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NOVEL DETERMINATION OF THE DIMERIZATION MECHANISM FOR THERMAL POLYMERIZATION OF α-METHYLSTYRENE

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This study discussed the phenomena on thermal polymerization of α-methylstyrene (AMS). A curve scanned by temperature-programmed technique was performed by differential scanning calorimetry (DSC). Heat of polymerization (ΔH) and onset temperature of exothermic (T_0) behavior were determined to be 280±10 J g^{-1} and about 138±1°C, respectively. A dimer formation mechanism was proposed for initiation of the propagating chain. Spectroscopic identification of dimer structure was conducted by infrared (IR) spectroscopy in the wavenumber from 650 to 1100 cm^{-1}associated with molecular fingerprint characteristics. The mechanism of thermal polymerization on α-methylstyrene proposed in this study was similar to that of styrene suggested by Mayo.

Keywords: *dimer formation mechanism, DSC, IR, α-methylstyrene (AMS), thermal polymerization*

Introduction

Styrene is a staple commodity used in various polymerization processes to produce polystyrene (PS), styrene–butadiene–rubber (SBR), acrylonitrile–butadiene–styrene (ABS), and other copolymers. It is manufactured commercially by dehydrogenation of ethylbenzene in the petrochemical industry. In Taiwan, its annual production was about 1.2 million tons in 2003 [1].

During storage and transportation, styrene may undergo an exothermic and self-accelerating reaction under an environment of about 50°C [2–4]. Under such a circumstance, styrene may result in various kinds of incidents with different degrees of damage. From 1994 to 2001, several serious accidents occurred in Taiwan, as reported by Chen *et al*. [5].

The related accidents incurred by styrene and its derivatives were mainly ascribed to:

- Lack of knowledge about its reaction kinetics and thermodynamics.
- Inadequate information on process design and operating conditions.
- Human errors with unsafe behaviors [2, 3].

The kinetics of thermal polymerization plays an essential role in the application to industrial production of resins and to establishing safety designs during manufacturing, preparation, handling, processing, storage, transportation and disposal. To accurately confirm kinetic parameters, understanding the reaction mechanism of specific substance is a very important approach combining with either microscopic viewpoint or spectroscopic data.

Even now, the major intermediate is not completely resolved in the reaction mechanism on styrene polymerization, including its derivatives. The aim of this study was to identify the critical reaction step for styrene polymerization dominated with the dimerization by α-methylstyrene (AMS) monomer, possessing steric hindrance with a methyl group. We also investigated previous mechanisms by different analytical methods which utilized calorimetric and spectroscopic measurements [6, 7].

Experimental setup and material

Having a methyl group in the double bond, AMS was used for comparing the dimerization or polymerization behavior on styrene. For thermal analysis, differential scanning calorimetry (DSC) conducts screening tests on AMS monomer. DSC curves reveal the exothermic phenomena produced by dimerization or polymerization. The sample acquired from the programmed temperature was related to the dimerization or different isothermal tests by the degree of polymerization. Intermediates or products were proposed by the identification of functional groups conducted by infrared (IR) spectrometry.

AMS monomer sample

AMS monomer with 99 mass% purity purchased directly from the supplier (Sigma–Aldrich Chemical Corp.) was measured and determined for both density and concentration. The sample was then stored at 4°C in a refrigerator.

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Table 1 Experimental rates data of exothermic reaction of AMS monomer conducted by DSC with scanning tests of 4°C min^{-1}

1st reaction			2nd reaction		
W/mg	T_0/°C	ΔH/J g^{-1}	T_0/°C	ΔH/J g^{-1}	Q_{total}/J g^{-1}
7.70	139.14	13.06	360.81	269.76	282.82
6.80	138.84	22.15	360.88	256.36	278.51
5.10	139.22	19.56	367.15	239.22	258.78
5.28	137.72	21.16	362.36	262.58	283.74
7.90	136.55	17.27	356.34	265.85	283.12
Average value	138.29	18.64	361.51	258.75	277.39
Literature [3, 4]	NA	NA	NA	NA	297.65

