

# A Study on Evaluation Methods for Preventing Recurrence of Accidents Involving Mixtures of Monomers and Initiators

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It is well known that radical polymerization reactions can release a large amount of energy. In recent years, unintended polymerization had progressed during storage and transportation, causing accidents. Therefore, chemical companies are examining evaluation methods. Since conventional thermal analysis equipment with temperature ramping measurements cannot adequately assess these monomers, a method using Polymerization Induction Time (PIT) obtained from isothermal measurements with high-sensitivity calorimeters is being established in recent years. However, these proposed methods target the evaluation of monomers alone. This study compared the results of isothermal measurements using a conventional high-sensitivity thermal analyzer and AKTS simulation analysis using DSC data for mixtures consisting of monomers, inhibitors, and initiators. The PIT estimation method by AKTS is a simpler method than the conventional isothermal method, but some samples were applicable while others were not. The difference is also discussed in terms of radical stability by computational chemistry.

## 1. Introduction

Thermally polymerizable substances are one of the polymer materials used to manufacture various everyday products and are highly useful substances, but they also have high potential energy. Therefore, it should be handled with care. In fact, an explosion of an acrylic acid storage tank (NIPPON SHOKUBAI, 2013) and an accident involving a container ship transporting divinylbenzene have been reported (Federal Bureau of Maritime Casualty Investigation, 2014). In 2017, regulations on thermally polymerizable substances were established under the UN transport recommendations, and the measurement of the Self-Accelerating Polymerization Temperature (SAPT) was made mandatory for transportation. Since SAPT testing requires large sample volumes and lengthy periods of time, previous studies have introduced a simpler evaluation method that shows a good correlation with SAPT. This method estimates the Polymerization Induction Time (PIT) using isothermal measurements with a high-sensitivity calorimeter (Min Sheng et al., 2019).

Additionally, it has been reported that the estimated PIT is influenced not only by temperature but also by factors such as dissolved oxygen, the concentration of polymerization inhibitors (Min Sheng et al., 2019).

On the other hand, in the polymer manufacturing process, to produce products with the desired functions, there are cases where various additives, including polymerization initiators, are pre-mixed with thermally polymerizable monomers in a mixing tank before being sent to the polymerization section. Attention must be paid to the fact that such mixtures exhibit different heat generation behaviour compared to pure thermally polymerizable monomers. In 2022, at one of our overseas affiliates, an incident occurred where a drum containing a mixed waste liquid of styrene and other substances ruptured. This mixed waste liquid contained not only monomers and polymerization inhibitors but also polymerization initiators. As a result of being stored outdoors in temperatures reaching around 40 °C, the waste liquid polymerized and underwent thermal runaway after about nine days. As part of the investigation into the cause of the accident, a simulation using the kinetic analysis software AKTS, based on DSC heating measurement data, was conducted. This successfully reproduced the conditions of the accident in the previous report. As a recurrence prevention measure for similar accidents, although it is suggested that the drums be managed at low temperatures, it's also necessary to evaluate a wide variety of combinations of different monomers, polymerization inhibitors, and initiators.

However, it takes a lot of time to conduct isothermal measurements using a high-sensitivity calorimeter for all brands. This study conducted a comparative analysis of isothermal measurements using a previous high-sensitivity calorimeter, along with the simpler evaluation methods of DSC measurements and AKTS simulation analysis, on mixtures of monomers, polymerization inhibitors and initiators.

## 2. Materials & experiment

### 2.1 Samples

The monomers used in the experiment were styrene(St), methyl methacrylate(MMA), glycidyl methacrylate(GMA) and methyl acrylate(MA). All of which were purchased from reagent manufacturers and used without further purification. The type of polymerization inhibitors used were 4-Methoxyphenol(MEHQ), 6-tert-Butyl-2,4-xlenol(6TBX), and 4-tert-Butylcatechol(TBC), with some added in a concentration range of 30 to 300 ppm. The initiators were t-Butyl peroxy-2-ethylhexanoate(PB-O) and di-t-butyl peroxide(PB-D), and the addition amount was fixed at 1 wt% for all samples. The atmosphere when placing the samples into the measurement cell was either air or nitrogen. Seven prepared samples are summarized in Table 1.

