

Studies on the effect of extraction of isophorone diisocyanate-based segmented polyurethanes

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Abstract. Linear segmented polyurethane was synthesised, using isophorone diisocyanate (IPDI), poly(tetramethylene oxide) glycol (PTMG) and 1,4 butanediol, for use in biomedical applications. The chemical stability of this polyurethane in hot methanol during Soxhlet extraction was studied by viscosity measurements, thermal studies, mechanical tests, ultraviolet and infrared spectral studies, and gel permeation chromatography. Hot methanol degrades the polymer at the allophanate linkages, while extracting low molecular weight polyurethane fractions. More urea linkages are formed in the extracted polymer.

Keywords. Polyurethane; isophorone diisocyanate; extraction; degradation; allophanate linkage.

1. Introduction

Polyurethanes embrace the greatest variety of elastomers, plastics, foams, coating materials etc and are the fastest growing segment of the polymer market. For biomedical uses aliphatic diisocyanates have an advantage over aromatic diisocyanates in yielding polymers which do not discolour rapidly in sunlight or degrade in UV light (Ulrich *et al* 1980; Frisch 1969). Isophorone diisocyanate (IPDI) is a cycloaliphatic diisocyanate which is recently being used for the synthesis of polyurethane. Khaub and Camberlin (1986) have prepared new polyurethane based on IPDI, poly(tetramethylene oxide) glycol (PTMG) and aromatic diamines. In the present work we have prepared a fully aliphatic segmented polyurethane based on IPDI, PTMG and 1,4-butane diol. Ono *et al* (1985) have found that the reactivity of the -NCO groups of IPDI is different owing to steric factors. The stability of the segmented IPDI-based polyether-urethane towards extraction medium such as methanol is expected to be different because of the differential reactivity of -NCO groups. Methanol has been considered as a good extraction vehicle for removing oligomers etc. from polyurethane for biomedical use. Bruck (1980) has found approximately 4–5% leachable components removed with boiling methanol after prolonged extraction of segmented polyurethane. (Cleaning of polymeric material is mandatory.) There are reports that the low molecular weight leachable fractions diffuse out of the polymer in a biological environment in long term use causing a

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cytotoxic effect (Borchard 1981; Guidoin *et al* 1980). The stability of IPDI-based polyurethane with allophanate linkages in extraction medium is not investigated yet. Therefore greater emphasis was placed on the synthesis of segmented aliphatic polyurethane with allophanate linkages based on IPDI and to study chemical stability during extraction with methanol.

2. Experimental

IPDI (Chemik He Werro Hcls, West Germany), poly(tetramethylene oxide) glycol, PTMG (Polymeg[®] 990, 2010, QO Chemicals, USA) and 1,4-butane diol (1,4-BD) (Sarabai Chemicals) were vacuum-dried before use. Distilled dimethylacetamide and tetrahydrofuran were used as solvents for synthesis and film casting, respectively. Dibutyl tin dilaurate was used as catalyst.

The polymers were synthesized by the prepolymer method. IPDI and PTMG were taken in the reaction flask in an N₂-atmosphere, and 0.1% catalyst was added. The exothermic reaction led to a maximum temperature of 120–130°C. After 100 minutes the reaction mixture was cooled to room temperature and the chain extender (butane 1,4-diol) was added. The reaction mixture was then maintained at 60°C for 30 minutes. The polymer was transferred to a glass plate kept in an oven at 60°C and cured for a period of 3 days.

All the polymers were similarly synthesized by varying the composition of the reactants with excess mole fractions of diisocyanate (table 1). The cured polymers were extracted thrice for 180 min with carbon tetrachloride and then once for 60 min with methanol using a Soxhlet extractor. The polymer samples (I – IPDI-based polyurethanes) were characterised before and after extraction.

A model IPDI polymer containing allophanate linkages was prepared by reacting IPDI, polypropylene glycol (mol. wt. 400) and butane diol with an excess of 1 mole of IPDI under the same conditions as above. The model polymer was extracted with methanol as described earlier.

Viscosity measurements were carried out using an Ubbelohde viscometer. Intrinsic viscosity was determined at 26°C using polymer solutions of concentration 1.5, 1.2, 0.9 and 0.6% prepared in dimethyl acetamide. The intrinsic viscosity of the polymers was found out before and after extraction.

