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A Study of the Influential Factors Regarding the Thermal Stability of Polymeric Materials

Shinichiro Goto

Process Safety Technology Group, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura Chiba 299-0265, Japan
Shinichirou.Gotou@mitsuichemicals.com

Mitsui Chemicals, Inc.(MCI) is a major petrochemical company worldwide. They produce polymeric materials resulting in high value-added products covering a wide range of industries. Normally, polymeric materials are polymerized under controlled radical polymerization, which releases a large amount of energy and increases temperature. Uncontrolled radical polymerization can occur, resulting in serious accidents. In the worst case, secondary reactions such as the decomposition of the polymer can occur, leading to more energy, pressure, and temperature increases. These secondary reactions can cause serious fires and explosions.
To avoid these major accidents, many studies about the stabilization of polymeric materials have been undertaken [1,2)]. For example, the addition of effective inhibitors and modeling of the inhibition mechanism have been reported [3,4)].
Acrylic acid is one of the most reactive of polymeric substances. An example of an accident with an acrylic acid tank occurred in 2012 [5)], after which, we re-evaluated how to treat acrylic materials safely from storage to disposal within our plants. But it's difficult to judge the optimum conditions. Therefore, MCI undertook to reveal the influential factors and their impact behind the thermal behavior of acrylic materials.
Commercially, acrylic acid is stabilized with p-methoxyphenol (MEHQ). It's known that the presence of dissolved oxygen is necessary for MEHQ to function effectively. Polymerization reaction is prevented by the consumption of oxygen and MEHQ (called the polymerization induction period). During polymerization induction periods, thermally produced radicals react with oxygen to form peroxide which can work as a radical initiator.
This paper reports on the thermal behavior of acrylic acid and its esters as a result of using a differential scanning calorimeter (DSC) and an accelerating rate calorimeter (ARC) under different conditions involving oxygen and inhibitor concentration. The unique thermal behavior involving acrylic acid and its esters were found.

1. Experiment

Samples

Acrylic acid (AA, Figure 1, 99%), isobutyl acrylate (IBA, Figure 2, 99%) and MEHQ (Figure 3, 99%) were purchased from Tokyo Chemical Industry (TCI). Inhibitor remover were also purchased from TCI. Dissolved oxygen in AA and IBA were removed by the bubbling of nitrogen for 5 minutes.

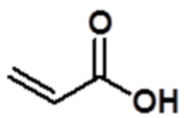

Figure 1 AA

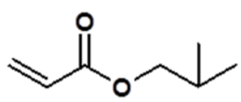

Figure 2 IBA

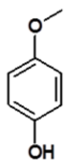

Figure 3 MEHQ

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Conditions of analysis

DSC and ARC measurements was used for evaluating the thermal behavior of the acrylic monomers. Condition of DSC analysis is summarized in Table 1. Condition of the ARC analysis is summarized in Table 2.

Table 1: Condition of DSC analysis

Equipment	NETZSCH 3500 Sirius
Range of temperature [℃]	30～450
Heating rate [K/min]	10
Crucible material	Stainless steel, Gold plated stainless steel
Sample mass [mg]	About 1
Sample treatment condition	Air, nitrogen

Table 2: Condition of ARC analysis

No.	THT ES-ARC
Range of temperature [℃]	90～122
Measurement method	Isothermal
Sensitivity [K/min]	0.02
Crucible material	Hastelloy C-276
Crucible mass [g]	About 14
Sample mass [mg]	About 2
φ correction	About 2.5
Sample treatment condition	Air, nitrogen

Glove box which was filled with nitrogen was used to prepare the under nitrogen samples.
In the isothermal mode, the equipment keeps the isothermal at set temperature until heat generation is detected.

2. Results and discussion

DSC

Results of DSC measurements are summarized in Table 3 and 4.

Table 3: Results of DSC measurements

No.	Sample	Crucible material	Q J/g	Tdsc ℃
1	AA	Stainless Steel	904	211
2		Gold plated	1080	165
3	IBA	Stainless Steel	618	197
4		Gold plated	700	199

sample treatment condition: air

Table 4: Results of DSC measurements

No.	Condition	MEHQ ppm	Q J/g		Tdsc ℃	
			1st	2nd	1st	2nd
1	N2	94	45	427	135	310
2	Air	6	602	-	169	-
3		1100	564	-	230	-
4		94	618	-	197	-

sample treatment condition: air, 1st means first peak, 2nd means second peak

Effect of crucible material

Figure 4 and 5 show the results of these DSC measurements as a curve relative to AA and IBA respectively for each condition. These results correspond to No.1～4 in Table 3.

