

Effect of Oxygen on Vinyl Acetate Polymerization

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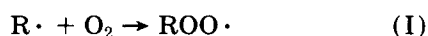
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SYNOPSIS

Various conflicting reports in the literature regarding the effect of oxygen on the stability of vinyl acetate (VA) toward polymerization led us to reexamine this topic using both isothermal stability tests and quasi-adiabatic calorimetry. Both commercial VA stabilized with 5–20 ppm by weight of hydroquinone (HQ) and purified, unstabilized VA exhibit lower stability to thermally initiated polymerization (at 50–120°C) in the presence of oxygen than in its absence. However, when stabilized with 3–5 ppm of HQ, both air-saturated and oxygen-free VA exhibit adequate thermal stability at normal transport and storage temperatures (25–50°C). Oxygen destabilization of VA is probably caused by the relatively low stability of VA polyperoxide rather than by the oxidation of acetaldehyde impurity to peroxyacetic acid. The length of VA polymerization induction periods is about –0.4 order in oxygen partial pressure.

INTRODUCTION

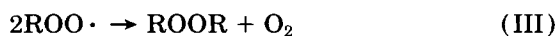
The dual role of oxygen in the polymerization of vinyl monomers has been recognized for some time.^{1,2} One effect of oxygen on such systems is its rapid reaction with carbon-centered radicals to form less reactive peroxy radicals.



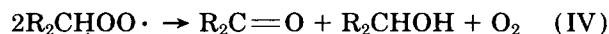
Reducing the reactivity of these radicals results in a slower effective rate of chain propagation compared to that in the absence of oxygen:



In addition, chain termination can take place via the combination of peroxy radicals^{2,3}:



or



The formation of peroxidic compounds by either re-

action II or III leads to the second effect of oxygen on vinyl polymerization, namely, initiation. If these peroxides are unstable under reaction conditions, their decomposition yields radicals that initiate polymerization. The global effect of oxygen on the rate of polymerization of any monomer will depend on the relative importance of these two opposing effects. In most cases reported the overall effect is retardation or even complete inhibition of polymerization.

The impact of oxygen becomes even more complicated when a free radical trapping compound (polymerization inhibitor) is added to stabilize the monomer. Many of these polymerization inhibitors (especially phenolic compounds) are much more efficient at trapping oxygen-centered radicals than carbon-centered radicals. This results in synergism between dissolved oxygen and phenolic inhibitors in stabilizing monomers.^{4,5}

Over the years, there have been some conflicting reports on the overall effect of oxygen on the polymerization of vinyl acetate (VA). Some of this confusion has resulted from the varying conditions under which its effect was tested. As early as 1931, Staudinger reported that at 100°C, carefully purified VA would not thermally polymerize in the absence of oxygen for a period of 6 weeks, whereas it completely polymerized in about one day under air.⁶

Nozaki and Bartlett reported that VA would not

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thermally polymerize in the absence of oxygen at 100°C in a Pyrex vessel but would polymerize in soft glass in a nonreproducible manner.⁷

Barnes¹ and Taylor⁸ reported that oxygen inhibits the photoinduced polymerization of VA at 0 and 100°C, respectively. The benzoyl peroxide-initiated polymerization of VA at 45–60°C was reported to be inhibited by oxygen as well.^{7,9}

All of the work cited above was carried out with carefully purified VA from which the stabilizer [usually hydroquinone (HQ)] had been removed by distillation.

It was our immediate objective to determine the effect of oxygen concentration in the gas blanket atmosphere on the stability of shipments of bulk quantities of commercial VA. This VA contains less than 10 ppm (by weight) of acetaldehyde impurity; one grade is stabilized with 3–5 ppm hydroquinone and another with 14–17 ppm hydroquinone.

EXPERIMENTAL

Hoechst Celanese Chemical Group, Inc. VA (stabilized with 4 ppm HQ as analyzed by liquid chromatography) was used in these studies without further purification unless otherwise indicated. This VA contained 2 ppm acetaldehyde, 5 ppm acetic acid (both analyzed by gas chromatography), and 30 ppm water (by titration with Hydranal Composite 5K).

Preparation of Inhibitor-Free Vinyl Acetate

Purified, hydroquinone-free VA was prepared by atmospheric distillation of Hoechst Celanese VA in a 1-in.-diameter, 20-tray Oldershaw column under nitrogen using HQ to prevent polymer fouling in the column. The product was stored at 0°C under nitrogen in Pyrex bottles covered with aluminum foil to keep out the light.