Thermal properties were determined using a thermal analyser (M/s. Du Pont Instruments). Differential thermal analyses (DTA) of the polymers were carried out

Table 1. Composition of polyurethanes.

Polyurethane	IPDI (mol)	PTMG (mol)	1,4-BD (mol)	NCO/OH	Excess NCO (mol)
I ₃	0.06	0.01 (990)*	0.03	1.5	0.020
I ₄	0.05	0.01 (990)	0.03	1.25	0.010
I ₆	0.075	0.0125 (2010)	0.05	1.2	0.0125

* The molecular weight of the polyol is given in parentheses
I – IPDI-based polyurethane

at a heating rate of 10°C/min. A sample weighing approximately 10 mg was heated from room temperature to 300°C. Fine grade glass beads supplied by M/s. Du Pont Instruments (USA) were used as the reference for DTA analyses. Thermogravimetric (TGA) analyses were carried out at a heating rate of 10°C/min for temperatures ranging from the ambient to 600°C. Gel permeation chromatographic (GPC) analysis was carried out (Water Associates, USA) using a μ -styragel column (10³, 10⁴, and 10⁵ Å) and a 280 nm UV filter. Dimethylacetamide was used as the mobile phase.

Tensile properties were determined by the ASTM D 882 method using an Instron universal testing machine. Six specimens were used for each sample.

Ultraviolet spectra of all the samples were recorded using a Hitachi 220 UV-visible spectrophotometer. The scan speed was 20 nm/min. A 1% solution in ethanol free from benzene and a cell path length of 1 cm were used for the spectral analysis.

Infrared spectral analyses of all the polymer samples were carried out on a Perkin Elmer Infrared spectrophotometer - 597. The polymer samples were cast on a sodium chloride window using THF. The regions 1550–1750 cm⁻¹ were recorded in expanded form with high concentrations.

3. Results and discussion

The chemical stability of the newly synthesized segmented polyurethane with allophanate linkages towards the extraction medium methanol can be visualized from the viscosity data (table 2). All the polymer samples attain low intrinsic viscosity after extraction. It may be due to fragmentation of the polymer chain during extraction. The fragmentation may be either a cleavage at the polyurethane backbone or at the crosslinks of the polymer. Such changes in macromolecular structure can be followed from spectral and GPC studies. Ratner (1981) has reported that methanol-acetone extraction degrades the polymer at the urethane -NH-C(=O)- linkage. Bruck (1980)



also reported that boiling methanol degrades the polymer at the urethane linkage to give carboxylic acid-terminated polyamides and low molecular weight polyurethanes which are subsequently extracted from the polymer. In the present studies, investigations are confined to the extracted polymer. The present investigations are aimed at possible attack on the allophanate linkage during the extraction.

The IR spectra of the extracted polymer (figure 1) indicates the possible changes in the molecular structure. IR spectral peaks are noticed for the stretching frequency of

Table 2. Properties of polyurethane before and after extraction.

Polymer	Intrinsic viscosity (dl/gm)		Tensile strength (kg/cm ²)		Elongation (%)		GPC retention time (min)	
	Before	After	Before	After	Before	After	Before	After
I ₃	0.120	0.021	31.72	25.87	375.5	172.5	0	31.4
I ₄	0.159	0.027	27.27	*	302.5	*	0	32.4
I ₆	0.210	0.054	†	39.2	†	704.4	0	30.8

* Too brittle to test; † Too soft to test

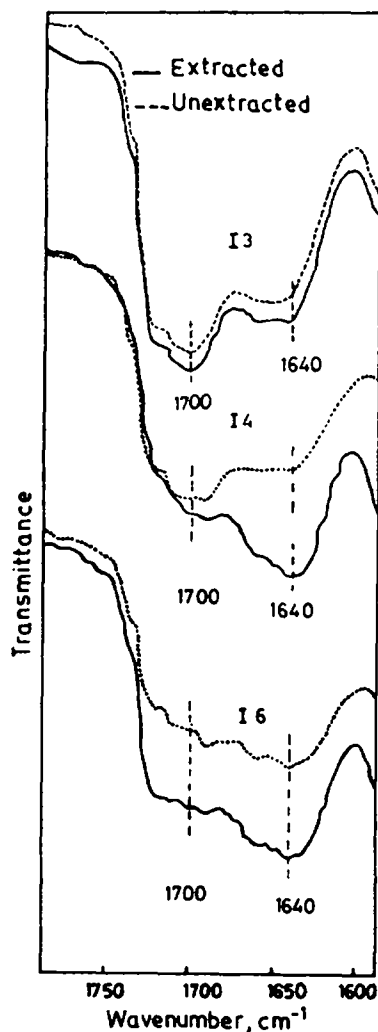


Figure 1. IR spectra of the polymers.

