessels by Venting

Considering the information obtained from runaway experiments, venting was an option to protect vessels from the runaway bulk polymerization of vinyl acetate monomers.

In incidents or accidents reported, it was observed that on depressurization of vessels where the runaway polymerization occurred, a polymeric material was released and that the vessel was found empty after venting. In addition, the release was always violent and almost instantaneous. Long vent lines with bends should therefore be excluded. Following this information, it was assumed that the vessel content behaved homogeneously during venting and that the whole vessel inventory was released. On the basis of our experimental results, the runaway polymerization of VAM was considered as a high vapor system as long as the polymer decomposition onset temperature was not reached (280−300 °C).

Choice of the Vent Sizing Equation. The vented material is made of viscous polymeric materials; however, the vent flow is not a viscous flow but a highly turbulent flashing flow carrying small pieces of polymers. At the moment, there is no particular flow model for such a fast transient phenomenon. Flashing flow methods are currently used. See ref 15. Leung's analytical vent-sizing equation can be used.[16]

$$A_0 = \frac{m_0 \frac{C_{PL}}{2} \Phi \left[\left(\frac{dT}{dt} \right)_{T_S} + \left(\frac{dT}{dt} \right)_{T_{max}} \right]}{G \left[\left(\frac{V_0}{m_0} T_S \frac{dP}{dT} \right)^{1/2} + (C_{PL} \Delta T)^{1/2} \right]^2}$$

In this equation: A_0 is the ideal vent area (m^2), m_0 is the vessel inventory (kg), V_0 is the vessel volume (m^3), G is the two-phase mass flux obtained from Leung's Omega method[17] (kg/m^2/s), C_{PL} is the reaction mixture specific heat (J/kg/°C), Φ is the experiment Φ factor or thermal inertia (nondimensional), T_S is the reaction mixture boiling point (K) at the vent actuation pressure, P_S.

$$\left(\frac{dT}{dt} \right)_{T_S} \text{ and } \left(\frac{dT}{dt} \right)_{T_{max}} (\text{°C/s})$$

are the experimental heat rates at T_S and T_{max}. T_{max} is the reaction mixture boiling point at P_{max}, the maximum allowable pressure in the reaction vessel. $\Delta T = T_{max} - T_S$ is the temperature rise related to the pressure rise $\Delta P = P_{max} - P_S$. dP/dT is the slope of the pressure versus temperature curve (Pa/°C).

However, in the present case, due to very fast reaction, there is no benefit to take into account the energy balance to obtain reduced vent size. The required vent size is best discussed using Boyle's equation and considering emptying times short enough to prevent the reaction to become too fast before complete emptying.

$$A = \frac{m_0}{G \Delta t_p}$$

The emptying time Δt_p is chosen considering adiabatic temperature rise times obtained from VSP closed cell experiments. The experimental temperature rise times are corrected to adiabatic conditions using the zero-order correction method.[18]

$$\Delta t_{\Phi=1} = \frac{\Delta t_{\Phi>1}}{\Phi}$$

The Φ factor of the VSP experiments was 1.035 (VAM sample mass = 80 g, C_{PL} = 1964.6 J/kg/K).

Choice of Vent Actuation Pressure and Emptying Time. The vent actuation pressure was chosen as low as possible and the emptying time was limited to exclude high heat-rates.

The minimum vent set pressure considered was $P_S = 1.1$ bar absolute to obtain critical mass flux and reasonable conditions for the rupture disk actuation pressure, allowing normal operation. The maximum pressure during venting was limited to $P_{max} = 1.7$ bar absolute so that the heat rate did not exceed 170 °C/min.

Vent Size Calculations. The vent size calculations using the Boyle equation are shown in Table 5.

In this table:

P_S is the vent set pressure or the vessel pressure (bar absolute).

T_S is the reaction mixture boiling point under P_S obtained from Figure 14.

$(dT/dt)_{T_S}$ is the experimental heat-rate obtained from Figure 13 (°C/min).

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(15) Leung, J. C.; Fauske, H. K. *Plant/Oper. Prog.* **1987**, *6*, 78−79.

(16) Leung, J. C. Simplified vent sizing equations for Emergency relief requirements in reactors and storage vessels. *AIChE J.* **1986**, *32*, 1622−1634.

(17) Leung, J. C. *J. Loss Prev. Process Ind.* **1990**, *3*, 27−32.

(18) Townsend, D. I.; Tou, J. C. *Thermochim. Acta* **1980**, *37*, 1−30.

