

Temperature-modulated DSC study of network formation via Thiol-Isocyanate “click” reaction

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(Manuscript Received on September 10th, 2015, Manuscript Revised March 29th, 2016)

ABSTRACT

The thiol-isocyanate chemistry was used to create crosslinked polymer networks without the use of solvent and catalyst. The preliminary study of a model thiol-isocyanate reaction was performed to confirm the “efficient linking” feature of the reaction, as indicated by online FT-IR method. Temperature-modulated differential scanning calorimetry (TMDSC) was used to

characterize the occurrence of the networks thiol-isocyanate reaction between multi-functional reactants, the influence of temperature on the reaction rate and the glass transition temperatures of the partially and fully cured networks. The investigation could pave the way for the design and tailoring of new cross-linked polymer materials for on-demand applications.

Key words: *Temperature-modulated DSC, thiol-isocyanate, click reaction.*

1. INTRODUCTION

Many polymerization reactions used to constitute polymer networks are complex and often require an initial resin formulation that undergoes a rapid transition from a relatively low viscosity liquid state to a highly crosslinked, glassy solid state with corresponding changes in different material properties. The ability to react and form networks with intimate control of the cross-linking dynamics and the final material

properties has enabled their use across various fields and contributed to many technological advancements [1]. The broad spectrum of applications in which polymer networks have become important vary from automobile and aircraft parts to biomedical devices to lithographic imprint materials and optical devices [2]. In this respect, network formation taking advantage of the powerful capabilities afforded

by the “click” reaction paradigm has recently attracted significant attention [3,4]. Various examples of “click” reactions that have been employed as cross-linking pathways are copper (I)-catalyzed azide alkyne cycloaddition, photoinitiated thiol-ene, base-catalyzed thiol-ene Michael addition, and base-catalyzed thiol-isocyanate reactions [1,5].

The base-catalyzed reaction of thiols with isocyanates to form thiourethanes has been known for over 50 years, but has only recently been recognized for its potential as a click reaction [6-9]. Recently, the utilization of the thiol-isocyanate nucleophilic addition reaction between a tetrathiol and an diisocyanate to yield highly cross-linked and uniform molecular networks has shown great promise in the preparation of thermoset films or in healing cracked epoxy thermosets [10-14] owing to its simplicity and high efficiency. Especially, catalyst-free reactions of mono-functional thiols with mono-functional isocyanates have also been reported [15].

A prerequisite in developing new crosslinked polymer networks is understanding the curing kinetics in order to successfully design and tailor materials for on-demand applications. Therefore, in this paper, we studied the kinetic aspect of the networks stoichiometric reaction between the tetrafunctional thiol pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol) and hexamethylene diisocyanate (HDI) as a function of temperature without addition of any catalyst via the temperature-modulated differential scanning calorimetry method (TMDSC). TMDSC subjects a sample to a linear heating ramp with a superimposed low-frequency temperature oscillation (modulation) resulting in a modulation in the heating profile [16]. TMDSC

analysis provides the “total” heat flow, such as that from conventional DSC, and the heat capacity-related (reversible) component of the heat flow. The difference between the reversing signal and the total is the non-reversing component. The reversing signal is excellent for quantifying the glass transition and separates the glass transition completely from other non-reversing processes such as enthalpy relaxation, crystallization, and cure reaction-related enthalpy changes [16]. To the best of our knowledge, a calorimetric study of a catalyst-free thiol-isocyanate curing mixture has not been previously reported.

2. EXPERIMENTAL

2.1 Materials

Hexamethylene diisocyanate (HDI, $\geq 99\%$), pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol, $>95\%$), isooctyl 3-mercaptopropionate ($>99\%$) and hexyl isocyanate ($>97\%$) were purchased from Sigma-Aldrich and used as received.

