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COMPARISON OF THERMAL POLYMERIZATION MECHANISMS FOR α-METHYLSTYRENE AND *trans*-β-METHYLSTYRENE

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The polymerization mechanisms of styrene and various derivatives by α-methylstyrene (AMS) and *trans*-β-methylstyrene (TBMS) were evaluated. Experiments were carried out for dimerization identification and thermal polymerization estimation by differential scanning calorimetry (DSC), thermal activity monitor (TAM) and Fourier transform infrared absorption spectrophotometer (FTIR). The results show that, under temperature ranges of 60–190 and 50–170°C, AMS and TBMS performed dimerization by benzene ring and ethylene double bond, respectively. AMS and TBMS would form unsaturated dimers, saturated dimers and trimers, etc., during the period of thermal polymerization. Through this study, one can estimate possible intermediates of the polymerization process for the monomer of interest in the petrochemical industry.

Keywords: *α-methylstyrene (AMS), differential scanning calorimetry (DSC), Fourier transform infrared absorption spectrophotometry (FTIR), thermal activity monitor (TAM), trans-β-methylstyrene (TBMS)*

Introduction

Styrene is most widely used to produce acrylonitrile-butadiene-styrene (ABS), polystyrene (PS), styrene-acrylonitrile (SAN), styrene-butadiene rubber (SBR) and other engineering plastics in the petrochemical industry. During production, 4-*tert*-butylcatechol (TBC) as an inhibitor is added to increase its stability and decrease reactive activity at the same time. This study conducted thermal polymerization on styrene influenced by the existence of TBC. For the operating safety goal, inhibited styrene was used to replace uninhibited styrene in process units and also in storage or transportation [1, 2]. From previous literature [3, 4], we can recognize that styrene has had arguments on initial reaction and reaction order (*n*). Identifying the dimerization of styrene would be a solution for initial reaction and reaction order. According to our previous study [5], we identified dimerization mechanisms of styrene by α-methylstyrene (AMS). This study investigated the differences of dimerization and thermal polymerization of AMS and *trans*-β-methylstyrene (TBMS) under dynamic conditions. Furthermore, this study could also be applied in polymerization processes to assess dangerous intermediates in the process industries during reaction. For another, styrene was oxidized to become formaldehyde, if the styrene contact formaldehyde in the process was changing this exothermic phenomenon.

Experimental

Samples

Analytical grade styrene monomer was purchased from Fluka Co.: Styrene, C8H8, M.W. 104.15, CAS: 00100-42-5; the styrene monomer must be stored at 0–4°C. Formaldehyde (J. T. Baker Co.) was used for DSC. HCHO, 37 mass% solution, M.W. 30.03 g $\mathrm{mol^{-1}}$, CAS. 50-00-0. Pure AMS and TBMS (Sigma-Aldrich, with 99 mass%) were used for a series of calorimetric and spectrometric experiments. AMS, $C_6H_5C(CH_3)CH_2$, M.W. 118.18 g $\mathrm{mol^{-1}}$, CAS: 98-83-9, is a colorless liquid with a melting point of –24°C. TBMS, $C_6H_5CHCHCH_3$, M.W. 118.18 g $\mathrm{mol^{-1}}$, CAS: 873-66-5, is a colorless liquid.

Equipment

Differential scanning calorimetery (DSC)

For estimating the kinetics of thermal decomposition, dynamic screening experiments were performed on a Mettler TA8000 system coupled with a DSC 821^e. The scanning temperature rate was chosen to be 4°C $\mathrm{min^{-1}}$.

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Thermal activity monitor (TAM)

Samples were dispensed into disposable calorimetric glass and stainless containers, capped and then respectively placed in the measuring and reference chambers. Measurements were conducted isothermally in the temperatures from 50, 70 and 90°C.

Fourier transform infrared absorption spectrophotometer (FTIR)

In infrared spectroscopy, FTIR 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.

