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THERMAL RUNAWAY EVALUATION OF α-METHYLSTYRENE AND *TRANS*-β-METHYLSTYRENE WITH BENZALDEHYDE

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Styrene is an important chemical in the petrochemical industry. In recent years, there have been sporadic releases, runaway reactions, fires, and thermal explosion accidents incurred by styrene and its derivatives worldwide. The purpose of this study was to estimate the impact of styrene and its derivatives of α-methylstyrene (AMS) and *trans*-β-methylstyrene (TBMS) contacting with benzaldehyde. Experiments were carried out to evaluate the thermokinetic parameters estimated by differential scanning calorimetry (DSC) and thermal activity monitor III (TAM III). TAM III was used to determine the fundamental thermokinetics under various isothermal temperatures, 80, 90 and 100°C. This autocatalytic reaction was demonstrated in thermal curves. After styrene was contacted with benzaldehyde, the exothermic onset temperature (T_0) and the total heat of reaction (Q_{total}) were altered by DSC tests. When benzaldehyde is mixed with AMS and TBMS, the reaction time will be shorter but the enthalpy reduced, as revealed by TAM III tests.

As AMS and TBMS, respectively, were contacted with benzaldehyde, both exothermic phenomena were changed during the reaction excursion. According to the results of this research, an operator should dictate the oxygen concentration in order to avoid any potential hazards during handling and transportation.

Keywords: *benzaldehyde, DSC,* α*-methylstyrene (AMS), thermal activity monitor III (TAM III), trans-*β*-methylstyrene (TBMS)*

Introduction

Organic peroxides (OPs) have caused many monumental explosions and runaway reactions, resulting from thermal instability, chemical pollutants, and even mechanical shock [1, 2]. Styrene is most broadly employed to produce polymerization materials, such as homopolystyrene, styrene–butadiene elastomers, acrylonitrile–butadiene–styrene terpolymers (ABS), unsaturated polyesters (UP), and emulsion polymers (EP) [3]. In Taiwan, in the petrochemical industry, styrene and its derivatives, α-methylstyrene (AMS) and *trans*-β-methylstyrene (TBMS), are more and more important with substantial consumption annually in Taiwan as displayed in Table 1 [4, 5].

From previous literature, in storage and transportation, styrene, AMS and TBMS, are normally added 10–30 ppm 4-*t*-butylcatechol (TBC) as an inhibitor. TBC is adding to increase its stability and decrease reactive activity at the same time [6]. If insufficient TBC was added, styrene, AMS and TBMS were oxidized to produce benzaldehyde, as shown in Fig. 1 [7]. If AMS and TBMS contact benzaldehyde in the operating process, storage and transportation was change of dimerization and thermal polymerization of exothermic phenomenon [8, 9].

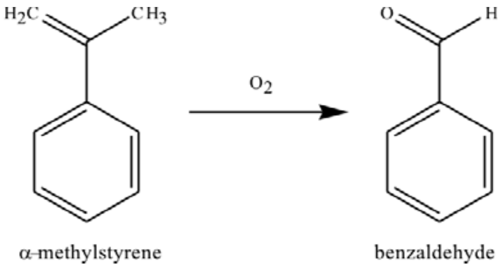

Fig. 1 α-Methylstyrene combined with O_2 to become benzaldehyde

Experimental

Samples

Analytical grade benzaldehyde (Sigma-Aldrich, with 99 mass%), C_6H_5CHO, M.W. 106.13 (g mol^{-1}), CAS: 100-52-7. AMS (Sigma-Aldrich, with 99 mass%), $C_6H_5C(CH_3)CH_2$, M.W. 118.18 (g mol^{-1}), CAS:

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Table 1 Annual throughput and demand for styrene in Taiwan between 2001 and 2005 (tons)

	2001	2002	2003	2004	2005
Domestic	1 146 140	1 249 184	1 274 113	1 247 194	1 248 492
Import	537 829	462 795	519 285	606 738	572 544
Export	5 731	40 349	72 704	51 888	70 854
Demand	1 678 238	1 671 630	1 720 694	1 802 044	1 750 182

98-83-9. TBMS (Sigma-Aldrich, with 99 mass%), $C_6H_5CHCHCH_3$, M.W. 118.18 (g mol^{-1}), CAS: 873-66-5.