Thermal Stability Tests in Pyrex Vials

The isothermal stability tests in this study were carried out in Pyrex vials illustrated in Figure 1. The bulb has an inner diameter of 18 mm and a height of 5.1 cm. The neck has outer and inner diameters of 6.35 and 3.80 mm, respectively, and a length of 15 cm.

For VA stability tests under air, it was ensured that the VA was initially saturated with air by sparging. The neck of the vial was capped with a $\frac{1}{4}$ -in. Swagelok cap fitting or sealed by melting and the vial immersed in a constant-temperature bath

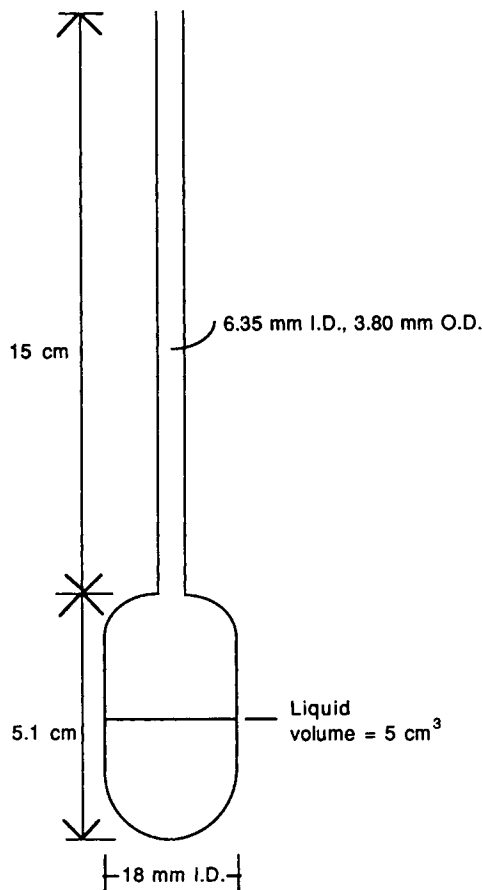


Figure 1 Pyrex vials used for vinyl acetate stability tests.

or placed in an oven. Onsets of polymerization were detected by visual increases in viscosity.

Samples of VA to be tested under nitrogen (or an air–nitrogen mixture) were equilibrated with the desired atmosphere by exhaustive sparging.

The carbon steel wires used in the tests indicated were 1 mm in diameter and 7 mm long. Unless it is specifically indicated that they were not pretreated, they were cleaned by surface abrasion and/or acid treatment followed by thorough rinsing and pre-soaking in VA.

Calorimetry

The calorimetry described in this report was carried out in a Reactive System Screening Tool (RSST) calorimeter (Fauske and Associates, Burr Ridge, IL). Modified software provided by the manufacturer allowed for rapid heating of the sample followed by incubation at a constant temperature.

Vinyl acetate samples to be used in RSST experiments were sparged for 45 min with the desired

Table I Stability of Vinyl Acetate at 48.9°C with Carbon Steel Wires^a

HQ, ppm	O ₂ , vol %	Time of Observation, Weeks						
		1	3	5	9	14	20	26
0	20	12*						
0	10	12*						
0	5	0	0	8	11*			
0	0	0	0	0	5*			
5	20	0	0	1	2	6*		
5	10	0	0	0	2	6*		
5	5	0	0	0	0	1	4*	
5	0	0	0	0	0	0	0	0
20	20	0	0	0	0	0	4	6*
20	10	0	0	0	1	5*		
20	5	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0

^a The asterisks indicate that all the samples in this set polymerized.

gas (air, nitrogen, or an air-nitrogen mixture). In air runs, the calorimeter was pressurized to 6 atm with dry air and the heating begun. For runs with atmospheres other than air, the system was alternately evacuated and pressurized to 6 atm with the chosen blanket gas composition four times before heating was started. All gases used (including air) were dried; the nitrogen used contained less than 5 ppm by volume of oxygen.

The 6-atm back pressure used in these runs assured that the VA would not boil at the incubation temperature, although some monomer typically vaporized during the exotherm. Calculated heat balances carried out for each run took this boiling into account.

RESULTS AND DISCUSSION

Isothermal Stability Tests

Effect of Oxygen Concentration in Blanket Gas

The first test series to determine the effect of oxygen on the thermal stability of VA was carried out in sealed Pyrex glass vials (see Experimental section) incubated in a constant-temperature bath set at 48.9°C. [The variation in temperature for baths and ovens used in this study was $\pm 0.2^\circ\text{C}$.] Samples of VA containing various concentrations of HQ were blanketed with air, and with 10 and 5% oxygen-nitrogen mixtures as well as with pure nitrogen.