Results and dicussion

Dimerization identification

From previous literature and our experimental results, we obtained comprehensive dimerization mechanisms of AMS and TBMS, as follows:

- A potential reaction (or initial reaction) in the thermal curves of AMS and TBMS by DSC, as shown in Fig. 1. Both AMS and TBMS had dimerization (1st peak) under temperature ranges, 60–190 and 50–170°C, respectively. The reaction heats (ΔH) were 19.48 and 42.60 J g^{-1} for AMS and TBMS, respectively, as displayed in Tables 1 and 2.
- The derivatives of styrene are AMS and TBMS; they can be oxidized to produce formaldehyde, which could inhibit the exothermal reaction for the styrene and its derivatives (para-methylstyrene, meta-methylstyrene, ortho-methylstyrene). SM, AMS, and TBMS spiked formaldehyde are shown in Figs 2–4. Exothermic onset temperature (T_0), ΔH and exothermic peak temperature decreased, as listed in Tables 3–5.
- As first formulated by Mayo, a dominant Diels–Alder reaction between two styrene molecules leads to a semi-benzene dimer. In pure

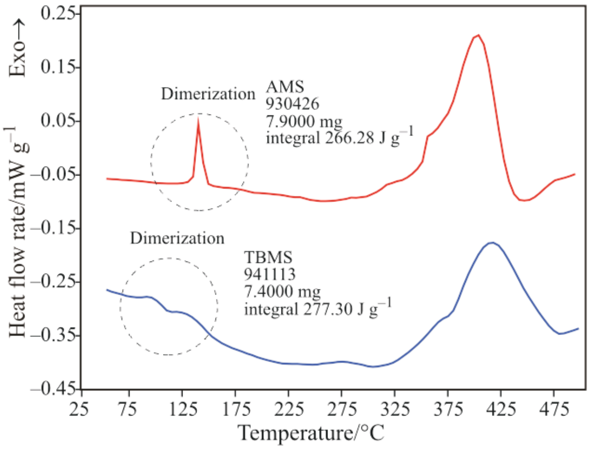

Fig. 1 Thermal curves (1st peak) of dynamic scanning of AMS and TBMS by DSC tests

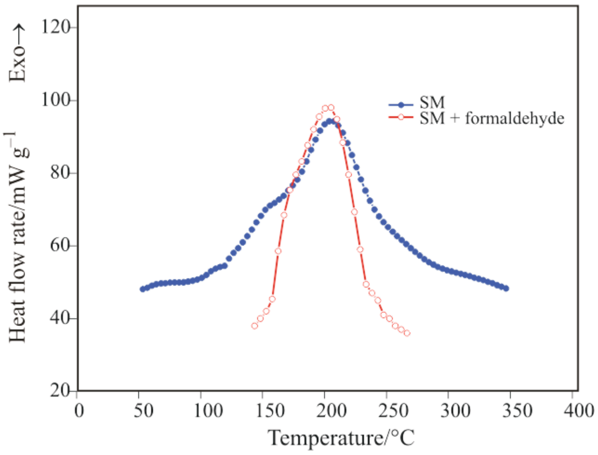

Fig. 2 Thermal curves of dynamic scanning of SM and SM with formaldehyde by DSC tests

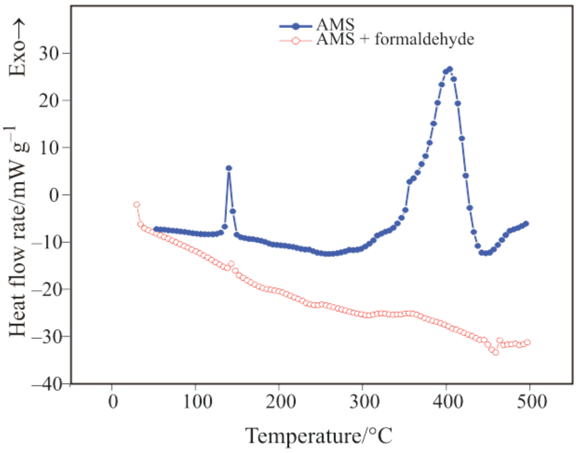

Fig. 3 Thermal curves of dynamic scanning of AMS and AMS with formaldehyde by DSC tests

