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Diphenylmethane diisocyanate self-polymerization: Thermal hazard evaluation and proof of runaway reaction in gram scale

Yoshihiko Sato [a,*], Ken Okada [a], Miyako Akiyoshi [a], Satoshi Murayama [b], Takehiro Matsunaga [a]

[a] Research Institute of Science for Safety and Sustainability (RISS), National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan
[b] Central Research Laboratory, Nippon Polyurethane Industry Co., Ltd., 440 Akiba-cho, Totsuka-ku, Yokohama, Kanagawa 245-0052, Japan

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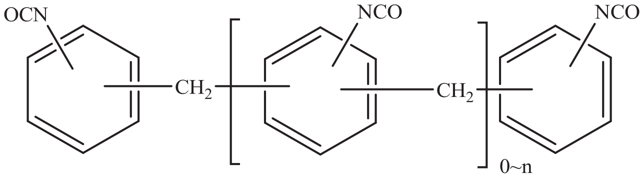
ABSTRACT

Thermal analysis by differential scanning calorimetry and thermogravimetric/differential thermal analysis mass spectrometry, adiabatic calorimetry, a gram-scale heating test, and infrared spectroscopy were performed to evaluate the thermal hazards of diphenylmethane diisocyanate (MDI) and prove the occurrence of a runaway reaction. The self-polymerization of MDI was found to occur at about 340 °C under rapid heating conditions. Carbon dioxide was eliminated and heat was generated to allow polymerization. Under adiabatic and closed conditions, the runaway reaction of MDI can begin at least from 220 °C. Besides it is highly probable that the runaway reaction of MDI can begin from a lower temperature in an actual process scale. More heat was generated than in the previous case and the pressure rose rapidly. A closed 2-mm-thick glass vessel exploded because of the runaway reaction of MDI even if the temperature was lower than 300 °C. Therefore, MDI could cause fatal runaway reactions below 300 °C, where MDI had been assumed to self-polymerize by eliminating carbon dioxide previously.

1. Introduction

Diphenylmethane diisocyanate (MDI) is commonly used to make polyurethane foams because of its high reactivity and easy handling (Herrington & Hock, 1998; Saunders & Frisch, 1962). The chemical structural formula of MDI is showed in equation (1).



(1).

MDI is generally synthesized from the phosgenation of diamino diphenylmethane (Herrington & Hock, 1998; Saunders & Frisch, 1962). Mixtures of 4,4′-MDI as well as MDI isomers and oligomers (dimers, trimers, etc.) of varying compositions are prepared depending on condensation (generation of amine compounds), phosgenation, and distillation conditions. Polymeric MDIs with different numbers of functional groups are used depending on applications (Herrington & Hock, 1998). Diisocyanates such as MDI react with polyols to produce polyurethanes. This reaction is exothermic. The reaction proceeds rapidly without additional external heating because of a large heat of reaction, making the heat of reaction an important property. Therefore, many studies have been conducted to examine the heat and rate of reaction between diisocyanates and nucleophilic reagents such as polyols and water (Aleksandrova & Tarakanov, 1972; Lovering & Laidler, 1962; Yevreinov et al., 1973). In addition, polyurethane foam has high heat insulating properties. Thus, the accumulation of heat from the reaction in the product can cause self-ignition. Hager and Brandien (1968) studied the relationship between heat accumulation and reactants, production and treatment conditions, and product size to prevent self-ignition. They found that self-ignition could occur in the case of deficient polyester flow even at formulation containing less than the critical water level and otherwise unchanged feedstream. Moreover, organic isocyanates are highly reactive and can decompose with accelerating rates. The heats of decomposition of some organic isocyanates have been measured (Urban, 2007) because of their potential contribution to heat accumulation and self-ignition. In contrast, aromatic isocyanates such as MDI are known to self-polymerize to form polymeric carbodiimide upon elimination of carbon dioxide above 300 °C (Saunders & Frisch, 1962). This reaction is exothermic and can accumulate heat in the products and progress at increasing rates. The reaction is shown in equation (2).

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* Corresponding author. Tel.: +81 29 861 4785; fax: +81 29 861 4784.
E-mail address: yoshihiko-satou@aist.go.jp (Y. Sato).

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$$\mathrm{R{-}NCO} + \mathrm{OCN{-}R} \longrightarrow \mathrm{R{-}N{=}C{=}N{-}R} + \mathrm{CO_2}$$

(2).

In 2007, an MDI tank burst in Japan. It was suggested that the reaction shown in equation (2) accelerated and the pressure in the tank increased because MDI was kept at a high temperature, causing the incident. As mentioned above, pressure may increase at a high rate upon elimination of carbon dioxide, allowing explosion accidents to occur. Therefore, quantitatively understanding the progress of the MDI reaction is important for preventing these accidents.