the urethane, allophanate and urea linkages. The samples before extraction have a broad band in the range $1600\text{--}1750\text{ cm}^{-1}$ with an intense peak around 1700 cm^{-1} characteristic of urethane and allophanate linkages. We found spectral variations for I_3 , I_4 and I_6 samples mostly in their percentage transmittance. No major variation is found in peak position. The variation in percentage transmittance is due to compositional variations in the present three polymers. The three monomers (i.e.) diisocyanate, polyol and diol were varied to get different physicochemical properties. After extraction of the polymers, the intensity of the peak at 1700 cm^{-1} reduces with an increase in intensity of the peak at 1640 cm^{-1} , which is characteristic of the urea linkage. Comparatively the I_4 sample shows an appreciable change with a good peak at 1640 cm^{-1} .

This is not clearly seen in I_3 and I_6 samples. This is mainly because the degree of allophanate linkage in I_4 should certainly be lesser than in I_3 under the same

experimental conditions; I_3 and I_4 samples were prepared with excess of 0.02 and 0.01 mole diisocyanate respectively. It can be reasoned that the period of extraction is sufficient to convert the allophanate linkages of I_4 sample to urea linkages.

The chemical changes in the polymer during extraction were further verified with UV spectral analyses. All the samples after extraction exhibit additional peaks at around 290 nm with a high absorbance, $E_{1\text{cm}}^{1\%}$, value characteristic of the transition of the carbonyl group (table 3 and figure 2).

Gel permeation chromatographic analyses were used to verify further the chemical changes in the polyurethane. The extracted polymer exhibits a peak with retention time (table 2 and figure 3). The verification with polystyrene standards (Waters Associates, USA) shows that the peaks with their corresponding retention time are equivalent to low molecular weight polyurethane. It is worth noting that these peaks are detected by a GPC UV detector with 280 nm UV filter. No such peaks are detected for any samples before extraction. This indicates that the extracted polymers alone contain GPC-UV (280 nm) detectable molecular chains. Based on IR, UV and GPC analyses it is inferred that methanol induces chemical degradation along with the removal of leachable components during extraction with the Soxhlet extractor; such chemical degradation could be at the allophanate linkage to form the linear urea linkage.

The degradation of the allophanate linkage of the present IPDI polyurethane was further investigated using model reactions involving IPDI, polyol and butane diol. The model polymer was analysed by IR spectral analyses. The peak at 1710cm^{-1} indicates the allophanate linkages in the model polymer (figure 4). David and Staley (1969) had attributed the peak at 1710cm^{-1} to allophanate linkage. It is generally formed with the addition of excess diisocyanate in the reaction mixture (Frisch 1969; Saunders and Frisch 1964). The peak at 1710cm^{-1} for model IPDI polyurethane is remarkably noticeable in comparison with the test polyurethanes. This is because of the higher degree of allophanate linkage formed in the model polyurethane. The model polyurethane was prepared with an excess 1.0 mole of diisocyanate. Since the reactivity of the primary isocyanate of IPDI is 3 times lower than that of its secondary isocyanate the stability of the urethane linkage in these sites is also considerably different (Cunliffe *et al* 1985; Hatada *et al* 1987). The IR spectrum of the extracted model polymer indicates the shift towards the peak at 1640cm^{-1} due to the formation of urea linkage (figure 4); the intensity of the peak at 1710cm^{-1} is decreased appreciably.