Table 1: List of prepared samples

No.	Monomer	Inhibitor		Initiator		Condition
		type	ppm	Type	%	
1	St	TBC	30	PB-O	1	Air
2				PB-D		
3	6TBX					
4	MMA	MEHQ	100			
5			GMA			
6			MA			
7						N <sub>2</sub>

### 2.2 Measurement conditions

Table 2: Measurement conditions

	DSC	C80
Sample mass [mg]	2	600
Crucible(cell) material	Stainless steel	Glass
Heat rate [°C/min]	0.5 to 8	- (isothermal)
Temp. range [°C]	30 to 300	70 to 100
Determination method of PIT	Isothermal prediction of AKTS (0.5% conversion point)	See below

The point at which the cell is inserted into C80 and measurements are started is defined as the PIT starting point, while the 0.5 % reaction point calculated from the average heat of reaction in the DSC measurement results is defined as the PIT endpoint. Examples of C80 measurement results and determination of the 0.5% reaction point are shown in Figure 1.

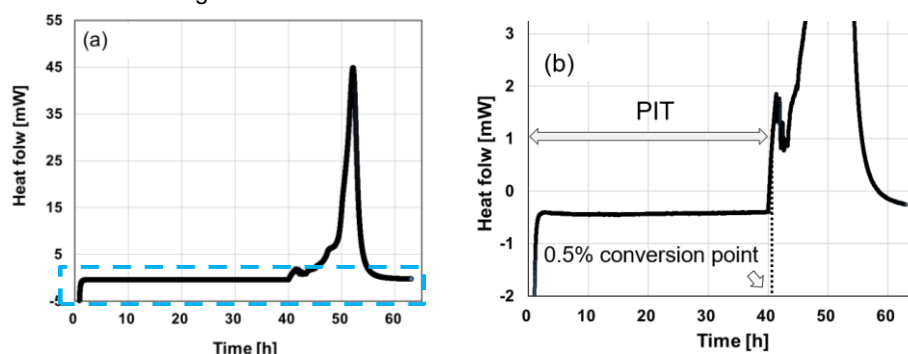


Figure 1(a): Examples of C80 measurement results (b): The area enclosed by the dashed line in (a) is enlarged.

### 3. Result and discussion

#### 3.1 DSC measurement and AKTS results

DSC measurements were performed under the conditions described above, and the average heat ( $Q_{AVE}$ ), standard deviation (SD), and  $SD/Q_{AVE}$  values were calculated by AKTS. They were summarized in Table 3. For No.1 (St, TBC, PB-O), the  $SD/Q_{AVE}$  is greater than 0.1, while for No.2 (St, TBC, PB-D), the  $SD/Q_{AVE}$  was 0.03. To confirm this difference, the details of the AKTS results were summarized in Table 4. For No.1 and No.2, their respective DSC charts were shown in Figures 2 (a) and (b). The half-life temperature of PB-O (10 hours half-life: 72.1 °C) is lower than that of PB-D (10 hours half-life: 123.7 °C), which manifest as a difference in the onset of the mixture (approximately 20 to 40 °C). Additionally, in No.1, the shape of the heat flow chart changed with the heating rate, showing that as the heating rate decreased, the heat generation tended to increase.

Table 3: Summarize of DSC measurement and AKTS results

No.	Monomer	Inhibitor		Initiator Type	R	$Q_{AVE}$ J/g	SD	$SD/Q_{AVE}$
		type	ppm					
1	St	TBC	30	PB-O	0.960	503.8	107.2	0.213
2					0.999	703.7	13.8	0.020
3					0.927	588.1	41.0	0.070
4	MMA	6TBX	100	PB-D	0.924	577.3	41.1	0.071
5	GMA				0.993	425.1	13.6	0.032
6	MA	MEHQ	300	PB-D	0.981	963.0	32.2	0.033
7					0.991	892.0	39.6	0.044

