

Thermal Stability and Thermal Degradation Reaction Kinetics of 4,4'-Diphenylmethane Diisocyanatetrimer†

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The trimer of 4,4'-diphenylmethane diisocyanate (MDI) is synthesized using 2,4,6-tris(dimethylaminomethyl) phenol (DMP-30) as catalyst. The thermal stability of MDI and its trimer and thermal degradation reaction kinetics for MDI trimer are studied by thermo gravimetric analyzer, respectively. The properties and structure of the trimer of MDI are characterized by X-ray diffraction, Fourier transform infrared spectroscopy and TGA. The activation energy of degradation reaction of the trimer was obtained by Ozawa method. The results show that there are two stages of the trimer during thermal degradation process and the apparent activation energy of the first and the second stage are 200.99 and 259.94 kJ/mol, respectively.

Keywords: Trimer of 4,4'-diphenylmethane diisocyanate, Thermal stability, Reaction kinetics, Ozawa method.

INTRODUCTION

Aromatic or aliphatic isocyanate can be self-addition reaction to get isocyanurate. There is no active hydrogen atom in isocyanurate ring and the unit structure become more stable. The products containing isocyanurate ring possess high protective properties, good corrosion resistance and yellowing resistance, good heat resistance and flame retardant. Because of these properties, the isocyanate trimer had been widely used in many fields such as coatings, adhesives, sealant elastomers, foamed plastic, etc.

Now the published literature were reported more about toluene diisocyanate (TDI) trimer, 1,6-hexamethylenediisocyanatetrimer (HDI), isophoronediiisocyanate (IPDI) trimer, but little about diphenylmethanediisocyanate (MDI) trimer¹⁻⁸. In this study, MDI trimer is synthesized by using solution polymerization. The thermal stability of the trimer is compared with MDI monomer and their thermal degradation reaction kinetics has been explored.

EXPERIMENTAL

Characterization: The structure of the products was ascertained by XRD (D8 Advance, BRUKER, Germany) at 40 kV and 40 mA with a CuK α radiation source. The spectra were

recorded by using a WQF-300 spectrometer (Beijing, China) with 32 scans and 4 cm⁻¹ resolution at the range 4000-400 cm⁻¹. The DTG and TGA were measured used STA409PC (NETZSCH-Gerätebau GmbH, Germany) thermal analyzer with the heating rate at 10, 15, 20, 30 K/min, respectively and high pure N₂ as shelter gas. The range of temperature was controlled from 50-800 °C.

Preparation of the trimer of MDI: 100 mL of dehydrated toluene and 50 g of MDI are mixed under the protection of high purity N₂, MDI has absolutely dissolved in toluene by heating with stirring and adding proper amount of 0.05 % of DMP-30 as catalyst. Stirring is continued at 60 °C for 6 h. The excess MDI monomer and catalyst were removed by washing with toluene.

RESULTS AND DISCUSSION

Infrared spectroscopic analysis: There is only-NCO absorption peak at 2274 cm⁻¹ in MDI infrared spectroscopy as shown in Fig. 1 and the absorption peak intensity of MDI after polymerization at 2274 cm⁻¹ is weaker than MDI monomer. The absorption peak of isocyanurate ring are obviously found at 1720 and 1410 cm⁻¹, but the absorption peak of carbodiimide structure is not be found⁹. In general, the formation of carbodiimide structure cannot be happened unless at high temperature,

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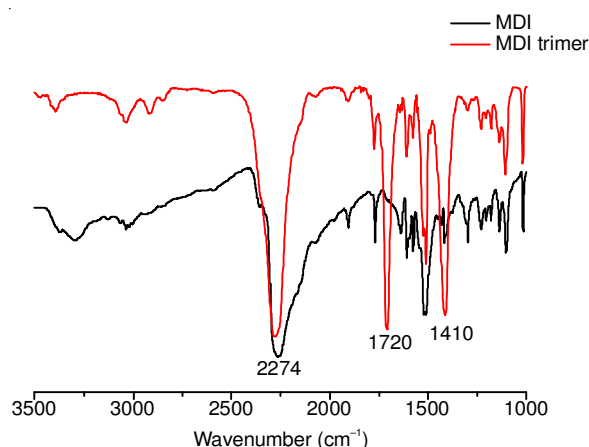


Fig. 1. Infrared spectroscopy of MDI and MDI- trimer

so the carbodiimide structure is not existed in the product. So the product is proved to be MDI trimer.