2.2 Kinetic investigation of stoichiometric reactions between thiols and isocyanates

To investigate the stoichiometric reaction between mono-functional thiol and mono-functional isocyanate, isooctyl 3-mercaptopropionate was mixed with hexyl isocyanate (molar ratio between the thiol and isocyanate functional groups of 1) and the reaction was performed at 90 °C under stirring, and was simultaneously monitored using the time-resolved online ATR FT-IR method.

To investigate the stoichiometric networks reaction between the tetrathiol and HDI, a well-mixed (for 15 seconds at room temperature) mixture of tetrathiol and HDI, with the molar ratio between the thiol and isocyanate functional

groups of 1, was subjected to TMDSC measurements.

2.3 Characterization

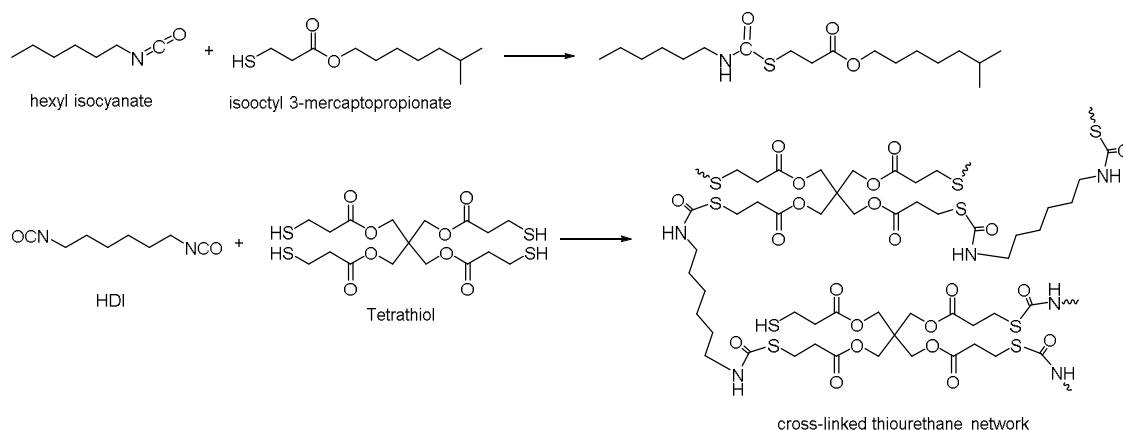
Time-resolved online ATR FT-IR spectra were recorded on a React-IR 4000 Instrument (Mettler Toledo AutoChem ReactIR) equipped with a silicon ATR probe (SiComp). For online monitoring, the silicon probe was introduced into a two-necked glass flask containing the reaction mixture (the IR probe was in contact with the reaction liquid) under stirring at 90°C and spectra were recorded for certain time intervals.

Temperature-modulated differential scanning calorimetry (TMDSC) thermograms were recorded using a TA-Instruments T-MDSC 2920 instrument. Nitrogen gas was used as purge gas. Liquid nitrogen was used to cool the system. The samples were studied in standard 40 μ L aluminum sample pans and at a scan rate of 2.5 K min⁻¹.

3. RESULTS AND DISCUSSION

In order to confirm the reaction between the isocyanate and thiol groups at elevated temperatures, the reaction of a liquid stoichiometric mixture of hexyl isocyanate and isooctyl 3-mercaptopropionate as mono-functional isocyanate and mono-functional thiol, respectively, was investigated (Scheme 1). The