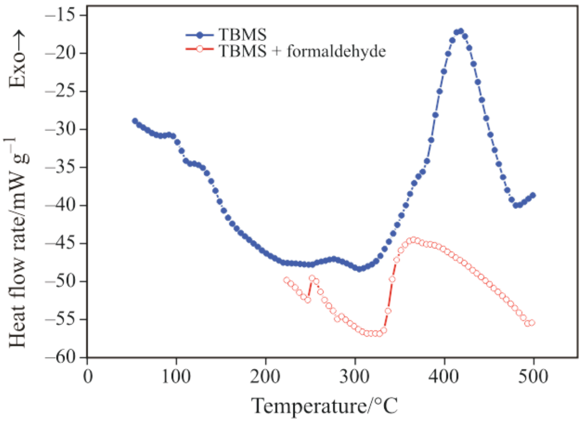

Fig. 4 Thermal curves of dynamic scanning of TBMS and TBMS with formaldehyde by DSC tests

Table 1 Experimental data on dynamic scanning of AMS by DSC tests

Sample mass/mg	Dimerization			Thermal polymerization			Total amount of exothermic heat Q_{total}/J g^{-1}
	Exothermic onset temp., T_0/°C	Reaction heat ΔH/J g^{-1}	Exothermic peak temp., T_{max}/°C	Exothermic onset temp., T_0/°C	Reaction heat ΔH/J g^{-1}	Exothermic peak temp., T_{max}/°C	
7.70	139.14	13.06	143.01	360.81	269.76	405.59	282.82
6.80	138.84	22.15	142.41	360.88	256.36	406.20	278.51
5.10	139.22	19.56	143.04	367.15	239.22	410.67	258.78
8.30	137.70	23.36	142.49	353.70	294.59	402.42	317.95
5.28	137.72	21.16	141.65	362.36	262.58	406.71	283.74
7.90	136.55	17.57	140.45	356.31	266.28	402.88	283.85
Average value	138.20	19.48	142.18	360.20	264.80	405.75	284.28

Table 2 Experimental data on dynamic scanning of TBMS by DSC tests

Sample mass/mg	Dimerization			Thermal polymerization			Total amount of exothermic heat Q_{total}/J g^{-1}
	Exothermic onset temp., T_0/°C	Reaction heat ΔH/J g^{-1}	Exothermic peak temp., T_{max}/°C	Exothermic onset temp., T_0/°C	Reaction heat ΔH/J g^{-1}	Exothermic peak temp., T_{max}/°C	
4.80	90.23	18.36	115.68	387.10	225.83	450.32	244.19
7.40	74.60	29.63	97.01	365.40	277.30	415.59	306.93
6.30	118.49	56.98	127.77	372.18	219.01	417.16	275.99
3.40	78.62	52.94	103.88	407.23	281.71	458.26	377.05
3.30	86.29	55.07	106.13	410.58	242.80	458.22	317.86
Average value	89.65	42.60	109.00	388.50	249.33	439.91	291.93

Table 3 Experimental data on dynamic scanning of styrene and styrene with formaldehyde by DSC tests

Sample	Mass/mg	Exothermic onset temp., T_0/°C	Reaction heat, ΔH/J g^{-1}	Exothermic peak temp., T_{max}/°C
Styrene	9.50	103.30	601.73	250.81
Styrene+fomaldehyde	5.38	148.06	490.13	205.30