Equipment

Differential scanning calorimetry (DSC)

To estimate the kinetics of thermal decomposition, dynamic screening experiments were performed on a Mettler TA8000 system coupled with a DSC 821^e [10, 11]. The scanning temperature rate was chosen to be 4°C min^{-1} [12, 13].

Thermal activity monitor III (TAM III)

Sample was dispensed into a disposable calorimetric glass and stainless containers, capped and then placed in the measuring and reference chambers, respectively. Measurements were conducted isothermally at 80, 90 and 100°C [14].

Results and discussion

DSC

- When AMS was combined with benzaldehyde, its dimerization process (1st peak) showed that exothermic onset temperatures (T_0) and exothermic peak temperature were diminished. Similarly, the total amount of exothermic heat (Q_{total}) was lessened to ca. 105.0 J g^{-1}, as shown in Table 2 and Fig. 2.
- In Table 2 and Fig. 2, the thermal polymerization process (2nd peak) revealed that T_0 was lessened from 360.2 to 276.2°C, whereas Q_{total} was enhanced from 284.3 to 389.3 J g^{-1}, along with a decrease of the exothermic peak temperature.
- As AMS was mixed with benzaldehyde, Q_{total} was augmented to ca. 105 J g^{-1}.
- After TBMS was combined with benzaldehyde, T_0 and Q_{total} were increased, but thermal polymerization T_0 and reaction heat that were corresponding to the dimerization process were both reduced, as demonstrated in Table 3 and Fig. 3.

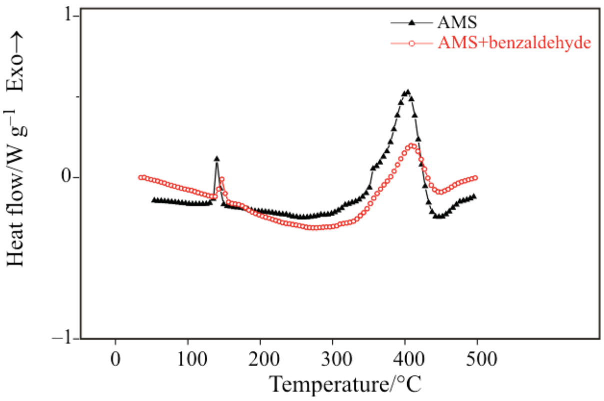

Fig. 2 Comparisons of dimerization and thermal polymerization curves of AMS and AMS with benzaldehyde by DSC tests

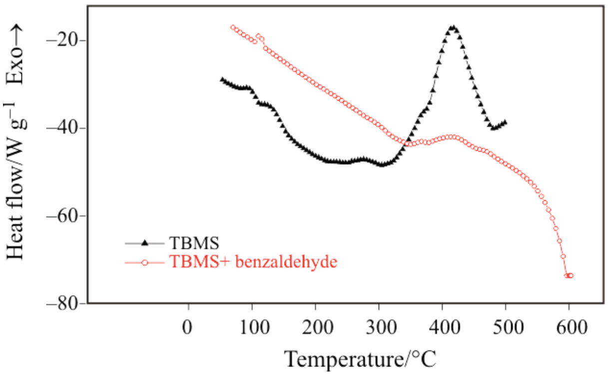

Fig. 3 Comparisons of dimerization and thermal polymerization curves of TBMS and TBMS with benzaldehyde by DSC tests

TAM III

- Under equilibrium conditions, we calculated the exothermal reaction under 80, 90 and 100°C isothermal temperature for the chemicals of interest. Through experiments, TAM III was employed to determine the thermokinetic and safety index of AMS and TBMS mixed with benzaldehyde [15], respectively. According to Tables 4 and 5 and Figs 4–7, when AMS and TBMS contacted benzaldehyde, its time to peak temperature, reaction time and reaction heat clearly decreased.
- Benzaldehyde could affect AMS and TBMS. Reaction heat was decreased, but it induced AMS

