# TG OF POLYTETRAHYDROFURAN/ISOPHORONEDIISOCYANATE REACTION PRODUCTS

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## Abstract

TG, swelling, and viscometric studies are presented for the residues, PTHF/IPDI polymer networks, and the extracts, the linear polymers and unreacted IPDI, after Soxhlet extraction of PTHF/IPDI reaction products. The products are obtained by reacting PTHF with 650, 1400, (2×650+1×2900), or 2900 of molecular mass with IPDI at various concentrations in bulk. The results on the swelling and the viscosity experiments suggest that the PTHF/IPDI reaction products have a usual expectable structure. All the TG curves are a double stage curve. The initial stage and the last stage seem to reflect decomposition of PTHF chains and vaporization of the remainder, IPDI, respectively. These are analyzed by a trial-and-error construction, supposing double event behavior. The values of ratio of mass loss associated with the initial event, $W0_1$, to the mass loss associated with the last event, $W0_2$, are smaller than the expectable those. This suggests that Event 2 involves vaporization of the decomposition products of PTHF moieties bonded to IPDI in addition to vaporization of IPDI.

**Keywords:** isophoronediisocyanate, polymer network, polytetrahydrofuran, reaction products, thermogravimetry

## Introduction

Polyether/diisocyanate reaction products are useful for polyurethane industry. Recently microcapsule researchers [1–3] are interested in research on polytetrahydrofuran (PTHF)/isophoronediisocyanate (IPDI) reaction products, because they have structural property suitable to a polyurethane backbone of ionomer. PTHF/IPDI reaction products contain many urethane linkages and a few allophanate bonds. Information on the allophanate bonds is important to fabrication of polyurethane, because the allophanate bonds sometimes contribute to formation of a polymer network [4]. This structural characteristic influences thermogravimetric (TG) data that are conducted in order to evaluate thermal stability of PTHF/IPDI reaction products in the industrial fabrication. PTHF and its derivatives are subject to thermal degradation [5–7]. This presentation is also trying to elucidate any relation between the thermal decomposition and the structure.

In the present paper, TG data are given for the residues after Soxhlet extraction of the products obtained by reacting PTHF with 640, 1400, (2×650+1×2900), or 2900 of molecular mass with IPDI at various concentrations in bulk, and are analyzed by a

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trial-and-error construction. The results of viscometry on the extracts solution and swelling experiment on the residues are presented in order to discuss characteristics of the residues. Relationships between TG parameters and molecular mass of PTHF or IPDI content are discussed, considering the results of the viscometry and the swelling experiment.

## Experimental

About 15 mL of PTHF with 650 (PTHF$_{650}$), 1400 (PTHF$_{1400}$), (2×650+1×2900) (PTHF$_{B1400}$), or 2900 (PTHF$_{2900}$) of molecular mass and IPDI were placed in flame-sealed glass tubes (20 mm diameter) at 1.0/1.0, 1.5/1.0, 2.5/1.0, or 3.0/1.0 of mole ratio. The reaction tubes were kept in 353 K thermostat for about 3 weeks. The linear polymers and excess IPDI were extracted with 100 mL THF for 5 h by using a Soxhlet extractor.

The TG experiment of the residues was performed, using a Perkin Elmer 7 series with UNIX TGA 7. A platinum TG pan was used and was flame-cleaned prior to each run. The TG data were recorded at the heating rates of 2, 5, 10 or 20 K min$^{-1}$ from a preheating temperature.

The intrinsic viscosity of the extracts solutions was measured by use of a Ubbelohde viscometer. The degree of swelling of the residues was determined from mass of the samples immersed in THF at 298 K till it becomes constant. The details are described elsewhere [8].

