A comprehensive analysis for styrene and its derivatives by calorimeters and spectrometers

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Syllabus

- Introduction
- Literature reviews
- Experiments
- Results and discussion
- Conclusions
- Recommendations
- Publications
- Future Prospects
- Acknowledgements
Styrene:

1. Characteristics.  
3. Purpose.

Global outturn:

1. Asia.  
2. Europe.  
3. USA.

Fig. 1. Various high economic products derived from styrene.
The main causes of accident incurred by styrene, derivatives, and its isomers were external and internally unsafe acts in Asia, Europe, and USA, as follows:

1. Human.                                        2. Equipment.
Introduction (3/5)

- **α-Methylstyrene (AMS).**

- **Trans-β-methylstyrene (TBMS).**

The aim of this study was to:
1. estimate thermokinetics parameters and identify polymerization mechanisms;
2. apply practical polymerization process; and
3. alleviate individual thermal hazard of accident occurrence to an acceptable level.

Fig. 2. α-Methylstyrene (AMS).

Fig. 3. Trans-β-methylstyrene (TBMS).
Fig. 4. The flowchart of manufacturing process on AMS.
Introduction (5/5)

Fig. 5. The flowchart of experimental procedure.

Selected accidents occurred in Asia, Europe, and USA

Styrene containing 4-tert-butylcatechol (TBC)
Blast furnace
Nuclear magnetic resonance spectrometer (NMR)
Fourier transform infrared absorption spectrophotometer (FT-IR)

Thermokinetic parameters estimation and polymerization mechanisms identification

Thermal activity monitor (TAM)
Differential scanning calorimetry (DSC)

α-Methylstyrene (AMS)
Trans-β-methylstyrene (TBMS)
Ortho-methylstyrene (OMS)
Meta-methylstyrene (MMS)
Para-methylstyrene (PMS)

Styrene

Fourier transform infrared absorption spectrophotometer (FT-IR)
Nuclear magnetic resonance spectrometer (NMR)
Fig. 6. Historical background on styrene development.
Fig. 7. Historical background on $\alpha$-methylstyrene, trans-$\beta$-methylstyrene, and its isomers development.
1. Differential scanning calorimetry (DSC)

- **Method** – The dynamic screening experiment performed on a Mettler TA 8000 system coupled with a DSC821e cell.

- **Conditions** – For the sake of better thermal equilibrium, the scanning rate for the temperature-programmed ramp was chosen to be 4 °C/min.

- **Obtained data** – Exothermic onset temperature, isothermal heat flow, enthalpy, etc.

2. Thermal activity monitor (TAM)

- **Method** – Sample were dispensed into the disposable calorimetric glass and stainless contains, capped and then respectively placed in the measuring and reference chambers.

- **Conditions** – Measurements were conducted isothermally in the temperature range from 12 to 90°C.

- **Obtained data** – Heat power, enthalpy, isothermal time to maximum rate, etc.
3. Fourier transform infrared absorption spectrophotometer (FT-IR)

Fig. 10. Fourier transform infrared absorption spectrophotometer.

In infrared spectroscopy, FT-IR radiation passes through a sample, which results in vibration transitions in functional groups.

The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample for spectroscopic identification.

4. Nuclear magnetic resonance spectrometer (NMR)

Fig. 11. Nuclear magnetic resonance spectrometer.

The solution NMR spectrum was obtained on a varian GEMINI 300 spectrometer, the solution spectra were obtained in quantitative conditions.

All solid state spectra were obtained on a varian INOVA 300 spectrometer.
Fig. 12. Comparisons of dimerization and thermal polymerization curves of styrene, styrene containing 10 ppm TBC, AMS, and TBMS by DSC tests.
Fig. 13. The flowchart for inhibition behavior by TBC.
Fig. 14. Comparisons of dimerization and thermal polymerization curves of OMS, MMS, and PMS by DSC tests.

Ortho-methylstyrene
950207
3.9000 mg
Integral 400.33 J/g

Meta-methylstyrene
950208
3.0000 mg
Integral 463.92 J/g

Para-methylstyrene
950209
4.2000 mg
Integral 327.65 J/g

Results and discussion (3/17)
Fig. 15. The energy level of resonance form on OMS, MMS, and PMS.
|                | Exothermic peak temperature
<table>
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<tr>
<td></td>
<td>(T&lt;sub&gt;max&lt;/sub&gt;, °C)</td>
</tr>
<tr>
<td><strong>Exothermic peak temperature (T&lt;sub&gt;max&lt;/sub&gt;, °C)</strong></td>
<td><strong>Reaction heat (ΔH, J/g)</strong></td>
</tr>
<tr>
<td><strong>Total exothermic amount (Q&lt;sub&gt;total&lt;/sub&gt;, J/g)</strong></td>
<td></td>
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**Results and discussion (5/17)**

<table>
<thead>
<tr>
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<th>Thermal polymerization</th>
<th>Dimerization</th>
<th>Total exothermic amount (Q&lt;sub&gt;total&lt;/sub&gt;, J/g)</th>
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<tr>
<td><strong>Exothermic onset temperature (T&lt;sub&gt;0&lt;/sub&gt;, °C)</strong></td>
<td><strong>Reaction heat (ΔH, J/g)</strong></td>
<td><strong>Exothermic peak temperature (T&lt;sub&gt;max&lt;/sub&gt;, °C)</strong></td>
<td><strong>Exothermic onset temperature (T&lt;sub&gt;0&lt;/sub&gt;, °C)</strong></td>
</tr>
<tr>
<td>Styrene</td>
<td>104.60</td>
<td>600.44</td>
<td>205.82</td>
</tr>
<tr>
<td>Styrene containing 10 ppm TBC</td>
<td>134.05</td>
<td>601.74</td>
<td>204.53</td>
</tr>
<tr>
<td>α-Methylstyrene</td>
<td>138.20</td>
<td>19.48</td>
<td>142.18</td>
</tr>
<tr>
<td>Trans-β-methylstyrene</td>
<td>89.65</td>
<td>42.60</td>
<td>109.00</td>
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<tr>
<td>o-Methylstyrene</td>
<td>201.64</td>
<td>369.95</td>
<td>206.82</td>
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<tr>
<td>m-Methylstyrene</td>
<td>184.35</td>
<td>447.42</td>
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<tr>
<td>p-Methylstyrene</td>
<td>140.06</td>
<td>285.11</td>
<td>147.83</td>
</tr>
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</table>