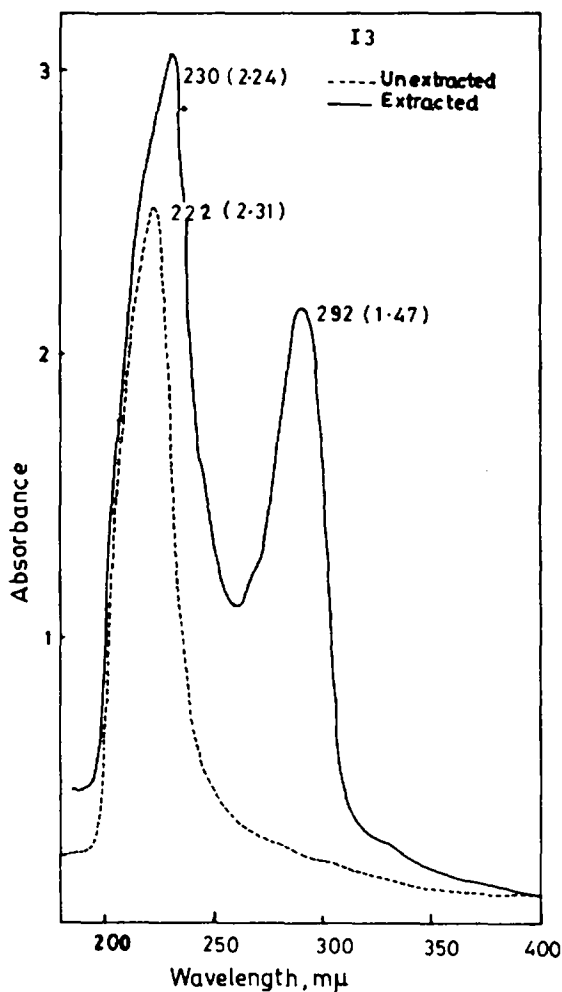
During the Soxhlet extraction with methanol, the polyurethane undergoes two changes. (i) Chemical attack on the polyurethane macromolecule, and (ii) extraction of leachables and degradation products. The present investigation on the extracted polyurethane confirms that the allophanate linkages of the test IPDI polyurethanes undergo dissociation during Soxhlet extraction to give urea linkages along with the generally known degradations (Bruck 1980; Ratner 1981) and the extraction of low molecular weight fractions derived from such reactions.

The formation of a urea linkage from the allophanate linkage during the extraction with methanol is suggested as shown in figure 5 (R, R¹ indicate the growing chain). During methanol extraction the allophanate linkage breaks to form the unstable carbamic acid end and then forms the urea linkage.

The thermal properties of the extracted polymers are given in figures 6 and 7 and in table 4. A representative TGA thermogram is shown in figure 6 for the I_4 polymer. All

Table 3. UV absorptions (nm) of extracted polyurethane samples.

Samples	$\lambda_{\max}(E_{1\text{cm}}^{1\%})$	
	Before	After
I ₃	222 (2.31)	(i) 230 (2.24) (ii) 292 (1.47)
I ₄	228 (2.38)	(i) 235 (1.86) (ii) 280–295 (2.21)
I ₆	229 (2.31)	(i) 231 (2.24) (ii) 291 (1.75)

**Figure 2.** UV spectra of the polymers [numbers on the curve refer to wavelength while those in parentheses are $E_{1\text{cm}}^{1\%}$ values].

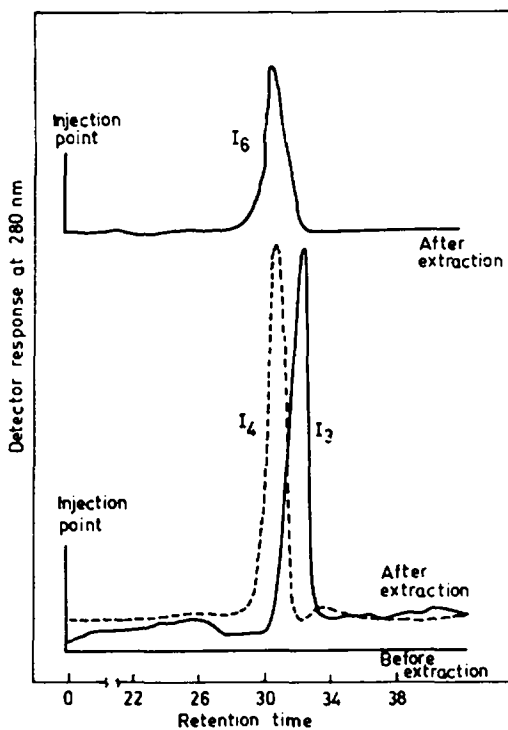


Figure 3. GPC chromatograms of the polymers.