Δt_{exp} is the time necessary for the pressure to increase from 1.1 bar absolute to the current pressure. This information was obtained from the VSP experimental data file.

$\Delta T_{\mathrm{exp}}/\Phi$ is the previous time difference, corrected to adiabatic conditions using the zero-order correction.

G_C is the HEM critical mass flux.

A is the vent area required for 1000 kg inventory.

Table 5 shows, for example that, if an emptying time of 11.2 s is allowed considering an average mass flux between 1.1 bar absolute and 1.7 bar absolute of $G = 1300$ kg/m^2/s, the ideal vent area required is:

$$A = \frac{m_0}{G\Delta t} = \frac{1000\ \mathrm{kg}}{1300\ \mathrm{kg/m^2/s} \times 11.2\ \mathrm{s}} = 0.0687\ \mathrm{m^2}$$

i.e. a 30-cm diameter vent.

Vent Line Considerations. The above ideal vent size is given as a minimum requirement. Provision must be made for vent line head losses. The vent line must be as short as possible and horizontal. At least one bend is necessary. A long vent line is likely to be plugged by polymers and would endanger the facility. The vent exit should be directed to a containment system or a stagnation plate[19] that could prevent polymers to be spread in the neighborhood. The design of a quench tank to contain the two-phase release is hindered by the fact that VAM is only slightly soluble in water. The possible solvents for VAM have a low flash point and could give flammable vapors. A very large containment vessel could be necessary. A long vent line to this tank would be a major drawback for the use of a quench tank.

Partial Pressure Containment. A total pressure containment of this runaway reaction is not realistic because the final pressure is at least 40 bar gauge without polymer decomposition. Nevertheless, enough pressure resistance should be given to the vessel to allow for variations in the runaway behavior and differences between design and a true venting scenario. Pressure resistance is useful up to the point where the reaction becomes very fast and the vent requirement becomes very large. This is approximately obtained when $T = 130$ °C and $P = 4$ bar absolute.

We suggest that the equipment have a pressure resistance of 4 bar gauge. This is usually granted for the type of equipment used in such operations.

Conclusion on the Venting Option. The above vent size calculations as well as the runaway events observed in industrial practice suggest that the vessel protection by venting remains a reasonable option even for such very fast polymerization reactions, provided that the vessel inventory is not too large and that a minimum pressure resistance of the vessel is provided. However, we recommend to consider accident prevention first, by eliminating the process conditions where such a runaway polymerization can occur.

Simulation of Vinyl Acetate Runaway Polymerization Using Win Sim

In this section, a kinetic model is proposed to represent the radical chain polymerization of vinyl acetate. The relevant kinetic data are obtained from the literature and discussed. The software used for the simulation is described. The use of this software is exemplified by the prediction of the runaway polymerization of vinyl acetate in the presence of dilauroylperoxide as an initiator i.e., to represent a premix vessel polymerization incident.

Kinetic Model. A reaction mixture containing the following stable components is considered:

- polymerization initiator (I)
- monomer (M)
- polymer (D)
- solvent (S)

The following radical components are also present:

- monomer radical (R•)
- polymer radical (P)

The kinetic model includes the following reaction steps: Initiation, Propagation, Termination together with the relevant kinetic equations. The kinetic model chosen is the model used in the "Polymer Plus" software of Aspen Tech using Arrhenius-type rate equations.

Reaction Mechanism. The model reaction steps and rate equations are the following:

initiator decomposition $\mathrm{I} \rightarrow n\mathrm{R}\bullet \quad \mathrm{R_d} = k_\mathrm{d}[\mathrm{I}]$

chain initiation $\mathrm{R}\bullet + \mathrm{M} \rightarrow \mathrm{P_1} \quad \mathrm{R_i} = k_\mathrm{i}[\mathrm{R}\bullet][\mathrm{M}]$

thermal generation of radicals $\mathrm{M} \rightarrow \mathrm{P_1} \quad \mathrm{R_{th}} = k_\mathrm{th}[\mathrm{M}]$

chain propagation $\mathrm{M} + \mathrm{P}_n \rightarrow \mathrm{P}_{n+1} \quad \mathrm{R_P} = k_\mathrm{p}[\mathrm{M}][\mathrm{P}]$

transfer to monomer $\mathrm{M} + \mathrm{P}_n \rightarrow \mathrm{D}_n + \mathrm{P}_1 \quad \mathrm{R_{trm}} = k_\mathrm{trm}[\mathrm{M}][\mathrm{P}]$

chain termination by disproportionation

$$\mathrm{P}_n + \mathrm{P}_m \rightarrow \mathrm{D}_n + \mathrm{D}_m \quad \mathrm{R_{td}} = k_\mathrm{td}[\mathrm{P}]^2$$

chain termination by combination

$$\mathrm{P}_n + \mathrm{P}_m \rightarrow \mathrm{D}_{n+m} \quad \mathrm{R_{tc}} = k_\mathrm{tc}[\mathrm{P}]^2$$