kinetics of the reaction between hexyl isocyanate and isooctyl 3-mercaptopropionate at 90°C was studied with in situ FT-IR by real-time monitoring of the peak areas of the S-H stretch at 2582 cm⁻¹ and NCO stretch at 2266 cm⁻¹ as well as the formed thiourethane (NHCOS) C=O stretch at 1687-1660 cm⁻¹. 3D online FT-IR waterfall plots showing the evolution of characteristic IR peaks for the thiol-isothiocyanate reaction between isooctyl 3-mercaptopropionate and hexyl isocyanate are given in Figure 1a. The occurrence of the reaction is indicated by decreases in the IR absorption intensities of the thiol and isocyanate bands and an increase in the intensity of the thiourethane band. In Figure 1b, the FT-IR band intensities, reflecting the concentrations of the reactants and the product (thiourethane) as a function of time, are shown. The decrease of the areas of the S-H stretch and the isocyanate C=O stretch were used to establish the kinetic profile. As shown in Figure 1b, simultaneous and equimolar consumption of the thiol and isocyanate was observed, indirectly suggesting that the reaction was clean and efficient. However, it is worth noted that side reactions, such as dimerization and trimerization of isocyanate, were not fully excluded, although it was not very likely without any catalyst [17]. Almost full conversion was obtained after 12 min.



Scheme 1. Thiol-isocyanate reaction of model mono-functional compounds and that between tetrathiol and HDI to form a crosslinked network.

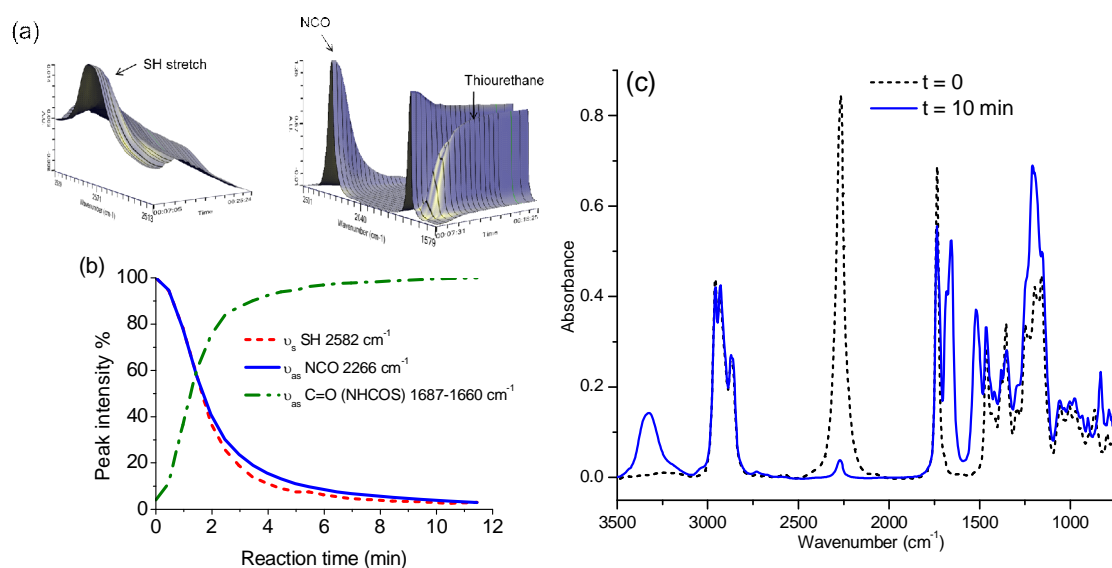


Figure 1. (a) 3D online FT-IR waterfall plots, showing the evolution of characteristic IR peaks for the thiol-isocyanate reaction between isooctyl 3-mercaptopropionate and hexyl isocyanate, (b) band intensities of thiol, isocyanate and thiourethane as a function of time reflecting the kinetic profile, and (c) a comparison of the full FT-IR spectra of the reaction at the start and after 10 min.

After the model study, the cross-linking reaction between tetrathiol and HDI was investigated by DSC. A non-isothermal DSC experiment showed that while heating the reactive mixture at a constant heating rate of 2.5 K min^{-1} , the reaction started at a temperature of about 18°C (Figure 2). The reaction was evidenced by a clear exothermic peak ranging

from 18°C to about 150°C. The reaction was not finished at the time when the temperature reached 150°C. Upon cooling, the DSC curve (Figure 2) was still largely curved in the exothermic direction which is likely explained by the ongoing reaction. A glass transition at about -10°C of the reacted system was observed, which was also the case of the second heating step. The

second heating curve still showed evidence of ongoing reaction as the curve dropped in endothermic direction.