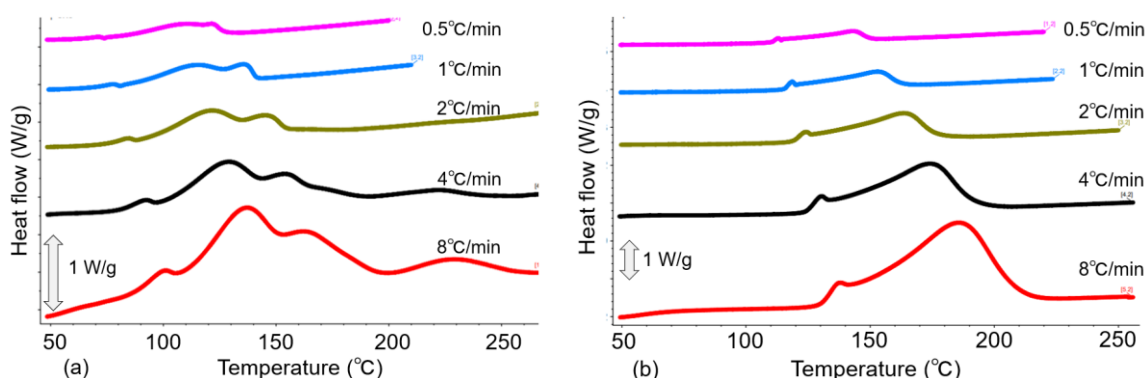


Figure 2: DSC chart of No.1 (a), and No.2 (b) respectively.

Table 4: AKTS results in detail

No.	8 °C /min		4 °C /min		2 °C /min		1 °C /min		0.5 °C /min	
	Onset °C	Q J/g	Onset °C	Q J/g	Onset °C	Q J/g	Onset °C	Q J/g	Onset °C	Q J/g
1	98.5	440.1	103.2	440.5	98.3	512.0	80.2	606.1	73.7	634.3
2	130.0	701.8	124.0	700.4	118.8	688.9	115.2	731.5	113.5	723.8

When polymerization is initiated using PB-O, the polymerization progresses from a lower temperature. Additionally, when the temperature is increased at a relatively fast rate, polymerization and thickening occur rapidly, hindering the diffusion of the monomer and polymerization inhibitors. Furthermore, the termination of polymer growth radicals by two molecules is inhibited, as is the termination of polymer growth radicals by polymerization inhibitors. These phenomena were referred to as the gel effect (Yu.L.Kuznetsova et al 2020), and it is presumed that the increased amount of unreacted monomer contributes to the variability in heat generation. According to the manufacturer's technical information, if the  $SD/Q_{AVE}$  is 0.1 or higher, the data is deemed unsuitable for use in AKTS. Therefore, No.1 was excluded from further evaluations, and PB-O was not used in combination with other monomers.

### 3.2 Comparison of AKTS Estimation Results and C80 Isothermal measurement results

From the literature by Min Sheng et al. assuming that the rate of consumption of the inhibitor at isothermal temperature is constant, the PIT can be shown in Equation (1)

$$\ln\left(\frac{1}{\text{PIT}}\right) = \ln(A_0) - \frac{E_a}{R} \frac{1}{T} \quad (1)$$

$$A_0 = \frac{A}{C_{\text{Inh}}} \quad (2)$$

PIT: min., preexponential factor A: 1/min., inhibitor concentration C: mol/L, activation energy  $E_a$ : J/mol

The PIT for each sample obtained from the C80 measurement was substituted into Equation (1) and plotted in Figure 3a with the inverse of temperature as the x-axis. The approximate equation for each plot, the activation energy ( $E_a$ ) calculated from the slope of the equation, and the activation energy obtained by AKTS estimation were summarized in Table 5. The activation energy of AKTS was set in the range of 0 to 0.5% reaction rate, which was the initial stage of the reaction. The activation energy of PB-D is 155 kJ/mol, which is relatively close for all samples in the C80 measurement. The activation energy calculated from AKTS for MMA as monomer, especially for No. 3, tended to be lower than that of PB-D. This may have affected the differences in each PIT, which will be discussed later.