The following constituent balances must be satisfied:

initiator $\dfrac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = -\mathrm{R_d}$

monomer radicals $\dfrac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}t} = n\cdot f\cdot \mathrm{R_d} - \mathrm{R_i}$

monomers $\dfrac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = -\mathrm{R_i} - \mathrm{R_{th}} - \mathrm{R_p} - \mathrm{R_{trm}}$

polymer radicals $\dfrac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = \mathrm{R_i} + \mathrm{R_{th}} - 2\mathrm{R_{td}} - 2\mathrm{R_{tc}}$

polymers $\dfrac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = -\mathrm{R_{trm}} + 2\mathrm{R_{td}} + \mathrm{R_{tc}}$

The quasi-stationary-state hypothesis is assumed and is written as follows:

$$\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}t} = 0 = f\cdot n\cdot \mathrm{R_d} - \mathrm{R_i}$$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = 0 = \mathrm{R_i} + \mathrm{R_{th}} - 2\mathrm{R_{td}} - 2\mathrm{R_{tc}}$$

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(19) Fauske, H. K. Practical containment concepts in connection with short-duration high-rate two-phase discharges. *J. Loss Prev. Process Ind.* **1990**, *3*, 130−135.

Hence:

$$R_i = f \cdot n \cdot R_d$$

$$[P] = \sqrt{\frac{R_i + R_{th}}{2(k_{tc} + k_{td})}}$$

Gel Effect. The gel effect or Trommsdorff effect is related to the reaction mixture increase of viscosity with increasing polymerization conversion ratio. The gel effect may induce an increase in the rate of polymerization due to the slower termination reaction caused by increased viscosity.

The kinetic interpretation of the gel effect is that given in the *Polymer Plus* software where the termination reaction rate constants are multiplied by a factor GF, depending on the polymer mass fraction in the reaction mixture.

$$k_t = GF \cdot k_{t0}$$

where

$$GF = \exp(-gf_1 X_P - gf_2\, X^2{}_P - gf_3\, X^3{}_P)$$

Dynamic Model. The reaction mixture is assumed to be enclosed in a vessel under constant volume conditions.

The initial mass, composition, temperature must be specified by the user.

In step one the model determines the reaction mixture thermodynamic state:

- vapor fraction
- composition of liquid and vapor phases
- vessel pressure
- vessel filling ratio

In step two, the boundary conditions are specified:

- vessel wall under constant temperature
- reaction mixture and vessel under constant temperature
- specified heat exchange through the vessel walls

The model determines the reaction mixture temperature, pressure, composition in the vessel, as a function of time.

The following system of differential equations is integrated using a variable step Runge Kutta method:

- enthalpy change = heat exchanged through the wall + heat of reaction released
- enthalpy change of the vessel wall = heat exchange with the reaction mixture + heat flux specified by the user
- change in number of moles of constituent = contribution of every reaction

The polymer molecular weight is calculated, assuming a constant total mass of the reaction mixture.

The following simplifying hypotheses are assumed:

- The liquid volume is constant during the polymerization reaction.
- The reaction mixture specific heat is constant during the polymerization reaction.

We know that both hypotheses are not true since the polymerization conversion ratio can be determined by measuring the reaction mixture volume and the liquid specific heat changes during the reaction. However, the relevant experimental data is not available and no model to account for these properties change was introduced.

The liquid volume and liquid specific heat are calculated for the initial conditions together with the reaction mixture thermodynamic properties.

Kinetic Data Obtained in the Literature

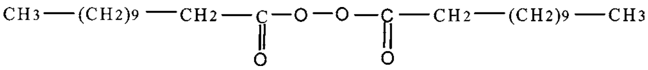
Polymerization Initiator Decomposition. The reaction is:

$$I \rightarrow nR\bullet$$

The initiator decomposition rate is:

$$-\frac{d[I]}{dt} = k_d[I]^{nd} = k_d \exp(-E_d/RT) \cdot [I]^{nd}$$

The initiator considered is dilauroylperoxide (LPO).



$$CH_3-(CH_2)_9-CH_2-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-CH_2-(CH_2)_9-CH_3$$

The following decomposition kinetics are available for dilauroylperoxide.