Since the curing reaction has not been complete at 150°C, the reaction was further investigated up to 190°C by TMDSC (Figure 3). The result shown in Figure 3 indicates that the reaction was nearly complete. The exotherm ranging from 18 to 170°C in the first heating scan did not appear in the reversing heating flow

because the curing process was non-reversing. On the other hand, the glass transition was around 24°C in the subsequent second heating scan. The glass transition temperature was shifted to 38°C in the third scan, and did not change upon further heating-cooling scans. The higher glass transition temperature (38°C) as compared to that (-10°C) in Figure 2 is attributed to the higher reaction conversion upon extending the reaction temperature to 190°C.

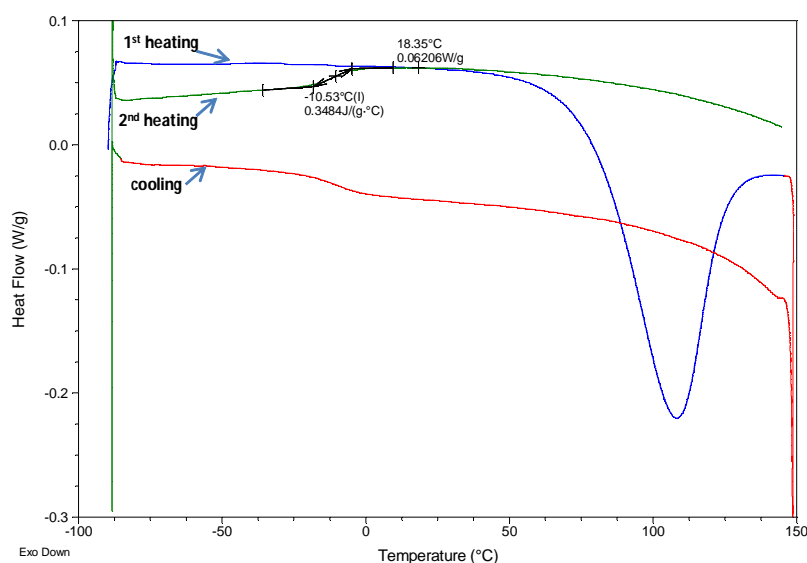


Figure 2. Non-isothermal DSC measurement at 2.5 K min⁻¹ from -80 to 150°C of a stoichiometric mixture of tetrathiol and HDI.

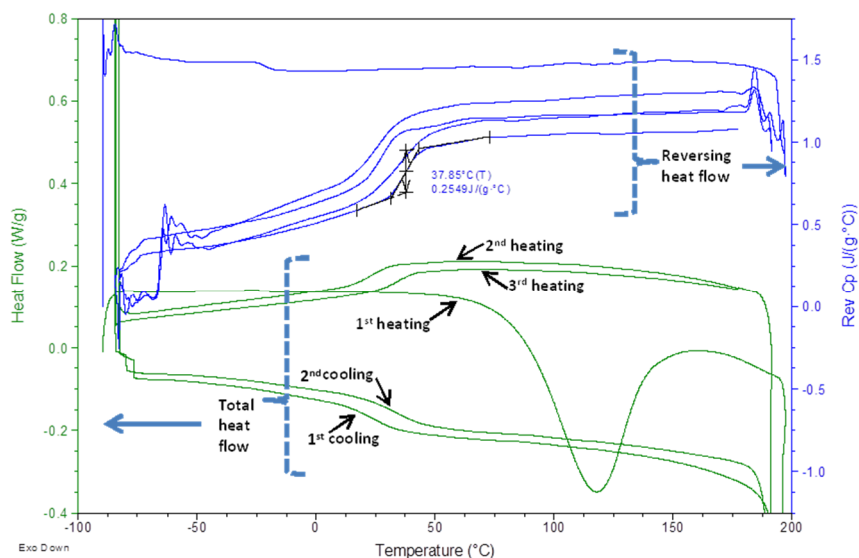


Figure 3. Non-isothermal DSC measurement at 2.5 K min^{-1} from -80 to 190°C of a stoichiometric mixture of tetrathiol and HDI (only heating scans are shown for reversing heating capacity).