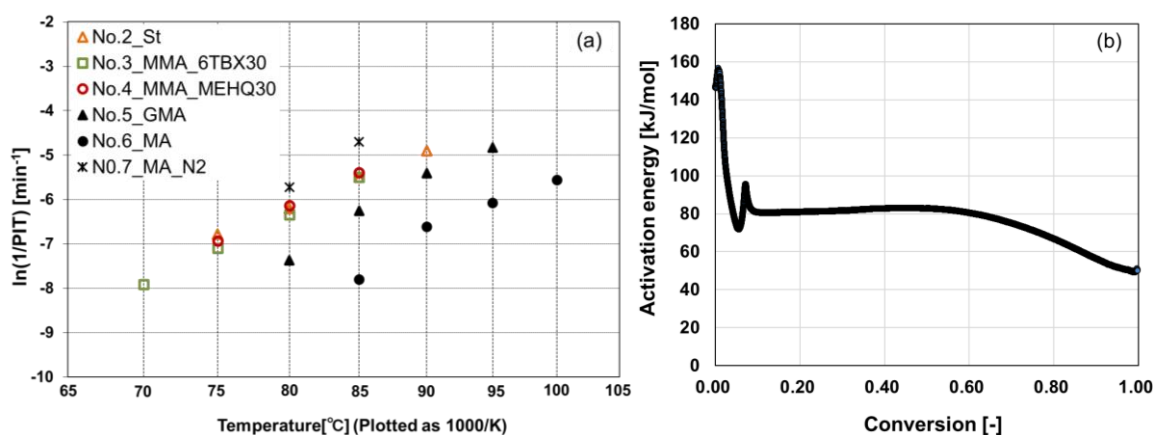


Figure 3: (a) plotted the PIT obtained from the C80 measurement substituted into Equation (1).  
(b) No. 2's conversion and activation energy calculated from AKTS.

Table 5: Summary of calculated activation energies

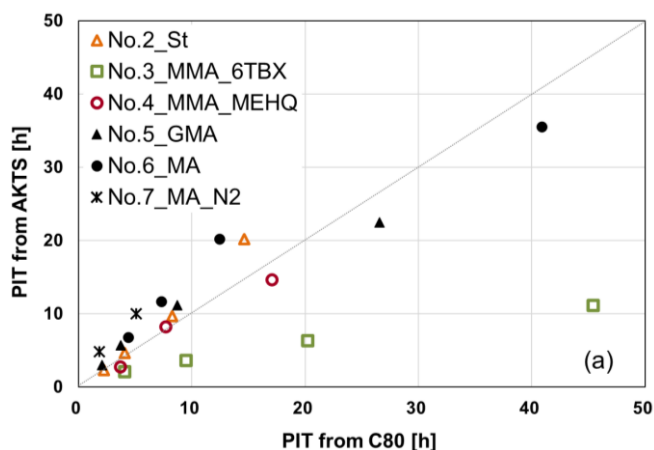
No.	Monomer	C80		AKTS
		Approximate equation	$E_a$ kJ/mol	Range* of $E_a$ kJ/mol
2	St	-15.979x + 39.092	132.8	146.6 to 155.0
3	MMA	-19.661x + 49.374	163.4	87.3 to 94.6
4		-19.142x + 48.056	159.1	112.6 to 115.2
5	GMA	-22.076x + 55.256	183.5	94.8 to 158.9
6	MA	-19.389x + 46.521	161.2	112.1 to 134.0
7		**		136.2 to 159.9

\*Conversion between 0 and 0.5%

\*\*Not calculated due to 2-point data

A plot of No. 2's conversion and activation energy calculated from AKTS is also shown in Figure 3b. The initial stage of the reaction was dominated by the influence of the initiator, with high activation energies, which gradually became lower as the reaction progressed. The activation energy of the styrene chain growth reaction is estimated to be about 33 kJ/mol (Masami Kamigaito, 2009), and it is assumed that the energy was close to that value. This trend was observed in all samples. The PIT obtained from each method is then compared.