Furthermore, organic isocyanates are highly reactive themselves and vigorously react with nucleophilic reagents (Urban, 2007). As a result, accelerated heat generation can occur. Water is a typical nucleophilic reagent, which upon mixing with organic isocyanates, leads to immediate generation of heat and carbon dioxide (Urban, 2007). This reaction is responsible for some of the worst chemical engineering accidents. One major accident is the methyl isocyanate release in Bhopal, India, in December 1984 (Lees, 1996). In this accident, a large amount of methyl isocyanate was stored, despite a continuous process. In addition to the exothermic reaction of methyl isocyanate, continuous heat generation caused a large pressure rise in this process because of a lack of a cooling system. Hydrolysis and carbon dioxide generation under acid or chlorine contamination are important processes in this exothermic reaction (D'silva, 1986; Urban, 2007). Because of the Bhopal accident, the reaction between organic isocyanates and water is generally recognized as an important hazard factor when handling organic isocyanates (Urban, 2007). In contrast, the self-polymerization of isocyanates at a high temperature is not generally recognized as a hazard.

In this study, MDI was analyzed by thermal analysis and adiabatic calorimetry to evaluate the thermal hazards of its self-polymerization experimentally. A gram-scale heating test was also performed to prove that this self-polymerization causes explosions.

2. Experimental section

Thermal analysis by differential scanning calorimetry (DSC) and thermogravimetric/differential thermal analysis mass spectrometry (TG–DTA/MS), adiabatic calorimetry, a gram-scale heating test, and infrared spectroscopy were performed to evaluate the thermal hazards of MDI and prove the occurrence of runaway reactions. The objectives and features of these measurements are shown in Table 1.

2.1. Materials

Polymethylene polyphenyl polyisocyanate with more than 99% purity (Nippon Polyurethane Industry Co. Ltd.) was used in this study. The sample consists of a 3:2 mixture of 4,4′-diphenylmethane diisocyanate and higher functionality isocyanates ($n = 1, 2, 3$ in equation (1)). The mixture was poured into a 1 L steel can and stored in a refrigerator. The solid MDI was used without purification.

2.2. Thermal analysis using DSC and TG–DTA/MS

The endothermic and exothermic behaviors of MDI upon heating were determined by DSC. The reaction products obtained upon heating were also identified by TG–DTA/MS.

During the DSC analysis, a high pressure DSC2920 (TA Instruments) was used. The sample (4 mg) was placed in a stainless sealed cell (RIGAKU) and heated from room temperature to 500 °C at a heating rate of $10\ \mathrm{K\,min^{-1}}$ under a 0.1 MPa N_2 atmosphere.

A Thermo Mass system (RIGAKU) equipped with a Thermo Plus TG1820 thermogravimetry and differential thermal analyzer (RIGAKU) and an M-200QA quadrupole mass spectrometer (ANELVA) was used for the TG–DTA/MS measurements. This apparatus can analyze the mass of gases evolved from samples upon heating. The sample (1 mg) was placed in an aluminum cell with an open pinhole cap and heated from room temperature to 500 °C at a heating rate of $10\ \mathrm{K\,min^{-1}}$ under a $200\ \mathrm{mL\,min^{-1}}$ helium flow.

2.3. Analysis using an adiabatic calorimeter

The exothermic and pressure rise behaviors of MDI under closed adiabatic conditions, which are the most severe engineering conditions, were evaluated using an adiabatic calorimeter. Heat generation was investigated from 160 to 260 °C.

A SIKAREX adiabatic calorimeter (SYSTAG) (CCPS, 1995; Kars & Visser, 1996) was used in the analysis. A stainless sample vessel fitted with a glass liner was placed at the center of the equipment. A thermocouple was directly inserted in the center of the sample to directly measure its temperature. Pseudo adiabatic conditions were obtained by maintaining the jacket and sample temperatures equal. The vessel pressure was measured by connecting a pressure transducer to the sample vessel. The working pressure of the sample vessel was 15 MPa. This analysis was conducted once. The amount of sample was 20 g. Measurement was performed using the heat–wait–search mode (CCPS, 1995; Townsend & Tou, 1980). The sample vessel was first heated up to its initial temperature. Then, when a certain self-heating was detected within a fixed time period after reaching thermal equilibrium, it was automatically switched to strict adiabatic control. When exothermic heat was not detected, step heating was only conducted at preset values and a check was performed to see whether exothermic heat could be detected. In this analysis, the initial temperature was 160 °C. The temperature step was 10 K. Wait and search times were set as 30 min, respectively.

Table 1
Objectives and features of the tests.

Tests	Objectives	Sample mass scale	Adiabatic condition	Opened or closed condition
Thermal analysis using DSC	Observation of endothermic or/and exothermic behavior	mg	Not adiabatic	Closed
Thermal analysis using TG–DTA/MS	Identification of gaseous products	mg	Not adiabatic	Semi-open
Analysis using an adiabatic calorimeter	Observation of behavior of heat and pressure generation	gram	Adiabatic	Closed
Gram-scale heating test	Actual proof of runaway reaction	gram	Near adiabatic	Closed
Infrared spectroscopy	Identification of condensed products	mg	Without heating	Open