There were 12 replicate samples for each atmosphere case, each sample containing a clean carbon steel wire. [The length and diameter of the wire were chosen to simulate the metal surface-liquid volume ratio in a railroad car.] A maximum of 8 samples in any given set was removed for analysis prior to polymerization onset. The results are shown in Table I, where numbers with asterisks indicate that all the replicate samples in that set not removed from the oven for analysis had polymerized. The results indicate that higher oxygen concentrations destabilize VA at a given HQ concentration.

A stability test at 54.4°C was carried out on samples of VA containing 5 ppm HQ and clean carbon steel wires. Six replicate samples were used for each

Table II Stability of Vinyl Acetate at 54.4°C with 5 ppm HQ, Carbon Steel Wires

Atmosphere	Time of Observation, Weeks								
	1	2	3	4	5	6	7	8	26
	Cumulative Number of Samples Polymerized								
Air	0	0	0	0	5	5	6 ^a		
10.5% O ₂	0	0	0	0	0	0	0	0	0
Nitrogen	0	0	0	0	0	0	0	0	0

^a All the samples in this set polymerized. Each set had six samples; none was removed for analysis.

Table III Stability of Vinyl Acetate with 5 ppm HQ

Temperature, °C	Atmosphere	Number of Samples	Induction Period, h
110.2	Air	5	5.75-7.5
109.9	Air	10	6.4-7.9
110.2	Nitrogen	5	>29
65.0	Air	10	330-354

blanket atmosphere: air, 10.5% oxygen, and pure nitrogen; none was removed for analysis. The results, shown in Table II, again show that VA samples under higher oxygen concentration gas blankets polymerize much more rapidly.

Additional stability tests without wires were car-

ried out at 110°C (under 1 atm of air and under nitrogen) and 65°C (1 atm of air) in a constant-temperature bath. The air induction periods (the nitrogen-blanketed samples did not polymerize during the test) are listed in Table III and are included in Figure 2 along with calorimetric data discussed below.

Effect of Metal Wire Preparation

Since the results reported in Ref. 7 seemed to point to the importance of materials in contact with the VA, we decided to examine this effect further. Table IV shows the difference in stability at 48.9°C of samples of VA containing 5 ppm HQ and blanketed with 10% oxygen when these samples (all in Pyrex vials) contained no wire, a cleaned carbon steel wire (see Experimental section for method of cleaning),