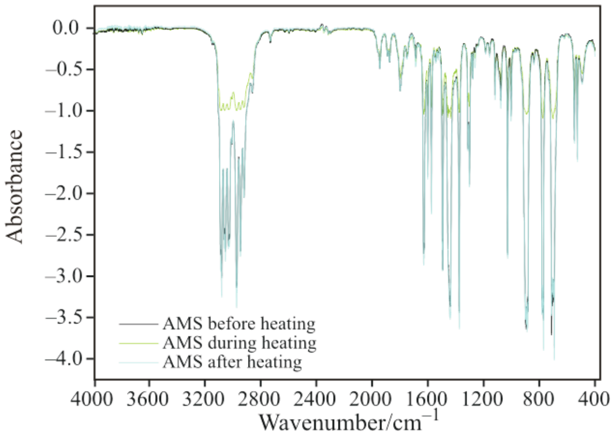

Fig. 5 Absorbance alterations before, during and after heating of AMS by FTIR spectra

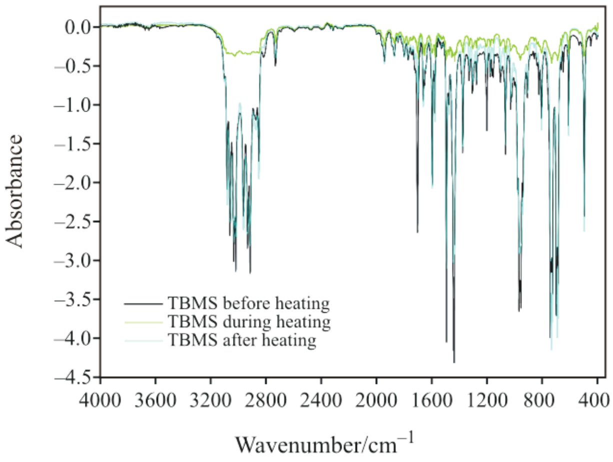

Fig. 6 Absorbance alterations before, during and after heating of TBMS by FTIR spectra

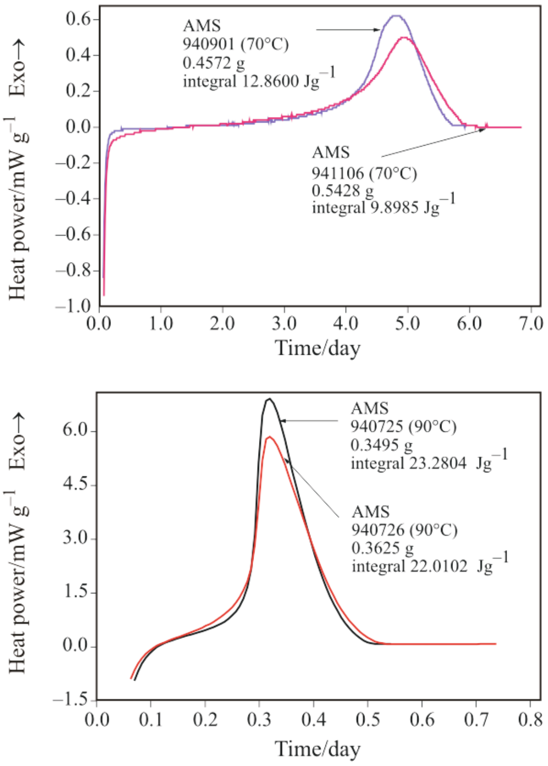

Fig. 7 Thermal curves of isothermal ageing of AMS at 70 and 90°C conducted by TAM

monomer, the dimers presumably undergo the retro–Diels–Alder reaction, and they react with styrene into the radicals [6].

- To date, as for the appearance alterations of AMS and TBMS, it was observed that the original chemicals, AMS and TBMS, are both colorless liquids. The colorless liquid gradually became white and murky liquid for AMS and TBMS under isothermal temperature (180°C) in one hour by blast furnace. Then, the white and turbid liquid slowly became colorless under room temperatures, 25–30°C, as revealed in Table 6.
- From FTIR spectra, we could observe the absorbance alterations on the chemical before heating, during heating of the chemical, and the chemical after heating, as shown in Figs 5 and 6. According to the above observations, we identified the dimerization mechanisms of AMS and TBMS.
- However, two continuously exothermic peaks for TBMS could be observed; the temperature range is 50–170°C, as can be seen in Fig. 1. A highly sensitive calorimeter is a suitable device to search for possible reaction pathways of two continuously exothermic peaks. Isothermal ageing measurements by TAM, AMS, and TBMS indicated an autocatalytic reaction and nth order reaction during the temperature ranges, 70–90 and 50–90°C, respectively (Figs 7 and 8).