W: sample mass (mg), T_0: exothermic onset temperature (°C), ΔH: reaction of polymerization (J g^{-1}), Q_{total}: total reaction of heat (J g^{-1}), NA: not applicable

Differential scanning calorimetry (DSC)

As one of the most popular instruments for establishing kinetic equations of thermal decomposition, dynamic screening experiments were performed on a Mettler TA8000 system coupled with a DSC 821^e measuring cell that can withstand relatively high-pressure crucible (100 bar). The STAR^e software [8] was installed for acquiring the DSC curves and isothermal traces. To obtain a better approach to thermal equilibrium, the scanning rate for the temperature-programmed ramp was chosen to be 4°C min^{-1}.

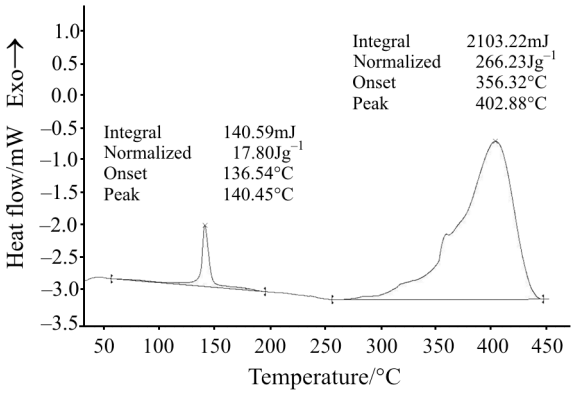

Fig. 1 DSC curve of AMS monomer

Infrared (IR) absorption spectrophotometry

In infrared spectroscopy, IR radiation passes through a sample, which results in vibrational transitions in functional groups. Some of the infrared radiation is absorbed by the vibration modes and some is passed through (transmitted). The resulting spectrum repre-

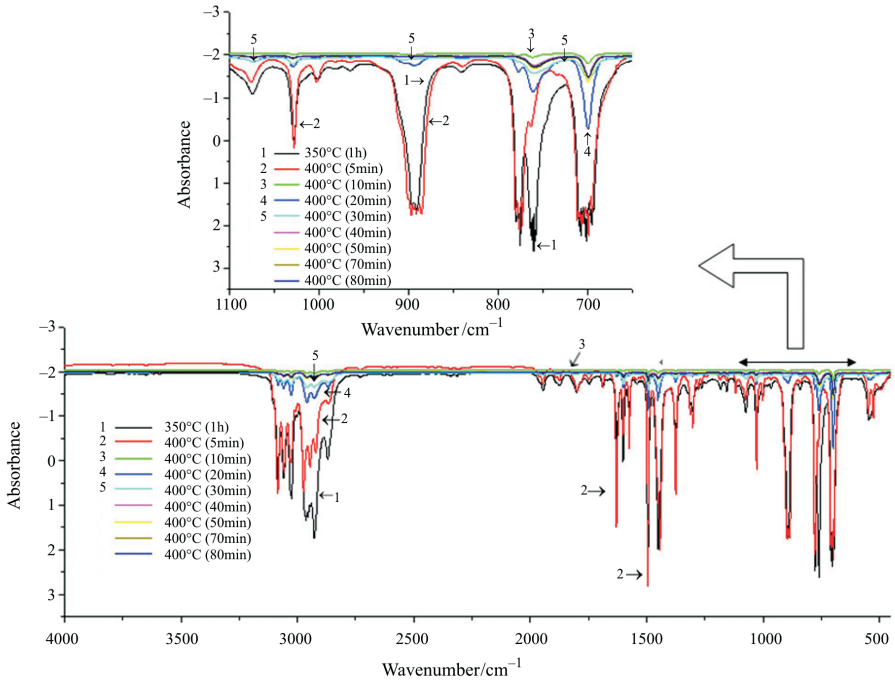

Fig. 2 Infrared absorption spectra of different degrees of polymerization of AMS monomer conducted by IR

sents the molecular absorption and transmission, creating a molecular fingerprint of the sample for spectroscopic identification.