## Results and discussion

All the TG curves seem to be a separable double stage curve. There are reports on multiple stage TG curves for aromatic polyamides [9], polyimide [10], a polyvinyl alcohol [11], a lignin-based polycaprolactone [12], and aromatic polyethers [13], etc. Previously we proposed a procedure for determing the activation energy, frequency factor, and the order of events corresponding to the respective stages of the iso-conversional multistage TG curves for a polymethylmethacrylate [14]. However, in this study, we analyzed the TG curves recorded at the slowest heating rate (2 K min$^{-1}$) by a trial-error-construction within 1% root mean square of residues by use of the following rate equation and Doyle [15] approximation of $p$-function, because they are not isoconversional [16].

$$-\mathrm{d}W/\mathrm{d}t = kW^{n} \quad k = A\exp(-E/RT) \tag{1}$$

$$\ln p(y) \approx -5.331 - 1.052y \quad y = E/RT \tag{2}$$

where $W$, $t$, $n$, $A$, $E$, $R$ and $T$ denote the mass, the time, the order of event, the frequency factor, the activation energy, the gas constant, the temperature, respectively. The mass of an event is derived as a function of $n$, $A$, $E$ and $T$, from Eqs (1) and (2), using the heating rate, $a$, and the total mass of the event, $W0$. The overall mass is the sum of masses of Events 1 and 2:

$$W(T) = W_1(n_1, A_1, E_1, W0_1, T) + W_2(n_2, A_2, E_2, W0_2, T)$$

where subscripts 1 and 2 denote Events 1 and 2, respectively. A constant frequency factor was used for the products derived from PTHF with a same molecular mass. The resulting TG parameters are summarized in Table 1. All the $E_1$ values are close to those of PTHF. Therefore, Event 1 may be associated with a Shimha-type [17] random decomposition of PTHF chain. This is supported by the onset temperatures is close to that of PTHF. The order of Event 1 is not the 1$^{st}$ order that is the order of event in the thermal decomposition of common polymers, but is the 2$^{nd}$ order. The Event 1 may be influenced by migration rate of the decomposition products to the surface from the bulk. The Event 2 may be associated with vaporization of IPDI that remains alone after decomposition of PTHF chains, because the larger the $W0_2$, the larger the IPDI content in feed. The TG samples are the residues after the extraction and therefore, IPDI units in the samples are attached to the polymers. If polymer chains are linear, $W0_1/W0_2$ values of PTHF$_{2900}$/IPDI, PTHF$_{1400}$/IPDI, and PTHF$_{650}$/IPDI are 13.0, 6.3 and 2.9, respectively. Table 2 shows all the values of $W0_1/ W0_2$. Contrary to the above expectation, the $W0_1/W0_2$ values increase with decreasing molar mass of PTHF. Except for PTHF$_{2900}$/IPDI (IPDI/PTHF=1.5), the degree of swelling and the intrinsic viscosity are almost constant as shown in Figs 1 and 2. This suggests that the length of oligourethane chain between cross-links is constant and independent of the IPDI content in feed and the molecular mass of PTHF. The excess of IPDI is considered to become pendent IPDI units with one isocyanate and one allophanate bond. The presence of such IPDI units is possible, because two isocyanates groups of IPDI have reactivity different from each other [3]. The deviation of results on PTHF$_{2900}$/IPDI (IPDI/PTHF=1.5) may be reflecting critical criteria of formation of cross-links. Now, we have to discuss the problem, 'why is $W0_2$ value of the products derived from PTHF$_{2900}$ larger'. The structure of samples is usual, as mentioned above. We cannot find the reasonable cause except Event 2 involves vaporization of the decomposition products of PTHF moieties attached to IPDI, in addition to vaporization of IPDI.
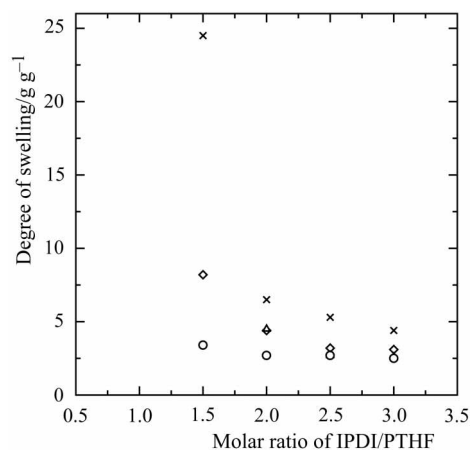


**Fig. 1** Plots of the degree of swelling *vs.* the value of IPDI/PTHF molar ratio in feed for o − PTHF$_{650}$/IPDI, △ − PTHF$_{1400}$/IPDI, ◇ − PTHF$_{B1400}$/IPDI and × − PTHF$_{2900}$/IPDI