In summary, AMS and TBMS were carried out for Diels–Alder reaction by benzene ring and ethylene double bond during the period of dimeri-

Table 4 Experimental data on dynamic scanning of AMS and AMS with formaldehyde by DSC tests

Sample	Mass/ mg	Dimerization			Thermal polymerization			Total amount of exothermic heat Q_{total}/J g^{-1}
		Exothermic onset temp., T_0/°C	Reaction heat ΔH/J g^{-1}	Exothermic peak temp., T_{max}/°C	Exothermic onset temp., T_0/°C	Reaction heat ΔH/J g^{-1}	Exothermic peak temp., T_{max}/°C	
AMS	6.85	138.20	19.48	142.18	360.20	364.80	405.75	284.28
AMS+ formaldehyde	4.03	138.32	3.29	143.73	321.95	39.46	360.90	42.75

Table 5 Experimental data on dynamic scanning of TBMS and TBMS with formaldehyde by DSC tests

Sample	Mass/mg	Dimerization			Thermal polymerization			Total amount of exothermic heat Q_{total}/J g^{-1}
		Exothermic onset temp., T_0/°C	Reaction heat ΔH/J g^{-1}	Exothermic peak temp., T_{max}/°C	Exothermic onset temp., T_0/°C	Reaction heat ΔH/J g^{-1}	Exothermic peak temp., T_{max}/°C	
TBMS	5.04	89.65	42.60	109.00	388.50	249.33	439.91	291938
TBMS+ formaldehyde	4.79	248.74	33.99	254.32	329.22	237.48	366.56	271.47

zation, respectively. However, the structure was very unstable and readily decomposed into two monomers for TBMS with temperature rise. Subsequently, two monomers quickly followed Diels–Alder reaction by benzene ring during the period of dimerization.

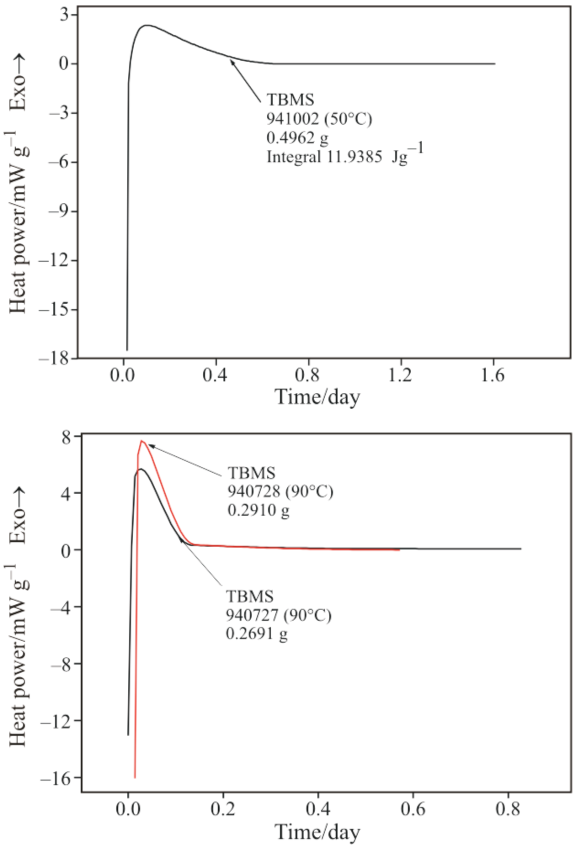

Fig. 8 Thermal curves of isothermal ageing of TBMS at 50 and 90°C conducted by TAM

Thermal polymerization estimation

From Figs 9–10, we can observe that thermal curves of AMS and TBMS gradually became flat after dimerization was finished. Thermal polymerization (2nd peak) occurred and formed a high molecular mass polymer by induction of initial reaction under dynamic conditions. From previous literature and experimental results, we can obtain comprehensive thermal polymerization mechanisms as follows:

- According to the above dimerization mechanisms, AMS was combined into a dimer from two monomers, and decomposed into two monomers from a dimer with temperature increase, which is similar to TBMS. Then, AMS and TBMS both had thermal polymerization (2nd peak) under temperature ranges of 260–450 and 310–490°C, respectively, as illustrated in Fig. 11. The reaction heats (ΔH) were 264.80 and 249.33 J g^{-1} for AMS and TBMS, respectively, as displayed in Tables 2 and 3.
- Amos *et al.* reported that pure AMS shows weak polymerization phenomena at room temperature to 200°C; a few dimers and trimers would be formed below a temperature of 250°C [7].
- By blast furnace, experiments had selected T_0 of AMS and TBMS and different isothermal times (1, 2, 3, 6 and 24 h) to observe appearance alterations of two chemicals during the period of thermal polymerization. From Tables 7 and 8, we can clearly see the alterations of sample color and status with passage of time.

By establishing the detailed mechanisms of thermal polymerization of AMS and TBMS, by searching and estimating certain reaction schema based upon information from the open literature [1, 5] and our experimental results (DSC and blast furnace), as

Table 6 Appearance alterations of dimerization for AMS and TBMS

	AMS			TBMS	
Sample appearance			Sample appearance		
Sample	Heating AMS	AMS after heating	Sample	Heating TMS	TBMS after heating
color	white and turbid liquid	colorless liquid	color	white and turbid liquid	colorless liquid

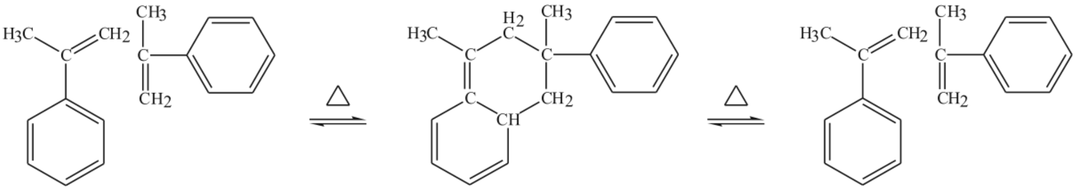

Fig. 9 Proposed scheme of dimerization mechanisms of AMS

Table 7 Appearance alterations of thermal polymerization for AMS taken from a blast furnace

	AMS				
Sample appearance					
	Red liquid	Black liquid	Black colloid	Black colloid	Black solid
Sample color	Isothermal: 360.20°C; Isothermal time: 1 h	Isothermal: 360.20°C; Isothermal time: 2 h	Isothermal: 360.20°C; Isothermal time: 3 h	Isothermal: 360.20°C; Isothermal time: 6 h	Isothermal: 360.20°C; Isothermal time: 24 h

Table 8 Appearance alterations of thermal polymerization for TBMS taken from a blast furnace

	TBMS				
Sample appearance					
	Yellow liquid	Black liquid	Black liquid	Black colloid	Black solid
Sample color	Isothermal: 388.50°C; Isothermal time: 1 h	Isothermal: 388.50°C; Isothermal time: 2 h	Isothermal: 3880.50°C; Isothermal time: 3 h	Isothermal: 388.50°C; Isothermal time: 6 h	Isothermal: 388.50°C; Isothermal time: 24 h