**Fig. 16.** The dynamic scanning data for styrene, styrene containing 10 ppm TBC, AMS, and TBMS.
Fig. 17. Comparison of polymerization curves of 2-chlorostyrene, 2,3,4,5,6-pentafluoro styrene, styrene, and styrene-D8.
Results and discussion (7/17)

Fig. 18. Heat power vs. time for polymerization of 99 wt% AMS under various isothermal conditions by TAM tests.
Fig. 19. Heat power vs. time for polymerization of 99 wt% TBMS under various isothermal conditions.
Fig. 20. The blast furnace tests on AMS and TBMS (1).
Diels-Alder reaction and Retro-Diels-Alder reaction, dimerization.

Free radical reaction, unsaturated and saturated dimer, thermal polymerization.

Initial reaction of styrene.

Fig. 21. Infrared absorption spectra of polymerization of AMS conducted by FT–IR.

Fig. 22. Infrared absorption spectra of polymerization of TBMS conducted by FT–IR.
Fig. 23. Nuclear magnetic resonance spectra of polymerization of AMS tested by NMR.

Fig. 24. Nuclear magnetic resonance spectra of polymerization of TBMS tested by NMR.
Fig. 25. The flowchart for dimerization on AMS.

Fig. 26. The flowchart for dimerization on TBMS.
Fig. 27. The blast furnace tests on AMS and TBMS (2).
Fig. 28. Estimation of the polymerization mechanisms on AMS.
Fig. 29. Estimation of the polymerization mechanisms on TBMS.
1. Reaction order:

\[ R = -\frac{d[A]}{dt} = -k[A]^{2.5} \]

\[ -kt = \frac{2}{3} \{ [A]^{3} - [A_0]^{3} \} \]

2. Reaction rate constant:

\[ k = \text{slope} = 0.0619 \, \text{(1/day)} \]

\[ = 7.16 \times 10^{-7} \, \text{(1/sec)} \]

<table>
<thead>
<tr>
<th>Reaction period (day)</th>
<th>Heat value alteration (Q)</th>
<th>Concentrations alteration (M)</th>
<th>Concentrations alteration (M)</th>
<th>- k t=2/3 { [A]^{3/2} - [A_0]^{3/2} }</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>670</td>
<td>8.700000000</td>
<td>[A]_0</td>
<td>0</td>
</tr>
<tr>
<td>0.001</td>
<td>607</td>
<td>7.881940299</td>
<td>[A]_0</td>
<td>0.0041477734</td>
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<tr>
<td>0.500</td>
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<td>[A]_0,5</td>
<td>0.0125711625</td>
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<td>0.0079282118</td>
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<tr>
<td>1.000</td>
<td>454</td>
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<td>0.0205961370</td>
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<tr>
<td>1.010</td>
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<td>0.0527282330</td>
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<td>1.501</td>
<td>329</td>
<td>4.272089553</td>
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<td>2.000</td>
<td>212</td>
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<td>0.1199820409</td>
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<td>2.010</td>
<td>185</td>
<td>2.402238806</td>
<td>[A]_2,0</td>
<td>0.1530747393</td>
</tr>
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</table>

\[ y = 0.0619x - 0.0177 \quad R^2 = 0.7812 \]
2. Frequency factor:

\[ k = A \times e^{-\frac{E_a}{RT}} \]

(1) \[ E_{a1} = 67 \text{ (kJ/mol)} \]
\[ 7.16 \times 10^{-7} = A \times e^{-\frac{67000}{8.314(273+70)}} \]
\[ A = 1.22 \times 10^4 \text{ (1/sec)} \]

(2) \[ E_{a2} = 84 \text{ (kJ/mol)} \]
\[ 7.16 \times 10^{-7} = A \times e^{-\frac{84000}{8.314(273+70)}} \]
\[ A = 4.76 \times 10^6 \text{ (1/sec)} \]
Conclusions

- The thermal curves on AMS and TBMS both showed *dimerization* and *thermal polymerization* under dynamic scanning tests by DSC.

- The initiation was triggered by *Diels-Alder reaction* from the *dimerization* of two AMS and two TBMS, respectively.

- A mechanism of the thermal initiation process was also proposed and was similar to the mechanism for the *thermal polymerization of styrene* suggested by *Mayo, 1960*.

- Through this study, *isomers* of different organic peroxides can be applied to have related *polymerization mechanisms* and *thermal hazard estimations*. 
Recommendations

- To identify the *critical reaction step* dominated with the dimerization by different substitutes, such as *bromine*, with functional group approaches.

- From results gained by this investigation, the basis to acquire the related kinetic parameters could be adequately *designed, established, implemented* and *evaluated* to a deeper extent.
Future Prospects

Thermal Analysis

Material Engineering

Chemical Engineering

HC

CH

CH3

C

HC

CH2

CH

HC

CH2

CH3

HC

CH2

CH3
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Thank you for your attention!