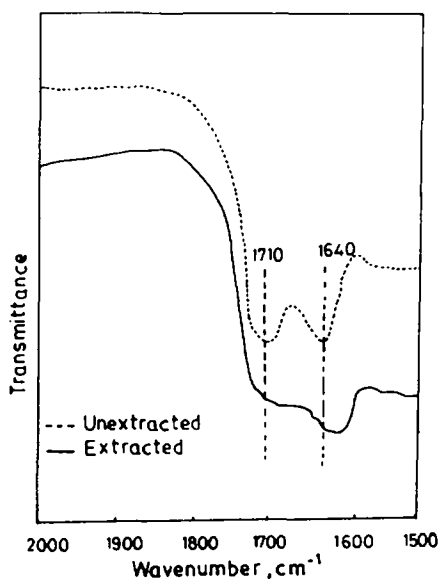


Figure 4. IR spectra of the model IPDI polymers.

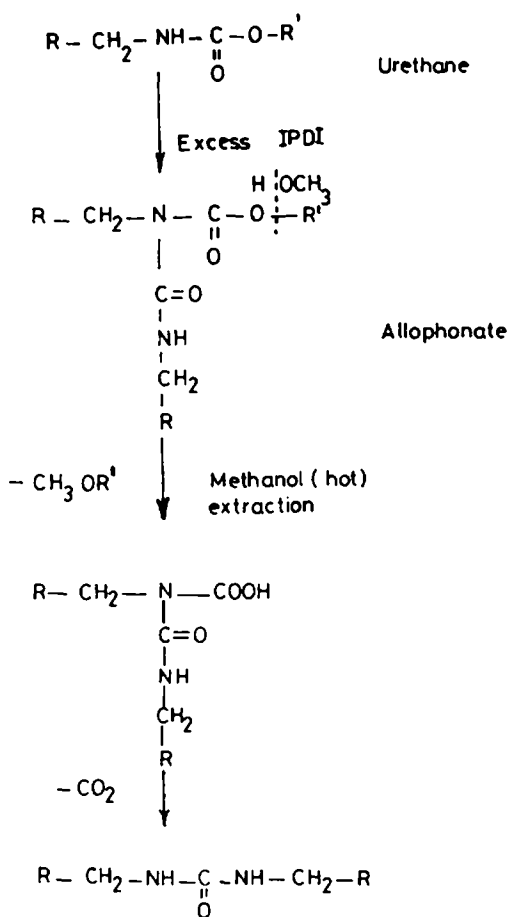


Figure 5. Formation of the urea linkage in the extracted polymers (R and R' refer to the growing chains).

the extracted polymers undergo a three-step decomposition. Interestingly the second-step decomposition temperature (T_{d2}) of the extracted polymers decreases as compared to that of the unextracted polyurethanes. The third-step of the decomposition, as denoted by its temperature T_{d3} , is observed for all the extracted polymers. The DTA thermograms are given in figure 7. The unextracted polymers I_4 and I_6 exhibit sharp endothermic peaks on softening. I_3 sample exhibits a broad softening peak. However the extracted I_3 , I_4 and I_6 samples exhibit a broad peak on softening. The data are given in table 4. The peaks appearing at lower temperatures disappear after extraction. The softening point for I_4 and I_6 samples is distinctly increased after extraction. The thermal properties of the extracted polymer confirm the macromolecular changes introduced in the extracted polymers.

The mechanical properties of the extracted polymers are given in table 2. Interestingly the I_4 sample becomes brittle after extraction. This is attributed to the fact that methanol also extracts the degraded and low molecular weight fragments as indicated earlier. On the other hand, the I_6 polymer prepared with high molecular