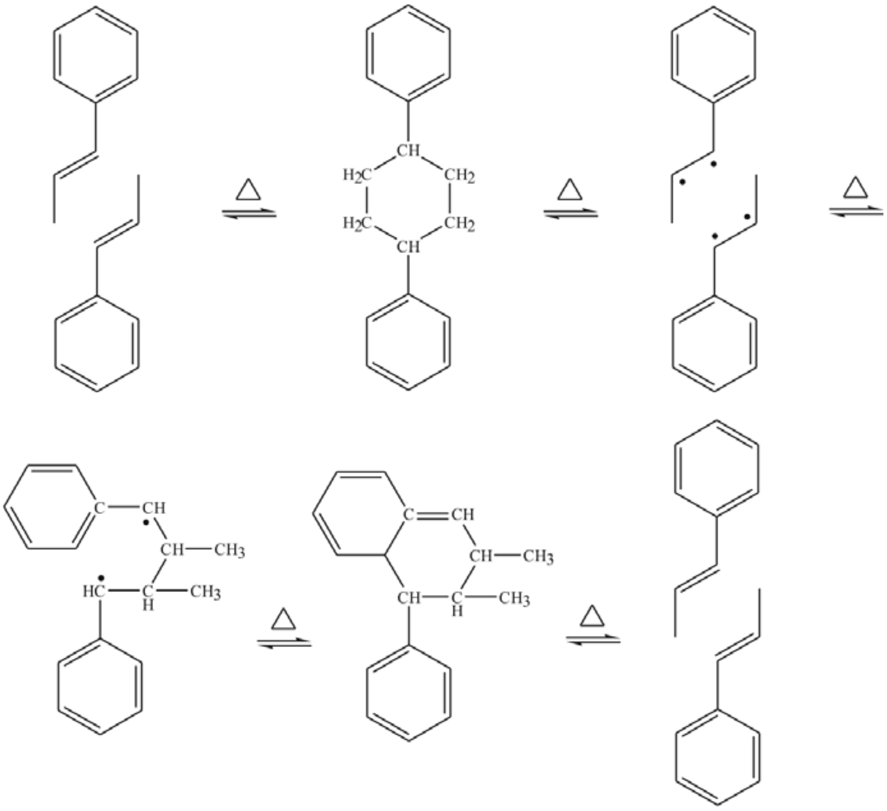

Fig. 10 Proposed scheme of dimerization mechanisms of TBMS

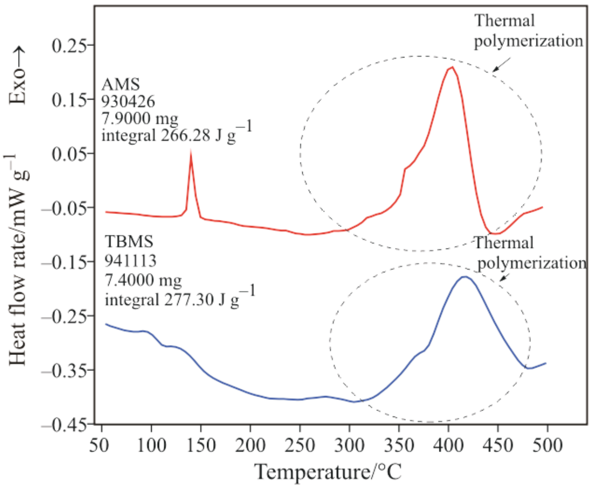

Fig. 11 Thermal curves (2nd peak) of dynamic scanning of AMS and TBMS by DSC tests

follows: after dimerization, all monomers formed five possible substances during the period of thermal polymerization. The unsaturated dimers were the key intermediates for high molecular polymer formation of AMS and TBMS; some monomers formed saturated dimers and trimers, and others did not have any alteration. Since the structure was very unstable for saturated dimers, it would decompose to generate two monomers with temperature increase. Furthermore, the chain transfer reaction was finished if monomers formed trimers, as indicated in Fig. 12.