Results and discussion

Thermal stability

By using the dynamic method scanned by DSC, AMS monomer was heated to observe its reaction behaviors. Table 1 summarizes several repeated experimental data, which can be scrutinized with reliable results. From DSC curves, we can observe that there were two exothermic peaks indicated in Fig. 1. Following the calorimetric results, isothermal aging was performed, which provided different degrees of polymerization samples. As planned, data from calorimetry and spectroscopy were compared for characterization of the dimers, intermediates, or metastable species.

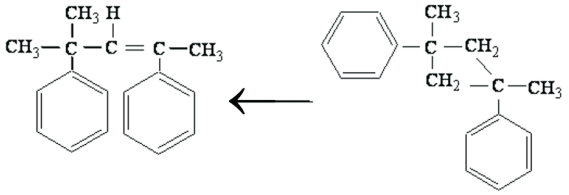

Fig. 3 Formation of unsaturated AMS dimer from its saturated one [4]

Infrared spectra

Figure 2 illustrates infrared absorption spectra for various samples in the polymerization process thermostated at different times and at the same temperature.

Significantly, we can observe the variations on functional groups in these samples. Judging from the changeless infrared absorption spectra when the sample was thermostated for 40 min at 400°C, AMS monomer was verified as the completeness degree of polymerization. Prior to completing the whole process of polymerization, we can look for the dimer by means of infrared absorption spectra.

The dimers from AMS monomer exist in both unsaturated and saturated forms, the latter being produced from the former by cyclization. The isomerization of the dimer is represented in Fig. 3. The characteristics of these dimers can be distinguished

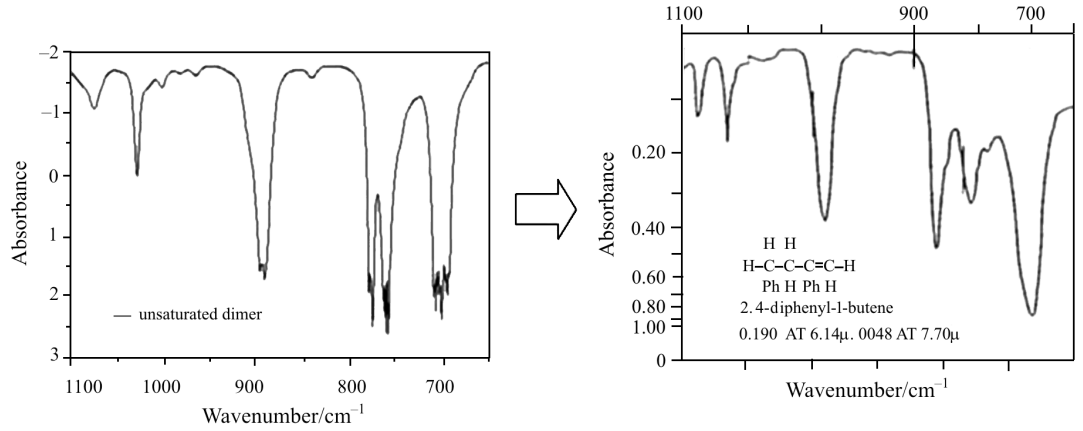

Fig. 4 Comparison of literature values with results for unsaturated AMS dimer in this study [9]