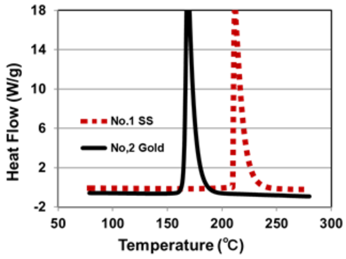

Figure 4 DSC measurement of AA

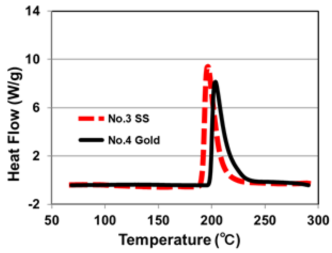

Figure 5 DSC measurement of IBA

In the case of AA, the results were completely different between when using the SS crucible and when using the gold plated one. On the other hand, in the case of IBA, the effect was found to be small. We decided to use IBA.

Effect of oxygen

Figure 6 shows the results of the DSC measurements as a curve. These results correspond to No.3 and No.5 in Table 4. As shown in Figure 6, the results of under air conditions were totally different to the results of the nitrogen conditions. There is a strong, sharp peak around 190 ℃ under air conditions. On the other hand, there are two broad peaks around 120 ℃ and 200 ℃ respectively.

This is because of the formation of monomer peroxide. It seems that under nitrogen conditions there exists a low risk state when polymerization is started.

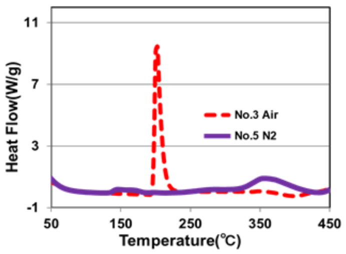

Figure 6 DSC measurement of IBA (effect of oxygen)

Effect of the concentration of MEHQ

These results correspond to No.3, 6, 7 in Table 4. As shown in Figure 7, the onset of the DSC was shifted to the high temperature side by the high MEHQ concentration. It is assumed that during the measurements, the polymerization starting temperature is dependent upon the concentration of the MEHQ. On the other hand, regardless of the concentration of MEHQ, the exothermic peaks of all samples were strong and sharp. All three samples had almost the same heating value.

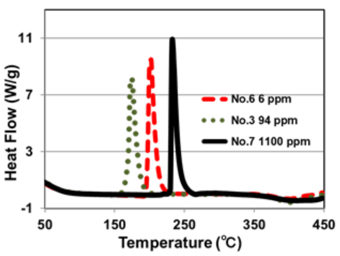

Figure 7 DSC measurement of IBA (effect of the concentration of MEHQ)

ARC measurement was conducted to study the thermal behavior of acrylic ester more detail.

ARC

Results of ARC measurements are summarized on Table 5. Hereafter, polymerization induction period was used for the time which is taken until the heat generation of 0.02 ℃ / min or more is detected.
And the adiabatic temperature rise express that temperature rising from the detection of heat generation until the heat generation rate becomes 0.02 ℃/min or less.

Table 5: Results of ARC measurements

No.	Conditions	MEHQ ppm	Polymer induction period hours	Adiabatic temp. rise ℃
1	Air	1100	66	38
2		94	36	78※
3		6	2.8	84※
4			8.8	84※
5			80	78
6		94	-	-
7	N2		3.7	61
8			-	-

※ reference value

Effect of the concentration of MEHQ

Figure 8 shows the results of ARC measurements as a curve of IBA with different concentration of MEHQ. This result corresponds to No.1, 2, 3 on Table 5. The higher concentration of MEHQ, the longer polymerization induction period was observed. But there is no linearity relationship between the concentration of MEHQ and polymerization induction period. Excess MEHQ seems to be less effective. The adiabatic temperature rise of No.1 is also smaller than that of No.2 and No.3. A part of monomer might be polymerized during ARC measurement even if under air condition.
Figure 9 shows heat rate as a function of reciprocal temperature. Heat rate of No.1 (MEHQ1100ppm) was very slow compared to No.1 and No.2. Almost all of the monomer peroxide must be reacted with MEHQ. So, it was no longer able to function as an initiator for polymerization.

Effect of the temperature

Figure 10 shows the results of ARC measurements as a curve of IBA with different isothermal temperature. This result corresponds to No.2, 4, 5, 6 on Table 5. When the Isothermal temperature was set to 90 ° C (No.6), exothermic reaction of 0.02 ° C/min or more wasn't observed. We think that remaining MEHQ prevent polymerizing.
Figure 9 shows there is a big difference between the heat rate of No.2 and No.5. The heat rate of No.5 is slower than that of No.2. We assume that there is a border temperature for monomer peroxide decomposition that is accelerating the polymerization of the acrylic esters. We decided to call that which is above the boundary a high temperature region. On the other hand, we decided to call that which is under the boundary as a low temperature region. Handling the acrylic monomer at a high temperature region is high risk.