Figure 4(a) shows comparison of the PIT from C80 and AKTS. Although some variability is observed, PIT from AKTS and C80 are approximately the same except No.3. Figure 4(b) is Table 6 summarizing the PIT results for No. 3 and No. 4 in detail. In PIT calculated from C80, No.3 tended to be longer than No.4. Generally, the lower the electron-donating property of phenolic inhibitors, the more effective they are as inhibitors, hence 6TBX > MEHQ is assumed (Ali Darvishi et al, 2019). On the other hand, the AKTS results were completely opposite. In addition, No.3's AKTS estimated PIT showed a linear correlation with the C80 isothermal measured PIT, it exhibited a shorter trend. This may be due to the smaller activation energy mentioned above. Figure 4(c) is a Table 7 summarizing the PIT results for No. 6 and No. 7. These results indicate that oxygen is necessary for the inhibitor to take effect even if an initiator is present (Sergio S. Cutie et al, 1996).



(b) Table 6: Summary of PIT for No.3,4

	C80		AKTS	
	No.3	No.4	No.3	No.4
75 °C	20.2	17.1	6.3	14.7
80 °C	9.5	7.7	3.6	8.3
85 °C	4.1	3.7	2.1	2.8

(c) Table 7: Summary of PIT for No.6,7 at 85 °C

	C80		AKTS	
	No.6	No.7	No.6	No.7
85 °C	40.9	1.8	45.6	4.9

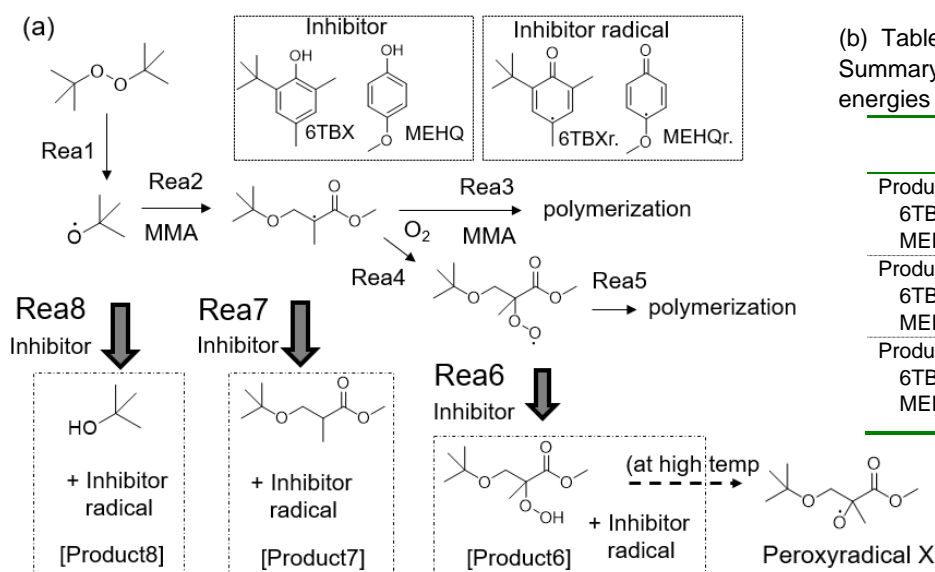
Figure 4: (a) Comparison of the PIT from the C80 and AKTS.

(b) Table 6 summarizing the PIT results for No. 3 and No. 4

(c) Table 7 summarizing the PIT results for No. 6 and No. 7 at 85 °C

### 3.3 Approach to Further Analysis Using Computational Chemistry

As showed in Figure 4(b), the strengths of inhibitors 6TBX and MEHQ in the C80 and AKTS results were exactly opposite. To consider these in more detail, an approach to analysis was implemented from the estimation of the stability of each radical by computational chemistry. Calculated reactions of No.3 or No.4 are shown in Figure 5(a). Rea1: Cleavage of initiator, Rea2: Addition of Rea1's product to monomer, Rea3: polymerization by Rea2's product, Rea4: Peroxidation of the Rea2's product, Rea5: polymerization of Rea4's product. Rea6: inhibition of Rea4's product, Rea7: inhibition of Rea2's product, Rea8: inhibition of Rea1's product. The stabilization energies for inhibition reaction for Product6,7 and 8 in Figure 5(a) were summarized in Table 8.