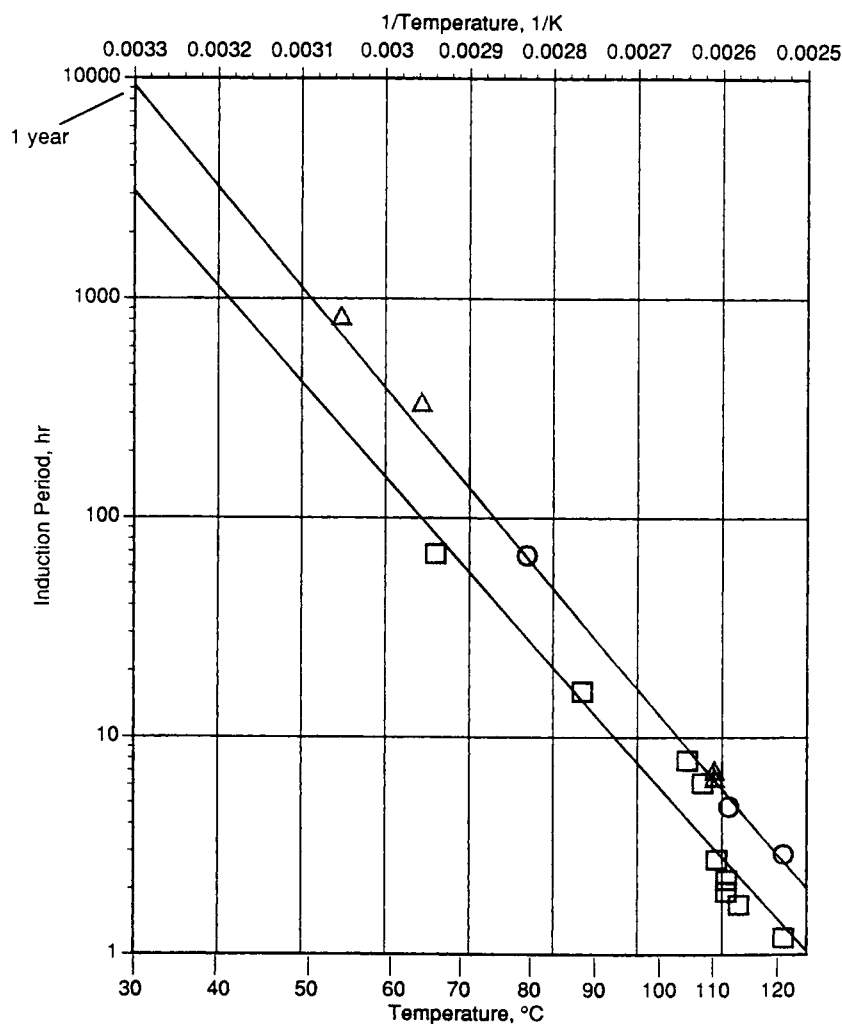


Figure 2 Vinyl acetate polymerization induction periods in RSST calorimeter [under (□) 1.25 atm oxygen; (○) 0.216 atm oxygen] and in vials under air (△).

Table IV Stability of Vinyl Acetate at 48.9°C with 5 ppm HQ, 10 vol % O₂ Atmosphere; Effect of Carbon Steel Wire

Wire	Time of Observation, Weeks								26
	1	2	3	4	5	6	7	8	
	Cumulative Number of Samples Polymerized ^a								
None	0	0	0	0	0	1	1	4	4
Clean	0	0	0	0	0	0	0	0	0
Untreated	0	1	4	8	10	10	10	10	10

^a Each set consisted of 12 replicate samples. No samples were removed for analysis during the test.

and an untreated carbon steel wire (12 replicates for each case; none removed for analysis). The difference in results is profound, indicating that cleaned wires have a strong stabilizing influence but untreated wires have a destabilizing influence on VA compared to monomer with no wire at all.

Effect of Acetaldehyde Impurity

Butcher theorizes that the initiating effect of oxygen on VA depends on the oxidation of acetaldehyde impurity to peroxyacetic acid, the actual radical generator.¹⁰ We carried out the following experiments to test this contention.

A sample of commercial-grade VA stabilized with 4 ppm HQ was analyzed for acetaldehyde content by gas chromatography and found to contain 2 ppm. A portion of this VA was "spiked" with 53 ppm of acetaldehyde. Three samples of each material (the commercial VA and the acetaldehyde-spiked VA) were incubated under air and three under nitrogen at 54.4°C (all with clean carbon steel wires). The results are shown in Table V. Two of the three commercial VA samples under air polymerized within 3 months; the third polymerized after 7 months. Neither the commercial VA samples incubated under nitrogen nor the acetaldehyde-spiked VA samples under either atmosphere polymerized during the test period of 9 months. This rules out the dependence of oxygen's destabilizing effect on acetaldehyde impurity. In fact, the results indicate acetaldehyde to have a significant stabilizing effect on air-blanketed VA.

It will be noted that the induction periods of the VA samples under air (without acetaldehyde) were considerably longer in this experimental series than

those of the corresponding samples in Table II (which were also tested at 54.4°C). It is possible that this is a result of the two very different methods used to clean the carbon steel wires in the two series of tests. In this series the outer surface of the wires were abraded off with emery cloth and the wires soaked overnight in acetone and dried in air. In the runs shown in Table II, the wires were cleaned by washing several times with hydrochloric acid, repeated rinsing with deionized water, drying, and then soaking overnight in VA.

Uninhibited Vinyl Acetate

Commercial VA was freed from its HQ stabilizer by fractionation, and the polymerization induction period of the resulting material determined. Six tubes of the unstabilized material under air and 6 tubes under nitrogen were heated to 110°C in the constant-temperature bath. All six air-blanketed samples polymerized between 0.5 and 1.5 h; all six nitrogen-blanketed samples polymerized between 4.0 and 4.7 h. These results show that the destabilizing effect of oxygen holds true for hydroquinone-free VA.