(1) paper of Korbar and Malavasic[20]

		T = 65 °C		T = 75 °C		T = 85 °C	
order n_d	E_d (kJ/mol)	K_d (s^{-1})	$T_{1/2}$ (h)	K_d (s^{-1})	$T_{1/2}$ (h)	K_d (s^{-1})	$T_{1/2}$ (h)
1.1	135.7	0.22×10^{-4}	8.8	0.88×10^{-4}	2.20	3.27×10^{-4}	0.60

(2) data of manufacturer mentioned by Korbar and Malavasic[20]

		T = 65 °C		T = 75 °C		T = 85 °C	
order n_d	E_d (kJ/mol)	K_d (s^{-1})	$T_{1/2}$ (h)	K_d (s^{-1})	$T_{1/2}$ (h)	K_d (s^{-1})	$T_{1/2}$ (h)
–	127.3	0.28×10^{-4}	6.8	1.04×10^{-4}	1.90	3.56×10^{-4}	0.50

(3) data of Warson[21] used in Polymer Plus

			half-life = 60 s		half-life = 1 h		half-life = 10 h	
order n_d	E_d (kJ/mol)	K_d (s^{-1})	T (°C)	$T_{1/2}$ (h)	T (°C)	$T_{1/2}$ (h)	T (°C)	$T_{1/2}$ (h)
1	127.4	1.44×10^{15}	116		80		62	

(4) other data

Half-life periods are given in various works.

A half-life period of 10 h at 62 °C is mentioned in ref 22.

A half-life of 1 min at 115 °C is mentioned by SRI.

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(20) Korbar, A; Malavasic, T. Influence of different initiators on methyl methacrylate polymerization, studied by differential scanning calorimetry. *J. Therm. Anal.* **1995**, *44*, 1357−1365.

(21) Warson, H. *Per-compounds and per-salts in polymer processes*. Solihull Chemical Services, 1980.

(22) *Encyclopedia of Polymer Science and Engineering,* 2nd ed.; Kroschwitz, J. L., Ed.; John Wiley: New York, 1989; Vol. 11, p 4.

The following data were measured:

$T_{1/2}$ (h)	42	12	3.2	1
T (°C)	50	60	70	80

Thermal Generation of Radicals by the Monomer. The reaction is:

$$\mathrm{M} \rightarrow \mathrm{M}\bullet$$

The monomer radical generation rate is:

$$\mathrm{R}_{\mathrm{th}} = k_{\mathrm{th}}[\mathrm{M}] = k_{\mathrm{th}} \exp(-E_{\mathrm{th}}/RT)[\mathrm{M}]$$

No kinetic data is available on this reaction rate in the literature due to the many factors influencing the thermal generation of radicals by the monomer.

Chain Propagation. The reaction is:

$$\mathrm{M} + \mathrm{P}_n \rightarrow \mathrm{P}_{n+1}$$

The heat of polymerization is basically the heat of propagation reaction. The data available on this reaction is:

(1) the data of Flory[23]

ΔH_{r} (kJ/mol)	k_{p} (mol L^{-1} s^{-1})	E_{p} (kJ/mol)
–	24×10^7	30.5

(2) the data of the *Encyclopedia of Polymer Science and Engineering*

ΔH_{r} (kJ/mol)	k_{p} (mol L^{-1} s^{-1})	E_{p} (kJ/mol)
87.5–89.1	3.2×10^7	26.2

Termination Reaction. The chain termination can occur following two reactions:

by combination $\mathrm{P}_n + \mathrm{P}_m \rightarrow \mathrm{D}_{n+m}$

by disproportionation $\mathrm{P}_n + \mathrm{P}_m \rightarrow \mathrm{D}_n + \mathrm{D}_m$

The data from the literature suggests that the combination reaction is negligible compared to the disproportionation reaction. The data on the disproportionation reaction are:

(1) the data of Flory[23]

K_{td} at 60 °C	K_{td} (mol L^{-1} s^{-1})	E_{td} (kJ/mol)
7.4×10^7	2.1×10^{11}	21.8