To further investigate the curing thiol-isocyanate reaction, a series of isothermal measurements has been performed on the system (Figure 4). The heat flow signal of each measurement shows exothermic signals originating from the reactions. Upon increasing

the isothermal temperature, the reaction rates were increased considerably (the maximum peak height was obtained after more than 90 min at 60°C whereas only a few minutes at temperatures above 90°C). The total heat of the reaction was about 300 J g^{-1} .

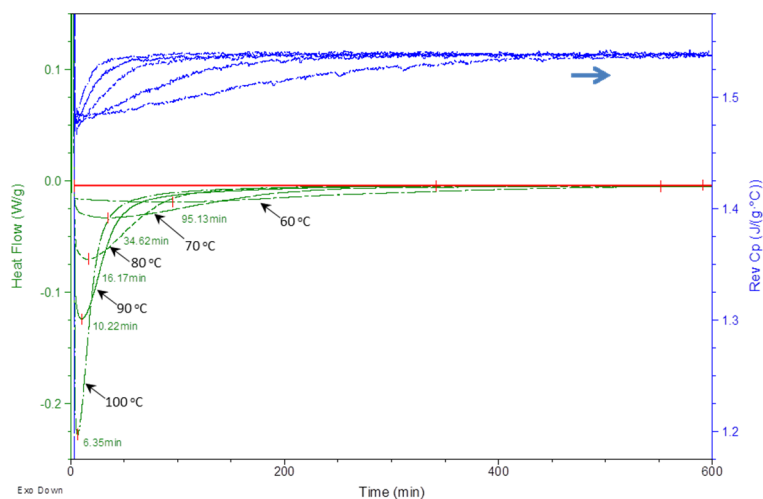


Figure 4. Isothermal TMDSC measurements at various temperatures of the stoichiometric mixture of tetrathiol and HDI.

After the isothermal TMDSC measurements, a series of heating and cooling cycles were performed. The first cycle was performed in order to investigate residual reaction. This could be due to time limitation. The second and third additional cycles were used to evaluate the final glass transition of the network, considering that the reaction has been complete. Figure 5 shows the additional heating scans (3 cycles) of the isothermal TMDSC measurements. From the first cycle DSC curves, the glass transition temperatures of the partially cured networks right at the end of the isothermal measurements range from about -10 °C to almost 25 °C. Because the glass transition temperature

of a thermosetting polymer system increases with increasing reaction conversion, this DSC result indicates that higher reaction conversions were obtained for isothermal DSC measurements at higher temperatures. On the other hand, the additional cycles after the second cycles for all samples almost overlapped with one another, showing one glass transition. Because the glass transition temperatures appeared the same in the third and second DSC scans (regarding the sample previously cured at 100°C), no further DSC scan was conducted. The main conclusion that can be drawn is the confirmation of the final glass transition temperature of about 35-38°C.