Calorimetric Studies

Quasi-adiabatic calorimetry was used to confirm the destabilizing effect of oxygen observed in the isothermal experiments and also to estimate the rate of temperature increase during the polymerization of VA. Several series of experiments were carried out using the RSST calorimeter described in the Experimental section. Runs were carried out under 6 atm of air (1.25 atm oxygen partial pressure), under 6 atm of an oxygen-nitrogen mixture containing 3.6 vol % oxygen (0.216 atm oxygen partial pressure,

Table V Effect of Acetaldehyde on Vinyl Acetate Stability at 54.4°C with 5 ppm HQ, Carbon Steel Wires

Material Tested	Atmosphere	Induction Period, months
VA	Air	3-7
VA	Nitrogen	>9
VA + 53 ppm acetaldehyde	Air	>9
VA + 53 ppm acetaldehyde	Nitrogen	>9

simulating that in atmospheric air), and under pure nitrogen. The results are discussed below.

Calorimetry at 1.25 atm Oxygen Partial Pressure

Nine runs were carried out on commercial VA in the RSST calorimeter under 6 atm air at temperatures ranging from 67 to 123°C. The observed induction periods in this series of experiments are shown in Table VI and are plotted in Figure 2. The "inverse" Arrhenius plot is described by the following equation ($R^2 = 0.93$):

$$\text{Induction period, hours} \\ = 1.0327 \times 10^{-11} \exp(20,097/RT)$$

The rate of temperature rise during the exotherm in all but two of the runs was greater than 100°C/min, and energy balance calculations gave heats of polymerization that generally ranged from 14 to 26 kcal/mol (the reported value¹¹ is 21 kcal/mol). This range is reasonable considering the experimental complications (see Experimental section) and the physical limitations of the screening tool calorimeter used.

Calorimetry at 0.216 atm Oxygen Partial Pressure

Three RSST runs were carried out under 6 atm of an oxygen-nitrogen mixture containing 3.6 vol % oxygen (0.216 atm oxygen partial pressure) to confirm that the key atmosphere-related variable is oxygen partial pressure and not total pressure. These induction periods are presented in Table VII and plotted in Figure 2. These induction periods are consistent with those determined in the constant-temperature bath under air; the latter are also included in Figure 2. The "inverse" Arrhenius equation ($R^2 = 0.997$) describing the induction periods under 0.21–0.22 atm oxygen is

Table VI Calorimetric Results with Vinyl Acetate with 4 ppm HQ under 1.25 atm Oxygen

Temperature, °C	Induction Period, h	Maximum Temperature, °C	Maximum Rate, °C/min
122.5	1.19	156	15
114.4	1.69	171	110
112.1	1.94	172	176
112.1	2.15	176	123
110.5	2.74	167	222
108.1	6.18	152	15
105.6	7.82	178	1417
88.5	16.15	189	553
66.9	6.6	173	1142

Table VII Calorimetric Results with Vinyl Acetate with 4 ppm HQ under 0.216 atm Oxygen

Temperature, °C	Induction Period, h	Maximum Temperature, °C	Maximum Rate, °C/min
122.5	2.91	144	2.4
112.6	4.82	151	6.9
80.2	67.5	176	215

$$\text{Induction period, hours} \\ = 7.3407 \times 10^{-12} \exp(20,936/RT)$$

These induction periods average about twice as long as those with 1.25 atm oxygen at corresponding temperatures, reflecting a kinetic order of about -0.4 in oxygen partial pressure. The maximum rates of temperature rise during the exotherms in these calorimetric runs were significantly slower than those in the runs carried out under 6 atm of air.

Determinations under Nitrogen

A carefully deoxygenated sample of VA (see Experimental section) was held under nitrogen at 105°C in the RSST calorimeter for 25 h with no evidence of an exotherm. The equipment was cooled down, opened, and the sample found to be unpolymerized. The material was replaced in the calorimeter and heated to 113°C under 6 atm air. It polymerized after 2.3 h with an exotherm rate typical of those observed in 6-atm air runs. The initial nitrogen incubation of the sample evidently did not affect its subsequent polymerization under air. A second such experiment was carried out in which the deoxygenated sample was heated at 107°C for 66 h under nitrogen without any polymerization. It was then heated to 110°C under 6 atm air and it polymerized within 4.8 h with a normal exotherm.

In another RSST experiment, a VA sample was heated under 6 atm air at 105°C for 1.25 h. The run was interrupted before any exotherm was detected and the absence of polymerization confirmed by examination of the sample. The sample was replaced in the calorimeter, deoxygenated, and an attempt made to heat it to 110°C under nitrogen, but it polymerized during heatup at about 93°C.