(2) the data of the *Encyclopedia of Polymer Science and Engineering*

K_{td} at 60 °C	K_{td} (mol L^{-1} s^{-1})	E_{td} (kJ/mol)
2.9×10^7	3.7×10^9	13.3

Transfer to Monomer. There is a scarcity of data on the transfer to monomer reaction. *Encyclopedia of Polymer Science and Engineering* gives data on the ratio

$$C_{\mathrm{m}} = kt_{\mathrm{m}}/k_{\mathrm{p}}$$

$$C_{\mathrm{m}} = 1 \times 10^{-4} \quad \text{at } T = 0\ ^\circ\mathrm{C}$$

$$C_{\mathrm{m}} = 3 \times 10^{-4} \quad \text{at } T = 70\ ^\circ\mathrm{C}$$

C_{m} may influence only the polymer mean molecular weight.

Gel Effect. Limited data are available concerning the gel effect of vinyl acetate polymerization. The factor values of Polymer Plus are assumed:

gf1	0.44
gf2	6.36
gf3	0.17

Use of the Model. The model described above is used for the simulation of vinyl acetate bulk polymerization but could be used also for any other polymerization with or without a solvent, provided that the thermodynamic properties are available through UNIPHY. The program run provides various information displays.

Main screen: pressure, temperature, temperature gradient, and liquid-/gas-phase compositions as a function of time. Secondary displays: kinetic descriptions – initial conditions – vessel characteristics – alarm conditions.

Application to the Simulation of the Bulk Polymerization of Vinyl Acetate. The software is used to simulate the bulk polymerization of vinyl acetate in the presence of 1.8% dilauroylperoxide under isothermal temperatures of 37 °C and 47 °C in a VSP test cell.

The test conditions are the following: test cell volume: 115 cm^3; charge: 81.7 g; dilauroylperoxide: 1.8% w/w; initial pressure: 1 bar absolute.

The following kinetic parameters are used:

	K	E (kJ/mol)
initiator decomposition	1.44×10^{15}	127.4
thermal generation of radicals	0	0
propagation	3.2×10^7	26.2
transfer to monomer	0	0
termination by combination	0	0
disproportionation	3.7×10^9	13.3

initiator efficiency factor: $f = 0.6$

enthalpy of polymerization $\Delta H_{\mathrm{r}} = 88$ kJ/mol.

A first simulation was made without gel effect.

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[23] Flory, P. J. *Principles of Polymer Science*; Cornell University Press: Ithaca, NY, 1958.

A progressive polymerization was obtained which did not represent the runaway polymerization obtained in the VSP because the rate of polymerization decreased as a function of time. If a gel effect was introduced using the Polymer Plus parameters, an induction period phenomenon was obtained. For an isothermal exposure at 47 °C, an isothermal induction period of 90 min was obtained. The gel effect was found to occur for a conversion ratio of approximately 50%. By tuning the kinetic parameters and the heat losses from the test cell, the simulation could be adjusted to represent the experimental data.

Conclusion

The prediction of the runaway polymerization of vinyl acetate based on a simulation using a kinetic model and kinetic data from the literature provides an estimate of the polymerization isothermal induction period. In the model used, the only cause of chemical acceleration is the gel effect obtained for a conversion ratio of 50%. The radical chain reaction is not found to speed up the reaction under isothermal conditions and the presence of a polymerization inhibitor is not taken into account. Much effort should be devoted to better define the initial and boundary conditions to represent experimental conditions. The simulation is specific for a premix vessel containing a high concentration of polymerization initiator.

For monomer storage vessels, the polymerization induction period near ambient temperature is controlled by the inhibitor consumption as explained in this paper. The initial inhibitor concentration, the thermal production of free radicals by the monomer, and the production of radicals by trace concentration of the polymerization initiator in the case of recycled monomer are the governing factors. The runaway polymerization accidents may then result from a long residence time under too high a temperature. This explanation is supported by the experimental results presented in this paper.

The protection, by emergency relief vents, of premix vessels or storage vessels from over pressurization caused by VAM bulk polymerization is an option, provided that enough pressure resistance is provided through the vessel design. As the reaction may become very fast, the required vent area is significant. Therefore, the prevention of accidents in this field would best rely on prevention measures and a good control of operating conditions.

The case histories and the explanations presented in this paper are not specific of vinyl acetate monomer and may also apply to other reactive monomers and to processes where the same circumstances are present. This paper is an invitation to revisit polymerization processes to check that the weaknesses described are absent.

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