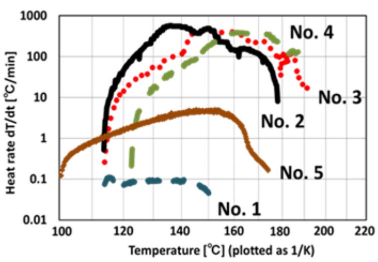

Figure 8 ARC curve of IBA (Effect of the MEHQ)

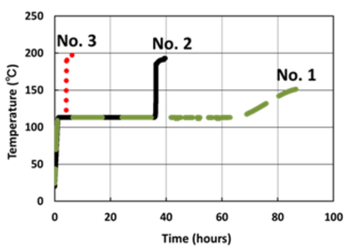

Figure 9 ARC curve of IBA (Heat rate vs temperature)

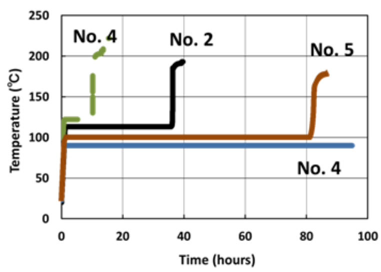

Figure 10 ARC curve of IBA (Effect of temperature)

Effect of oxygen

Figure 11 shows the results of ARC measurements as a curve of IBA with different sample treatment conditions. This result corresponds to No.7, 8 on Table 5. Under nitrogen conditions at 113 ℃ (No.7), the polymerization induction period was shorter and the adiabatic temperature rise was lower than under air conditions at 113 ℃. The ARC could not detect the heat generation at 90 ℃(No.8), but the sample was polymerized after the ARC measurement.
One of the reasons for this is that quinone- based polymerization inhibitors such as MEHQ cannot work efficiently without oxygen. We assume that during the polymerization induction period, monomer concentration decreases because polymerization at heating speed 0.02 ℃/min or less has progressed. The molecular weight of the sample were analysed to prove the above assumption.

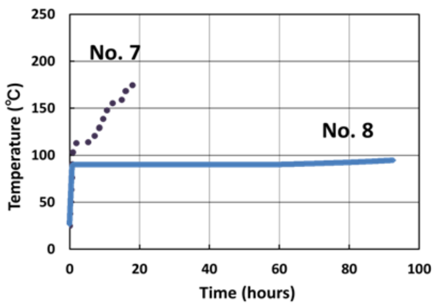

Figure 11 ARC curve of IBA (Effect of the oxygen)

GC and GPC

Gas Chromatography (GC, Agilent technologies 6890) was used to analyse the residual concentration of the MEHQ in the sample. Gel Permeation Chromatography (GPC, Shimadzu, Columnoven:CTO-6AS, Pump:LC-10AD) was also used to analyse the molecular weight of the sample. Results of GC and GPC analysis are summarized in Table 6 and Table 7 respectively. The sample which was used for the ARC measurement or taken during the ARC measurement were selected. The state of the sample is as follows: After 94 hours of ARC measurement at 90 ℃ under air conditions see (No.1), After 16 hours of ARC measurement at 113 ℃ under air conditions see (No.2), and after 48 hours of ARC measurement at 90 ℃ under nitrogen conditions see (No.3)

Table 6: Results of GC analysis

No.	Conditions	ARC Tempeature ℃	MEHQ concentration (ppm) at each time			
			0h	16h	48h	94h
1	Air	90				56
2	Air	113	94	72		
3	N2	90			※	

※The sample was polymerized.

Table 7: Results of GPC analysis

No.	Conditions	ARC Tempeature ℃	Molecular weight (as poly-St standard)			
			0h	16h	48h	94h
1	Air	90				178
2	Air	113	178※	178		
3	N2	90			※※	

※178 means monomer
※※About one million.

From the results of the GC, we found that the MEHQ remained after the ARC measurement with both of the samples under air conditions (No.1 and No.2). But we could not analyze under nitrogen condition sample (No.3) because of the polymerization.
From the results of the GPC, samples of No.1 and No.2 did not polymerize at all. It is confirmed that if a certain amount of the MEHQ remains, polymerization does not occur. On the other hand, sample No.3 was polymerized. Oxygen is necessary to prevent polymerizing. It is said that there is no reduction of MEHQ under nitrogen3), future analysis such as Liquid Chromatography (LC) etc. will be examined to reveal it.

3. Conclusion and future

Useful and interesting results were obtained from this work.
1) Effect of the concentration of MEHQ
The concentration of MEHQ is affect to DSC onset but almost constant calorific value was detected for any sample regardless of MEHQ concentration.
The polymerization induction period was extended by MEHQ at ARC measurement.
2) Effect of oxygen
We observed a sharp peak under air condition on DSC measurement. We assume that this is because of the monomer peroxide formation.
MEHQ cannot work efficiently without oxygen. The polymerization will occur with relatively slow speed during ARC measurement under shortage oxygen condition.
At a high temperature region, oxygen reacts with monomers to form monomer peroxide. Monomer peroxide decomposes and accelerates polymerization. MEHQ cannot work as an inhibitor efficiently at the high temperature region. We therefore decided to handle acrylic monomers in the low temperature region. To prevent polymerization, it is necessary to control the concentration of MEHQ and oxygen
Management of peroxide concentration is also important. Future studies will focus on the analysis of amount of the monomer peroxide. We also interested the relationship among monomer peroxide generation, oxygen concentration, and monomer structure.
We did not investigate the thermal stability of acrylic acid in detail because of its reactivity with metal in this paper. We also try to reveal them in the future.

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