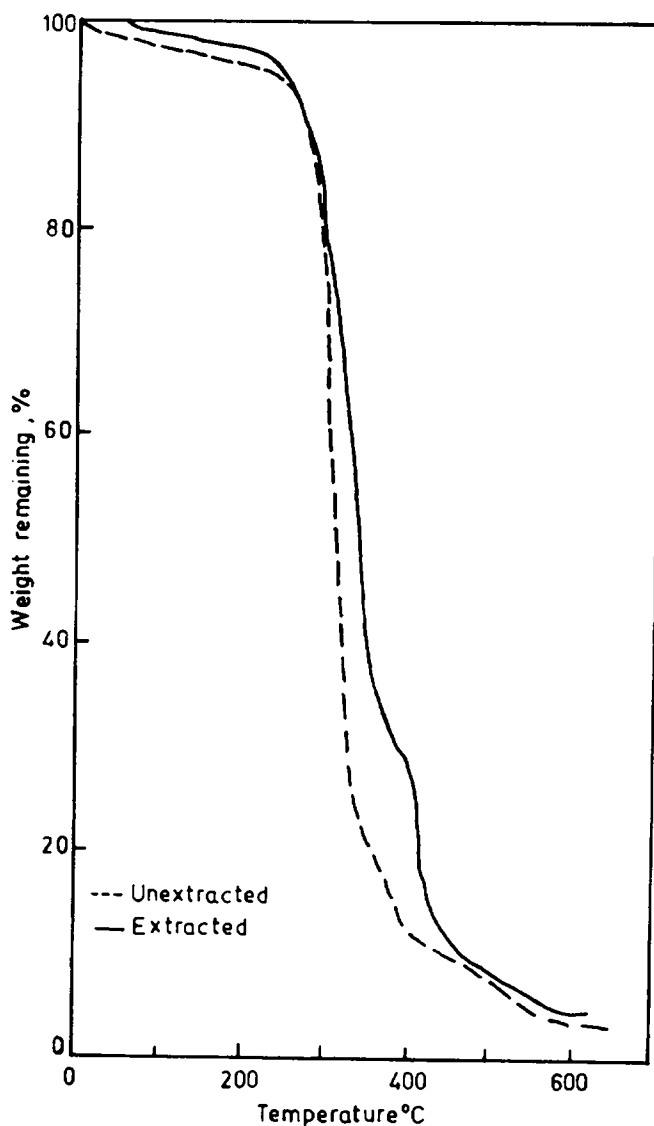


Figure 6. TGA thermograms of the I₄ polymer.

weight polyol (2010) showed an increase in tensile properties mainly due to the loss of low molecular weight fractions. Before extraction, the I₆ sample contains higher amounts of low molecular weight fractions. This is evident from the appearance of many peaks due to low molecular weight fractions in the softening range in the DTA thermogram and the disappearance of these peaks after extraction.

In conclusion, the studies on the extracted IPDI-based polyurethane indicate that the methanol not only attacks urethane linkages as observed by Bruck (1980) and Ratner (1981), but also leads to chemical degradation at the allophanate linkage during degradation. The extracted polymer exhibits different thermal and mechanical properties due to the formation of a linear structure with urea linkages.

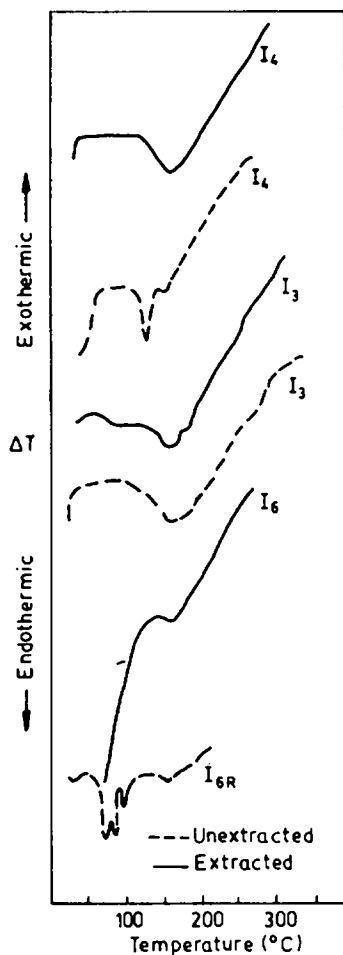


Figure 7. DTA thermograms of the polymers.

Table 4. Thermal properties of polyurethane before and after extraction.

Sample	Before					After				
	Softening point (°C) from DTA scan		Decomposition temperature (°C) (weight loss %) from TGA scan			Softening point (°C) from DTA scan		Decomposition temperature (°C) (weight loss %) from TGA scan		
	Inception	Peak	Td_1	Td_2	Td_3	Inception	Peak	Td_1	Td_2	Td_3
I ₃	95	160	315 (83.2)	505 (16.4)	—	112.5 (62.5)*	160	330 (74)	400 (18.8)	520 (6.8)
I ₄	100	115, 140	295 (88)	485 (8.8)	—	100	150	312 (68)	395 (20)	495 (8)
I ₆	50	75, 95, 115	330	500	—	140	150	310 (58)	410 (30.8)	500 (9.6)

* Endothermic

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