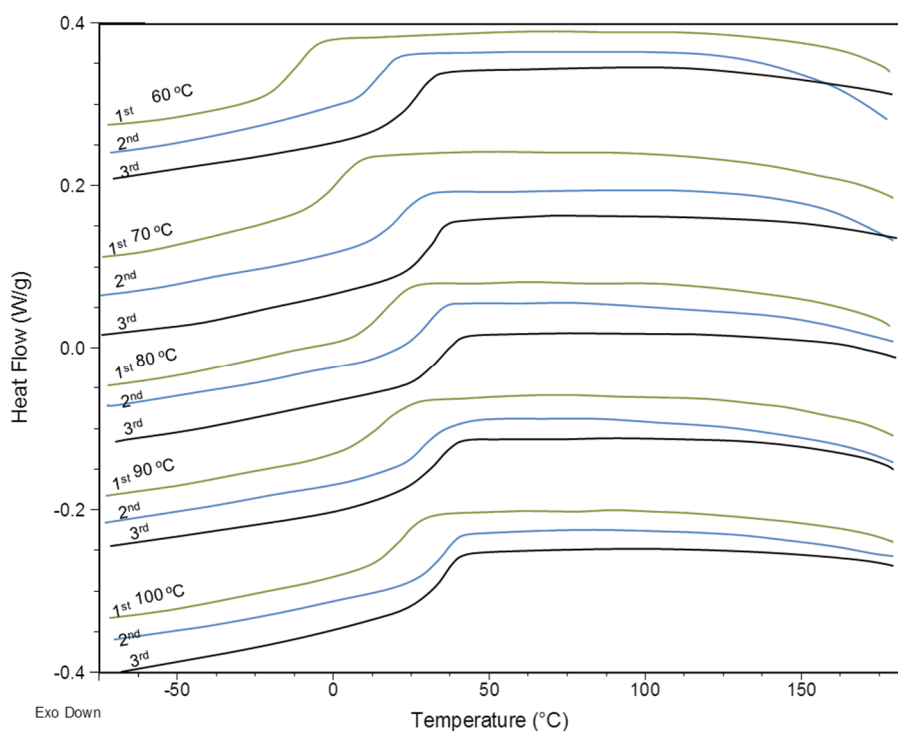


Figure 5. DSC heating scans after isothermal TMDSC measurements at different temperatures (60-100 °C, previously shown in Figure 4).

4. CONCLUSIONS

The kinetics of the model stoichiometric reaction between mono-functional thiol and isocyanate as well as the cross-linking reaction between a tetrathiol and diisocyanate were investigated, using in situ FT-IR and temperature-modulated DSC methods, respectively. The TMDSC analysis of the curing system showed that the thiol-isocyanate reaction was complete by heating at 2.5 K min^{-1} up to 170°C . The glass transition temperature of the cured system increased with increasing reaction conversion. The total heat of the reaction was about 300 J g^{-1} .

Isothermal heating of the reactant mixture at various temperatures from 60 to 100°C yielded partially cross-linked materials with glass transition temperatures varying from -10 to 25°C . The glass transition temperature of the finally cured system was found to be around 38°C .

Acknowledgments: This research was supported by project “TX2015-20-06/HĐ-KHCN” from Ho Chi Minh City University of Technology - Vietnam National University – Ho Chi Minh City, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam.

Nghiên cứu chuyển biến nhiệt bằng phương pháp DSC của sự hình thành mạng bằng phản ứng “click” thiol-isocyanate

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TÓM TẮT

Hóa học “click” thiol-isocyanate được sử dụng để tạo ra hệ polymer nối mạng mà không sử dụng dung môi và chất xúc tác. Khảo sát ban đầu, bằng phương pháp online FT-IR, mô hình phản ứng thiol-isocyanate được thực hiện để xác nhận các đặc trưng của phản ứng “Click”, nhằm khẳng định đặc tính “click” của phản ứng. Phương pháp “temperature-modulated differential scanning calorimetry” (TMDSC) đã được sử dụng để nghiên cứu đánh giá quá đặc tính quá trình và động học

của phản ứng nối mạng thiol-isocyanate giữa các chất phản ứng đa chức, cũng như sự chuyển pha thủy tinh của mạng polyme tạo thành. Theo sự hiểu biết của chúng tôi, nghiên cứu nhiệt lượng của hệ nối mạng thiol-isocyanate không chất xúc tác chưa từng được công bố trước đây. Các kết quả này có thể mở đường cho việc thiết kế và chế tạo các vật liệu polymer nhiệt rắn mới đáp ứng nhiều ứng dụng theo yêu cầu.

Từ khóa: Temperature-modulated DSC, thiol-isocyanate, click reaction.

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