Conclusions

In summary, this study estimated polymerization mechanisms of various isomers by detailed mechanisms of dimerization and thermal polymerization of AMS and TBMS. In addition, possible dangerous

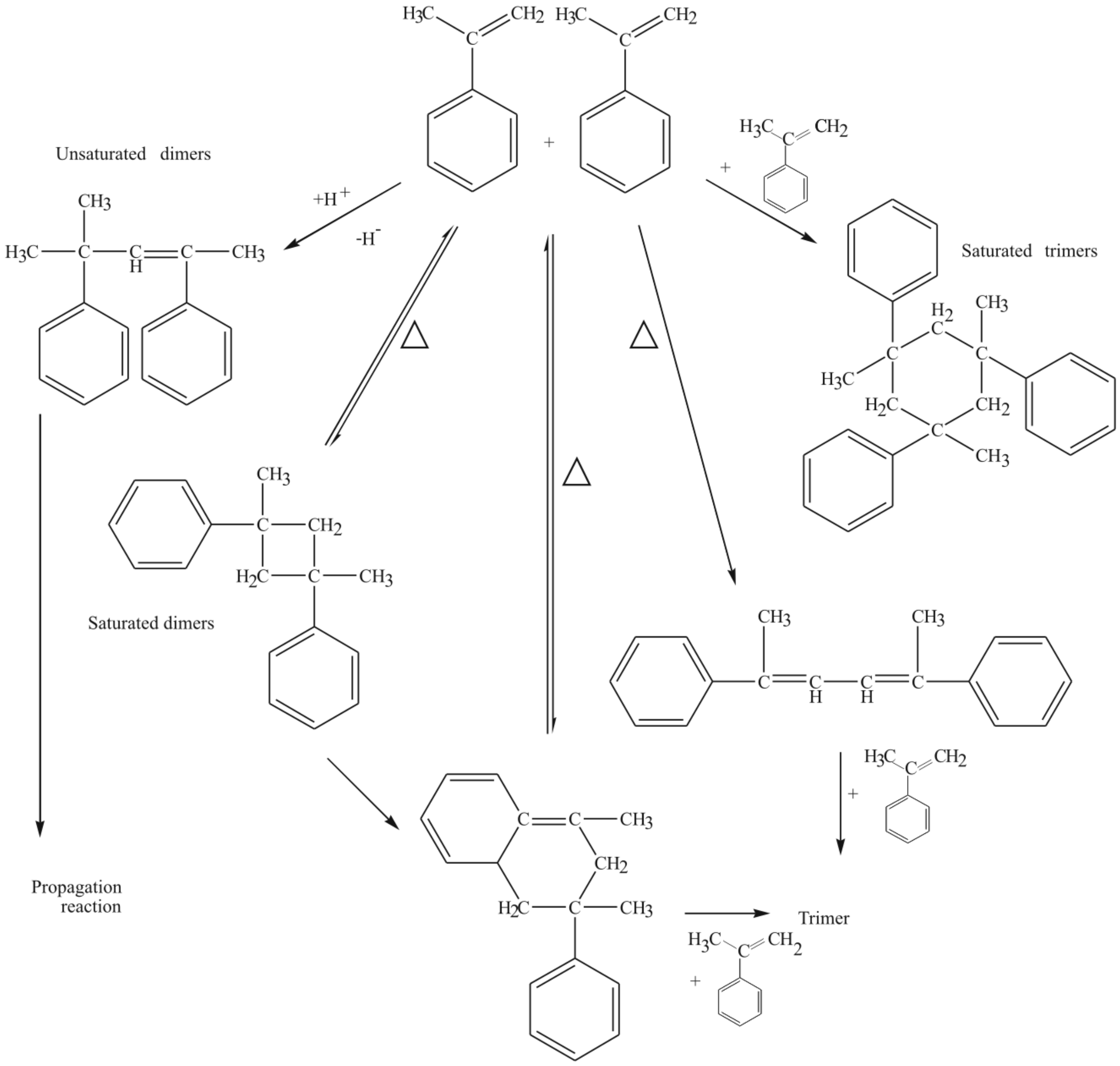

Fig. 12 Proposed and modified scheme of thermal polymerization mechanisms of AMS, as similar to TBMS (1)

intermediates during various processes in the petrochemical industry could also be anticipated and avoided.

After styrene contacted the formaldehyde, the exothermic onset temperature (T_0) increased, but the total heat of reaction (Q_{total}) decreased . The above reaction did not result in potential thermal hazards in the polymerization process, except for degrading its product quality.

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