Calorimetry with Uninhibited Vinyl Acetate

Unstabilized VA prepared by fractionation was tested in the RSST calorimeter at 109–110°C under

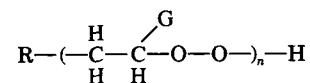
6 atm of air. The induction period was 0.9 h and the maximum rate of temperature rise during the exotherm was 105°C/min. Unstabilized VA was also tested under nitrogen in the RSST at 109–110°C. It showed no exotherm when heated for a period of 6.5 h. The system was cooled and examination of the sample showed it to have increased in viscosity. Evidently the rate of polymerization (and hence of heat liberation) was so gradual as to be undetectable due to heat leakage in the system.

Mechanistic Considerations

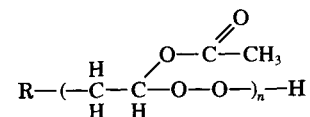
Calorimetric experiments under 6 atm air and under nitrogen were carried out on two other brands of VA (stabilized with 5 ppm HQ) to determine whether the destabilizing effect of oxygen could have been due to impurities specific to Hoechst Celanese VA. Not only was the directionality of oxygen effect the same for the other brands, but the induction periods were very close to those measured with the Hoechst Celanese VA at the same conditions. Nitrogen-blanketed samples did not polymerize when heated at 110°C for periods as long as those used for Hoechst Celanese VA. We therefore conclude that the destabilizing effect of oxygen on VA is a general phenomenon associated with that monomer.

The results of the RSST experiment in which VA was heated in air for a period less than its induction period and then heated under nitrogen are consistent with oxygen destabilization via formation of peroxides during the induction period. The material polymerized in a shorter total heating time than it would have under air at the same temperature because during the heating under nitrogen, oxygen had already worked its destabilizing effect (formation of peroxides) but was no longer present to slow down chain propagation. When the two effects of oxygen are experimentally separated in this manner, the destabilizing effect can even be observed with monomers in which the overall oxygen effect is stabilization.⁸ Thus the "dual effect" of oxygen in the polymerization of monomers proposed by Barnes and by Bartlett (see Introduction) is operative in the thermal polymerization of VA, but our results indicate that the destabilization due to radical generation by peroxide decomposition is much more important than oxygen's retardation of the chain propagation rate.

The question arises as to why oxygen's destabilizing effect is so much more important for VA than it is for styrene, acrylates, and other common monomers. It is likely that the answer lies in a relatively lower stability of VA polyperoxide.



In the case of styrene or ethyl acrylate, for example, the side chain group, G, is phenyl or carboxyethyl and is attached through a carbon-carbon bond. In the case of VA, G is an acetyloxy group that is attached to the polymer chain carbon atom through that atom's second carbon-oxygen bond. This formally relates the site to a typically unstable *gem*-diol:



This rationale is in agreement with Barnes's conclusions that VA forms a polyperoxide when heated with oxygen, and that this polyperoxide is significantly less stable than those formed in styrene or methyl methacrylate.¹² Under conditions where methyl methacrylate and styrene gave significant yields of polyperoxides with only small amounts of aldehydic decomposition products, VA gave more decomposition products than peroxide. The sensitivity of VA stability to the type of materials present in the monomer (i.e., cleaned or uncleaned steel wires) is probably a result of the catalysis of peroxide decomposition by such species as metal ions.

One possible explanation for the high stability of oxygen-free VA and the extreme destabilizing effect of oxygen might be that peroxide decomposition provides the only viable route to chain initiation because a purely thermal initiation mechanism is nonexistent. This concept seems inconsistent with the results observed with unstabilized VA; polymerization occurred at 110°C during a 6-h period with deoxygenated, unstabilized VA (compared to > 66 h with HQ-stabilized VA at the same temperature). This either reflects the existence of a thermal initiation process or testifies to the difficulty in obtaining a totally oxygen-free and peroxide-free sample of VA.

CONCLUSIONS

Both commercial VA stabilized with 5–20 ppm by weight of HQ and purified, unstabilized VA exhibit much lower stability to thermally initiated polymerization (at 50–120°C) in the presence of oxygen than in its absence. However, when stabilized with

3–5 ppm of HQ, both air-saturated and oxygen-free VA exhibit adequate thermal stability at normal transport and storage temperatures (25–50°C).

Oxygen destabilization of VA is not caused by the oxidation of acetaldehyde impurity but is probably due to the relatively low stability of VA polyperoxides. This destabilization is apparently exacerbated by substances that accelerate the decomposition of these peroxides, such as metal ions. The length of VA polymerization induction periods is about –0.4 order in oxygen partial pressure.

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