Thermal stability: Fig. 2 shows the results of TG and DTG of MDI and MDI trimer. There is only one stage in the thermal degradation process of MDI monomer that between 150 and 300 °C, which due to the volatilization of MDI. The weight loss of it is 91.11 %. While there is not obviously weight loss of MDI trimer before 300. There are two stages in the thermal degradation of MDI trimer. In the first stage that between 300 and 420 °C, the carbodiimide structure is formed because the remained -NCO group of MDI trimer continue to reaction and give off CO₂^{10,11}, as shown in Fig. 3, the weight loss of the first stage is 10.03 %. The second stage that between 420 and 620 °C, the polycarbodiimide is formed after decomposition of isocyanurate ring and give off CO₂. The polycarbodiimide decomposed at 580 °C and get a complex mixture of volatile products, leaving behind carbon residue.

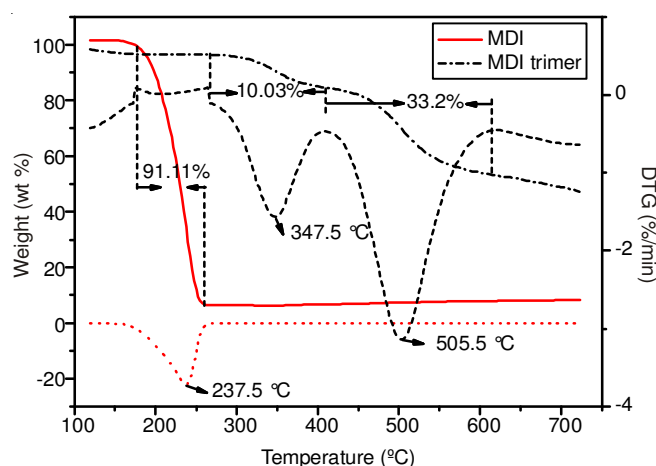


Fig. 2. TG and DTG of MDI and MDI- trimer

The decomposition product of MDI trimer under different temperatures are tracked by infrared as shown in Fig. 4. The absorption peak of cabodiimide structure is found at 2160 cm⁻¹ in MDI trimer after 400 °C carbonization, C-N stretching vibration peak is found at 1520 cm⁻¹ and C=O stretching vibration peak is found at 1600 cm⁻¹. There are not big difference between infrared spectroscopy of MDI trimer after 500 °C carbonization and after 800 °C carbonization. The Ar-H stretching vibration