(b) Table 8  
Summary of stabilization energies for inhibition reaction.

	value kJ/mol
Product6 6TBXr. MEHQr.	-37.1 -33.9
Product7 6TBXr. MEHQr.	-52.3 -49.0
Product8 6TBXr. MEHQr.	-100.3 -97.0

Figure 5: (a) Calculated reaction of the No.3 or No.4.

(b) Table 8 summarizing the stabilization energies for inhibition reaction.

The calculation program used was Gaussian 16 B.01 (M.J. Frisch *et al*, 2016), and the calculation level was set to D3-B3LYP/6-31+G(d). The larger the negative value of the calculation result, the more stable the product is. The rate constants for inhibition reaction (Rea6,7,8) were summarized in Table 9.

Table 9: Summary of rate constants for inhibition reaction (/s)

	inhibitor	25 °C		100 °C		200 °C	
		Forward	Reverse	Forward	Reverse	Forward	Reverse
Rea6	6TBX	$2.0 \times 10^7$	$2.8 \times 10^3$	$3.8 \times 10^6$	$4.7 \times 10^3$	$9.8 \times 10^5$	$7.7 \times 10^3$
	MEHQ	$1.1 \times 10^8$	$5.8 \times 10^4$	$1.5 \times 10^7$	$4.8 \times 10^4$	$2.9 \times 10^6$	$4.3 \times 10^4$
Rea7	6TBX	$3.4 \times 10^1$	$1.9 \times 10^{-8}$	$3.9 \times 10^1$	$2.5 \times 10^{-6}$	$4.5 \times 10^1$	$1.6 \times 10^{-4}$
	MEHQ	$2.3 \times 10^2$	$4.8 \times 10^{-7}$	$5.5 \times 10^2$	$9.1 \times 10^{-5}$	$1.2 \times 10^3$	$7.7 \times 10^{-3}$
Rea8	6TBX	$1.9 \times 10^{11}$	$5.1 \times 10^{-7}$	$7.6 \times 10^9$	$8.3 \times 10^{-5}$	$5.3 \times 10^8$	$6.3 \times 10^{-3}$
	MEHQ	$6.2 \times 10^{12}$	$2.2 \times 10^{-4}$	$9.0 \times 10^{11}$	$2.5 \times 10^{-2}$	$6.2 \times 10^{10}$	$1.4 \times 10^0$

As shown in the Table 9, the rate constants of 6TBX were smaller than those of MEHQ in all three reactions at all temperature range. A similar trend was observed in the reverse reaction. And as summarized in Table 8, the stability of the reaction products was higher for 6TBX. Therefore, 6TBX were less likely to be inactivated. AKTS results of No.3 was not explained by any of the calculations in this study. At high temperatures, product 6 is known to decompose to per oxyradical X. The difference in reactivity of the inhibitor to per oxyradical X may have an effect. Comparing the results of Rea6 and 7, Rea6 is by far the faster. It indicated that even in 6TBX that didn't need oxygen, the inhibitor was more effective in the presence of oxygen.

#### 4. Conclusions

As a simpler method for determining the PIT of mixtures of monomers, initiators, and inhibitors, the AKTS method was attempted. When PB-D was used as the initiator, it was found that the PIT estimation method using AKTS could be applied. Considering the electron donation and C80 measurements confirm that 6TBX was more effective than MEHQ as an inhibitor, but AKTS results were the opposite totally. It should be noted that the case of 6TBX can be overestimated in AKTS estimation. Alternatively, it is possible that per oxyradical X, which is not calculated in this study, is involved in the reaction during the temperature increase process. As well as the gel effect, this effect would be one of the factors affecting the applicability of the PIT estimation method by AKTS. More details will be discussed in the future.

#### Acknowledgements

This research was accomplished with significant support from colleagues and other departments. We thank all of them.

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