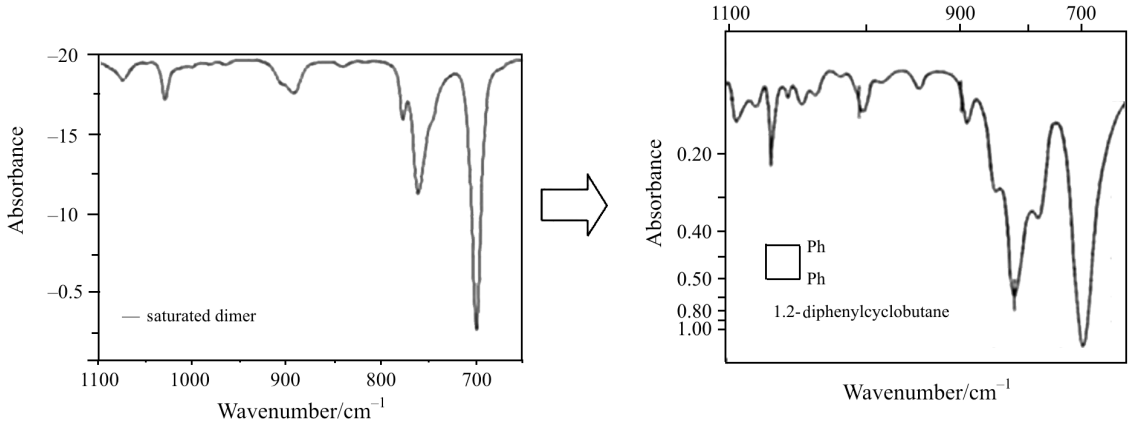

Fig. 5 Comparison of literature values with results for saturated AMS dimer in this study [9]

Initiation

$$(\alpha\text{–MS})_1+(\alpha\text{–MS})_1 \rightarrow (\alpha\text{–MS})_2$$

$$(\alpha\text{–MS})_2 \rightarrow 2(\alpha\text{–MS})_1$$

$$\left\{\begin{array}{l} (\alpha\text{–MS})_2+(\alpha\text{–MS})_1 \rightarrow 2R\cdot \\ (\alpha\text{–MS})_2+(\alpha\text{–MS})_1 \rightarrow (\alpha\text{–MS})_3 \end{array}\right\}$$

Propagation

$$R\cdot + (\alpha\text{–MS})_1 \rightarrow R\cdot + \text{Polymer–P}$$

Chain transfer

$$R\cdot + (\alpha\text{–MS})_2 \rightarrow \text{Polymer–T}$$

$$R\cdot + (\alpha\text{–MS})_1 \rightarrow \text{Polymer–T}$$

Termination

$$R\cdot + R\cdot \rightarrow \text{Polymer–T}$$

where $(\alpha\text{–MS})_1$, $(\alpha\text{–MS})_2$, $(\alpha\text{–MS})_3$, and $R\cdot$ are AMS monomer, dimer, trimer, and any benzyl radical, respectively.

Scheme 1 A proposed mechanism for thermal polymerization of AMS in this study

by IR spectra. Literature comparisons of the IR spectra at the fingerprint region are demonstrated by Figs 4 and 5. Accordingly, the results supported the observation of dimers in the pathway of the mechanism of polymerization.

Mechanism

From the above evidence, the thermal polymerization of AMS was initiated by combination of two AMS to produce a dimer. The mechanism which has received the most support was suggested by Mayo [9]. At the first step, AMS undergoes the Diels–Alder dimerization to form dimers. The dimer may be a saturated or unsaturated compound, which is proposed to be 1,3-dimethyl-1,3-diphenylcyclobutane or 2,4-diphenyl-4-methyl-2-pentene. In the second step, dimer reacts with a third AMS to produce one or two monoradicals. These radicals then initiate polymerization, propagation, chain transfer, and termination as usual. Therefore, we proposed a mechanism for thermal polymerization of AMS as shown in Scheme 1.

Conclusions

We reported a calorimetric study of the thermal polymerization of AMS. The initiation reaction is triggered by the Diels–Alder reaction from the dimerization of two AMS. These evidences of the existence of dimer were supported by calorimetric and spectroscopic measurements. A mechanism of the thermal initiation process was also proposed and was similar to the one for the thermal polymerization of styrene suggested by Mayo [9].

Acknowledgements

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