Table 2 Comparisons of dimerization and thermal polymerization curves for AMS and AMS with benzaldehyde by DSC tests

Sample	Mass/ mg	Dimerization			Thermal polymerization			Total amount of exothermic heat, Q_{total}/J g^{-1}
		Exothermic onset temperature, T_0/°C	Reaction heat, ΔH/ J g^{-1}	Exothermic peak temperature, T_{max}/°C	Exothermic onset temperature, T_0/°C	Reaction heat, ΔH/ J g^{-1}	Exothermic peak temperature, T_{max}/°C	
AMS	6.85	138.2	19.5	142.2	360.2	264.8	405.8	284.3
AMS+benzaldehyde	4.48	124.9	19.1	126.8	276.2	370.2	393.4	389.3

Table 3 Comparisons of dimerization and thermal polymerization curves for TBMS and TBMS with benzaldehyde by DSC tests

Sample	Mass/ mg	Dimerization			Thermal polymerization			Total amount of exothermic heat, Q_{total}/J g^{-1}
		Exothermic onset temperature, T_0/°C	Reaction heat, ΔH/ J g^{-1}	Exothermic peak temperature, T_{max}/°C	Exothermic onset temperature, T_0/°C	Reaction heat, ΔH/ J g^{-1}	Exothermic peak temperature, T_{max}/°C	
TMBS	5.04	89.7	42.6	109.0	388.5	349.3	439.9	291.9
TMBS+benzaldehyde	5.10	108.9	17.1	112.3	352.7	221.6	221.6	333.9

Table 4 Heat flow *vs.* time for polymerization of 99 mass% AMS with benzaldehyde under various isothermal conditions (80, 90 and 100°C) by TAM III test

Sample	Mass/ g	Vessel	Temperature/ °C	Time to peak temperature/h	Reaction time/h	Heat of decomposition/ J g^{-1}
AMS	–	Glass	80	–	–	–
AMS	0.2696	Glass	80	1.9	5.3	10.9
Benzaldehyde	0.3264					
AMS	0.5440	Glass	90	11.2	20.1	15.3
AMS	0.2710	Glass	90	1.2	2.4	10.3
Benzaldehyde	0.3225					
AMS	0.5296	Glass	100	4.9	8.4	16.0
AMS	0.2731	Glass	100	1.0	2.0	7.4
Benzaldehyde	0.3181					

Table 5 Heat flow *vs.* time for polymerization of 99 mass% TBMS with benzaldehyde under various isothermal conditions (80, 90 and 100°C) by TAM III test

Sample	Mass/ g	Vessel	Temperature/ °C	Time to peak temperature/h	Reaction time/h	Heat of decomposition/ J g^{-1}
TBMS	0.5363	Glass	80	1.9	12.3	20.5
TBMS	0.2776	Glass	80	2.3	8.3	19.1
Benzaldehyde	0.3215					
TBMS	0.5435	Glass	90	1.8	8.5	24.7
TBMS	0.2736	Glass	90	1.4	7.3	14.2
Benzaldehyde	0.3259					
TBMS	0.5378	Glass	100	1.3	5.3	23.3
TBMS	0.2766	Glass	100	1.2	4.9	12.6
Benzaldehyde	0.3207					

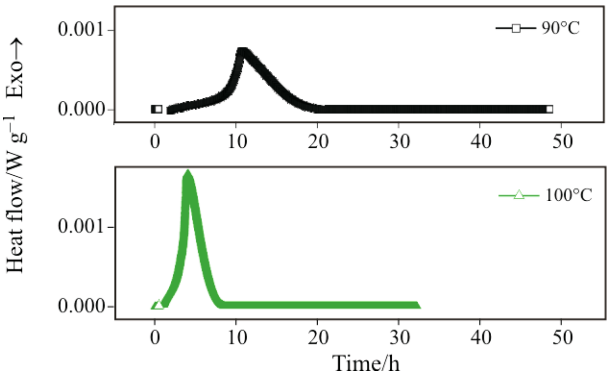

Fig. 4 Heat flow *vs.* time for polymerization of 99 mass% AMS under various isothermal conditions (90 and 100°C) by TAM III tests