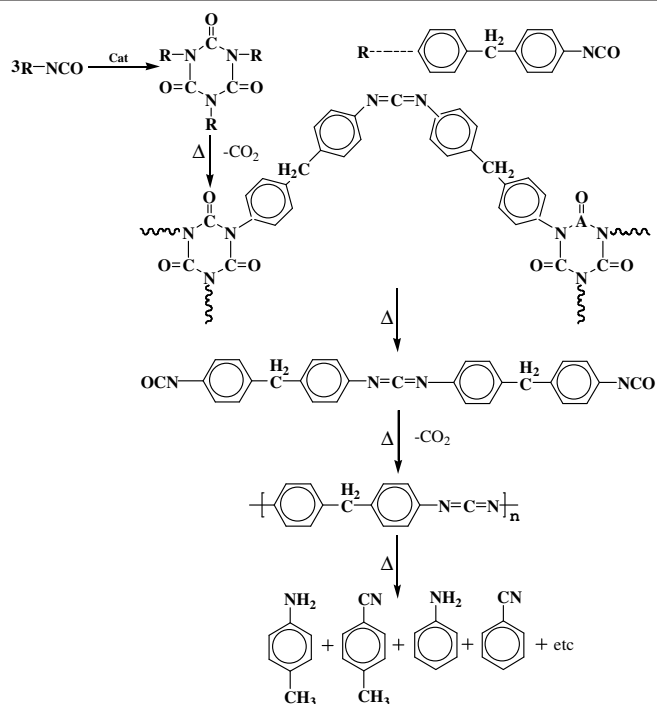


Fig. 3. Thermal degradation process of MDI-trimer

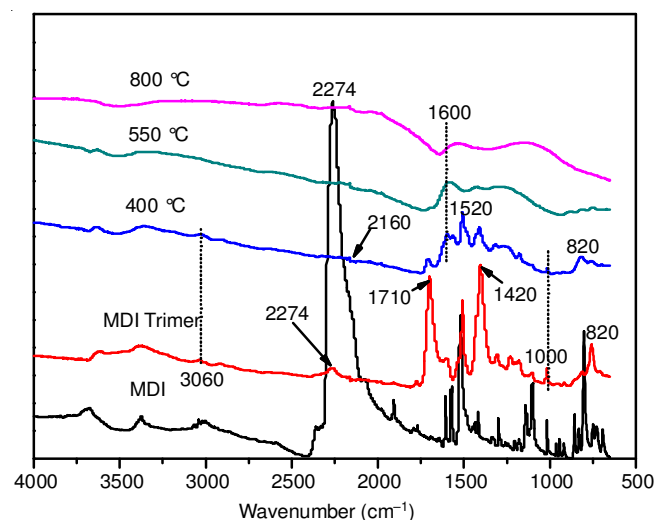


Fig. 4. Infrared spectroscopy of MDI-trimer before and after carbonization

peak is disappeared at 3060 cm⁻¹ and the disappearance of absorption peak at 820 cm⁻¹ is the result of para double instead Ar-C and Ar-N bond fission, remaining carbon residue at last.

X-Ray diffraction analysis: The MDI trimer and the product after carbonization are both present typical amorphous structures are shown in Fig. 5. The relatively narrow peak that has symmetrical peak shape is found at 18° diffraction angle in MDI trimer, which reflects the molecular space configuration is regular. The diffraction peak at 18° in the product after 400 °C carbonization is wider than it in MDI trimer, which mainly because the active-NCO groups of the MDI trimer react with each other and form a crosslinked structure. The diffraction peak gradually rises to a high angle with the carbonization temperature rises to 550 °C, the peak intensity become weaker and the peak type become wider, which shows that the molecular chain is broken and the arrangement of the chain segments are disorder after carbonization.

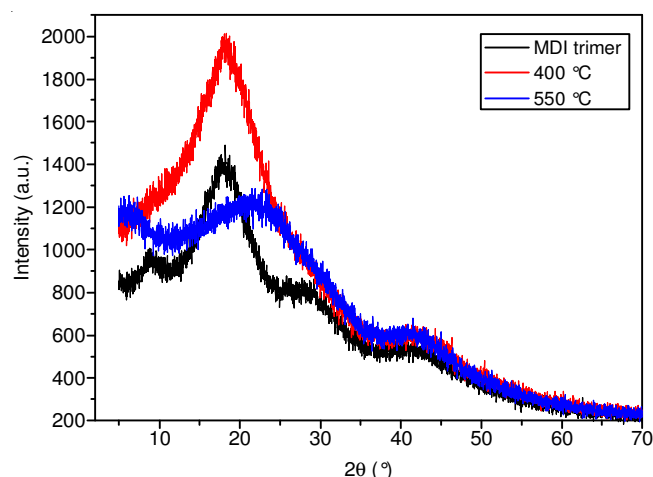


Fig. 5. XRD of MDI-trimer at different carbonization temperatures

Thermal degradation reaction kinetics: In this study, Ozawa method is used to calculate the activation energy. The activation energy (E) is calculated by using different DTG curve peak (T_p) under different heating rate β^{12} .

$$\log \beta = \log \left[\frac{AE}{RG(\alpha)} \right] - 2.315 - 0.4567 \frac{E}{RT}$$

The E can be calculated from the slope of the line that $\log \beta$ as Y axis and $1/T$ as X axis. The $\log \beta$ - $1/T$ fitting curve is got according to the Fig. 6 and Table-1.