**Table 1** TG parameters

| PTHF event | Molar ratio | 650 | | | | 1400 | | | | B1400 | | | | 2900 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1.5 | 2.0 | 2.5 | 3.0 | 1.5 | 2.0 | 2.5 | 3.0 | 1.5 | 2.0 | 2.5 | 3.0 | 1.5 | 2.0 | 2.5 | 3.0 |
| 1 | $A_1/s^{-1}\,g^{-1}$ | | $9.4 \cdot 10^{11}$ | | | | $4.2 \cdot 10^{11}$ | | | | $3.6 \cdot 10^{11}$ | | | | $6.83 \cdot 10^{10}$ | | |
| | $E_1/kJ\,mol^{-1}$ | 157 | 155 | 154 | 155 | – | 151 | 151 | 150 | 154 | 154 | 153 | 152 | 146 | 146 | 144 | 146 |
| | $n_1$ | | | | | | | | 2 | | | | | | | | |
| | $W0_1/w\%$ | 65.0 | 70.0 | 72.5 | 75.0 | – | 40.0 | 41.5 | 47.0 | 30.0 | 37.5 | 40.0 | 45.0 | 13.5 | 17.5 | 20.0 | 25.0 |
| 2 | $A_2/s^{-1}$ | | $3.5 \cdot 10^{19}$ | | | | $3.8 \cdot 10^{19}$ | | | | $3.8 \cdot 10^{19}$ | | | | $4.1 \cdot 10^{19}$ | | |
| | $E_2/kJ\,mol^{-1}$ | 267 | 268 | 269 | 268 | – | 271 | 271 | 270 | 270 | 270 | 271 | 270 | 270 | 270 | 270 | 270 |
| | $n_2$ | | | | | | | | 1 | | | | | | | | |
| | $W0_2/w\%$ | 35.1 | 30.0 | 27.5 | 25.0 | – | 60.0 | 58.5 | 52.5 | 70.0 | 62.5 | 66.0 | 55.0 | 86.5 | 82.5 | 80.0 | 75.0 |

Molar ratio is the value of IPDI/PTHF molar ratio in feed
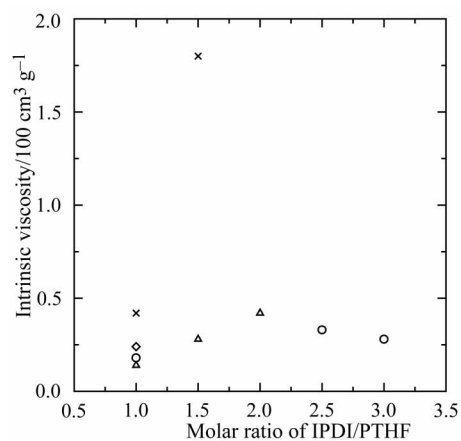
**Fig. 2** Plots of the intrinsic viscosity *vs.* the value of IPDI/PTHF molar ratio in feed for
o – PTHF$_{650}$/IPDI, △ – PTHF$_{1400}$/IPDI, ◇ – PTHF$_{B1400}$/IPDI and
× – PTHF$_{2900}$/IPDI

**Table 2** The values of $W0_1/W0_2$

| PTHF | Molar ratio | $W0_1/W0_2$ | | | |
|---|---|---|---|---|---|
| | | 1.5 | 2.0 | 2.5 | 3.0 |
| 2900 0.33 | | | 0.16 | 0.21 | 0.25 |
| B1400 0.82 | | | 0.43 | 0.60 | 0.67 |
| 1400 0.90 | | | – | 0.67 | 0.71 |
| 650 3.00 | | | 1.85 | 2.33 | 2.64 |

Molar ratio is the value of IPDI/PTHF molar ratio in feed

## Conclusions

The TG curves of the remainder, the polymer networks, obtained by Soxhlet extraction are a double-stage curve and are inapplicable to the isoconversional method. Thermogravimetric parameters obtained by a trial-and-error construction provide structural information on the polymer networks, and particularly, $W0_1/W0_2$ values reflect overall amount of IPDI, amount of pendent IPDI, amount of urethane bond in the main chain, and etc. The degree of swelling of the samples and the intrinsic viscosity of the extracted solutions are independent of the IPDI content in feed and the molecular mass of PTHF. This is one of bases that the above conclusions are derived by.

It may be concluded that TG measurements of PTHF/IPDI reaction products are very useful for polyurethane industry.

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