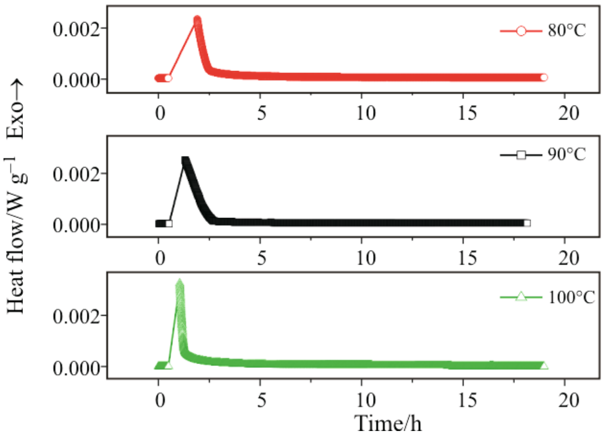

Fig. 5 Heat flow *vs.* time for polymerization of 99 mass% AMS with benzaldehyde under various isothermal conditions (80, 90 and 100°C) by TAM III tests

and TBMS to accelerate an exothermic reaction with shorter excursion time. In summary, the exothermic characteristics have potential thermal hazards in the polymerization process.

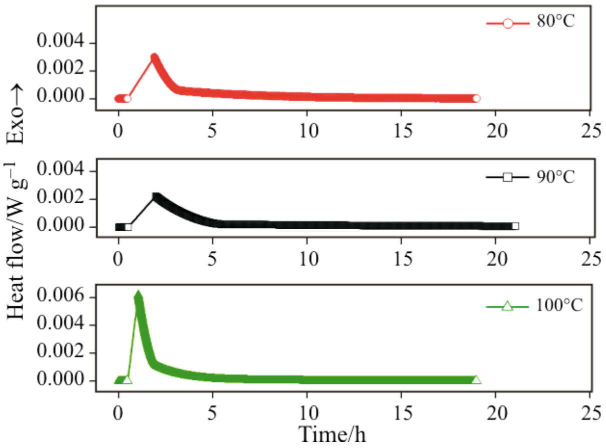

Fig. 6 Heat flow *vs.* time for polymerization of 99 mass% TBMS under various isothermal conditions (80, 90 and 100°C) by TAM III tests

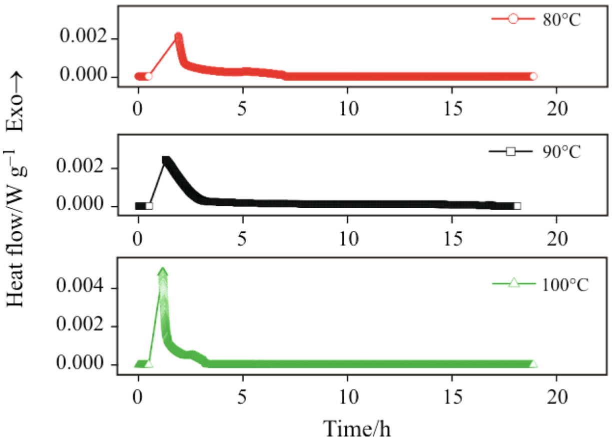

Fig. 7 Heat flow *vs.* time for polymerization of 99 mass% TBMS with benzaldehyde under various isothermal conditions (80, 90 and 100°C) by TAM III tests

Conclusions

In DSC tests, the contact of AMS or TBMS with benzaldehyde changed its exothermicity. The total exothermic reaction heat also increased, but this value did not reach a hazardous material level. In TAM III tests, time to peak temperature, reaction time and reaction heat for AMS and TBMS individually mixed with benzaldehyde were reduced. In a process, when AMS and TBMS are contacted with benzaldehyde, one must be careful of its reaction heat.

Through a series of DSC and TAM III tests, dosing benzaldehyde to AMS or TBMS individually will not significantly affect its thermal hazards under a reaction process, but care must be paid to the change of the exothermicity.

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