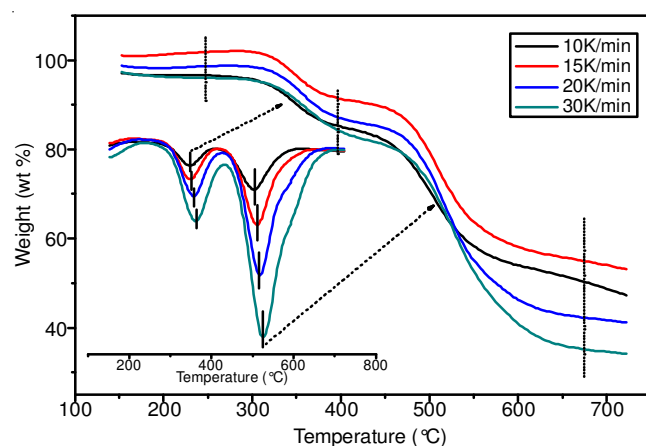


Fig. 6. TGA and DTG MDI-trimer at different heating rate

TABLE-1

T_p IN DTG OF MDI-TRIMER AT DIFFERENT HEATING RATE

Samples	Heating rate (K min ⁻¹)	T_{p1} (°C)	T_{p2} (°C)
MDI-trimer	10	347	505
	15	347.5	510
	20	357	517
	30	360	525

The two stages linear fitting curves are shown in Fig. 7. The first stage fitting curve equation expressed as $y = 18.88 - 11041.43x$, the line slope is -11041.43, the correlation coefficient is 0.925 and the calculated activation energy is 200.99 kJ/mol. The second stage fitting curve equation expressed as $y = 19.37 - 14279.18x$, the line slope is -14279.18, the correlation coefficient is 0.992 and the calculated activation energy is 259.94 kJ/mol. The result shows that the activation energy is relatively high in two stages.

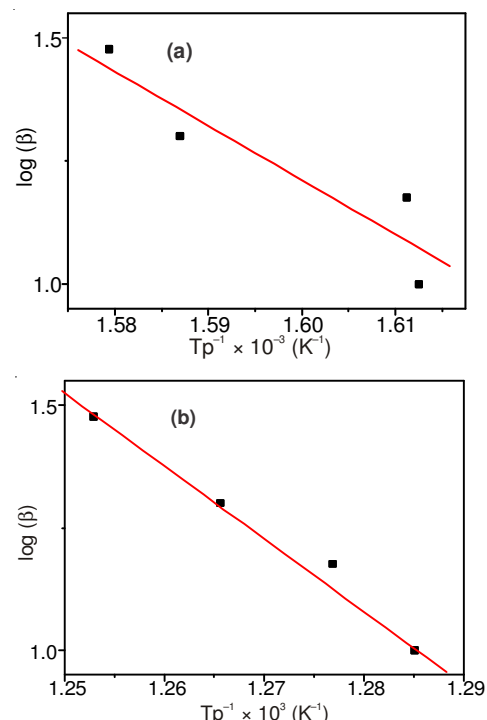


Fig. 7. Fitting curve of ozawa of MDI-trimer (a, the first stage; b, the second stage)

Conclusion

The product that synthesized by using solution polymerization is MDI trimer according to the result of Fourier infrared spectra. The thermal stability of MDI trimer is better than MDI. There are two stages through MDI trimer degradation process. The carbodiimide structure is formed in the first stage, the isocyanurate ring and carbodiimide structure resolved in the second stage. The activation energy of MDI trimer are calculated by Ozawa method.

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