

# Chlorinated Polyurethanes Based on 2,4-Toluenediisocyanate: Thermal Analysis and Flammability Evaluation

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**ABSTRACT:** A series of polyurethanes based on 2,4-toluenediisocyanate (TDI), with different amounts of 3-chloro-1,2-propanediol (CPDO), have been prepared. The process of thermal degradation was monitored by thermogravimetric analysis (TGA) alone or coupled with infrared spectroscopy (TGA/FTIR) and differential scanning calorimetry (DSC). Flammability of the polymers was determined using the oxygen index (OI) method. The influence of CPDO on the thermal decomposition parameters [e.g., initial decomposition temperature (IDT), char residue at 500°C, and DTG-max-temperature] and on the OI values have been discussed. Some correlations between thermogravimetric data and OI values were found, thus making it possible to apply the TGA method for certain flammability predictions of modified polyurethanes. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1465–1471, 1998

**Key words:** chlorinated polyurethanes; flammability; thermal analysis

## INTRODUCTION

Thermal degradation and flammability of polyurethanes have been a subject of numerous papers.<sup>1–4</sup> Because of a great number of application areas of different polyurethane systems, these materials were investigated by means of various laboratory-scale methods to provide a measure of their flammability, which itself is a very complex phenomenon. Four main processes are considered to be involved in polymer flammability: (1) preheating, (2) decomposition, (3) ignition, and (4) combustion and propagation. The last process is believed to be composed of a vapor phase in which the reactions responsible for the formation and propagation of the flame are taking place and a condensed phase in which fuel for the gas reac-

tions is being produced. According to this approach, flame retardancy can be improved by appropriately modifying either one or both of these phases.<sup>5</sup>

For evaluation of flammability of polymeric materials, several test methods have been developed so far, such as the oxygen index (OI) method,<sup>6</sup> the Factory Mutual fire test apparatus,<sup>7</sup> and the cone calorimeter.<sup>8</sup> Under the conditions of these techniques, a specimen is exposed to a constant heat flux and such data as the evolved gases produced by the burning specimen and mass loss are analyzed. The underlying principle common to these chemical heat release measurement techniques involves exposing a specimen in a furnace to a calibrated heat flux. This principle can be applied to the thermogravimetric analyzer, which is used through its display of the thermal degradation profile of minute samples to acquire fundamental information about burning material. Even more information can be obtained if the coupling of thermogravimetric analysis (TGA) with

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**Table I** Description of the Samples

Sample	3-Chloro-1,2-propanediol (mol %)	1,2-Propanediol (mol %)	POEOD (mol %)
1	0	80	20
2	20	80	0
3	20	60	20
4	20	40	40
5	20	20	60
6	40	40	20
7	40	20	40
8	60	20	20
9	80	20	0
10	80	0	20
11	100	0	0

evolved product analysis performed with a Fourier transform infrared (FTIR) spectrometry is used. A unique feature of this system is its ability to provide continuous monitoring of the IR spectra of evolving product as well as quantitative analysis of gases. In contrast to pyrolysis GC, in which all the gases produced by heating to a given temperature are separated and analyzed as a batch, TGA/FTIR offers the great advantage of sequentially identifying the gases for a comprehensive vapor-phase analysis.

It was decided to explore the feasibility of monitoring the degradation profile of this type of polyurethane and to examine first the effect of the amount of chlor-containing diol on the flammability and thermal decomposition.

## EXPERIMENTAL

### Materials

Polyurethanes used in the course of this work were prepared according to the method described in ref. 3. 3-Chloro-1,2-propanediol (Aldrich, Steinheim, Germany) and polyoxyethyleneoxidediane (POEOD, from ICSO, Kędzierzyn-Koźle, Poland) were used as received. The description of the samples is given in Table I.

### TGA

TGA was performed on a Derivatograph-C (MOM, Hungary) thermal analyzer, operating in a dynamic mode at a heating rate of 10 K/min. The conditions were: sample weight, ~ 10 mg; atmo-

sphere, air; temperature range, 25–500°C, reference material, Al<sub>2</sub>O<sub>3</sub>.

### TGA Coupled with FTIR Spectroscopy

TGA coupled with FTIR spectroscopy was carried out using a Perkin–Elmer 7 thermogravimetric analyzer (heating rate, 50 K/min; sample weight, ~ 15 mg; nitrogen flow, 50 cm<sup>3</sup>/min), and a Perkin–Elmer 1725X FTIR spectrometer. The thermogravimetric analyzer and spectrometer were suitably coupled to enable the passage of evolved products from the furnace to the gas cell over a short path, to minimize secondary reaction or condensation on cell walls. Moreover, the experimental conditions have been chosen to ensure that the condensable products form a submicron aerosol mist. This size aerosol has two advantages: (1) the particles follow the gas stream lines, thus minimizing condensation, and (2) the particles produce little scattering in the mid-IR, so the condensable products can be analyzed online in the FTIR cell.

### Differential Scanning Calorimetry

For the DSC measurements a Netzsch DSC 200, operating in a dynamic mode, was employed. A sample of ~ 4 mg weight was placed in sealed aluminum pan. The heating rate of 10 K/min was applied as the best choice to ensure high resolution of the DSC curves. Prior to use the calorimeter was carefully calibrated with an indium standard; an empty aluminum pan was used as reference.

**Table II Characteristics of the Samples**

Sample	$M_n$ (g/mol)	$M_w$ (g/mol)	$M_w/M_n$	Oxygen Content (%)	OI
1	1465	4569	3.12	27.22	18.50
2	1696	4442	2.62	26.15	19.03
3	1859	7078	3.81	25.43	—
4	2142	7608	3.55	23.73	—
5		Not soluble in THF		22.52	20.69
6	2448	7068	2.89	24.10	19.02
7		Not soluble in THF		22.26	25.49
8	2779	12960	4.66	24.88	—
9	1310	2310	1.76	24.18	—
10	2074	6415	3.09	24.47	24.00
11		Not soluble in THF		23.91	23.01

### Oxygen Index

Oxygen index measurements were performed on a standard flammability test apparatus, according to the procedure described in ref. 6.

### Gel Permeation Chromatography (GPC)

Molecular weight was determined by GPC performed at 25°C on a Knauer 64 GPC System with a refractometric detector, with two PL-Gel Mixed-E columns. Tetrahydrofuran was used as the eluant at a flow rate of 0.8 cm<sup>3</sup> min<sup>-1</sup>, and sample concentration was 5 mg cm<sup>-3</sup>. Polystyrene standards (Waters) were used to construct a calibration curve. GPC data were processed using a CHROMA program to calculate average molecular weights,  $M_n$  and  $M_w$ , as well as polydispersity,  $M_w/M_n$ . These data are summarized in Table II.

### Elemental Analysis

C, H, N analysis was done using a Perkin–Elmer 240 elemental analyzer. Cl content was determined by the Schoeniger method.<sup>9</sup>

## RESULTS AND DISCUSSION

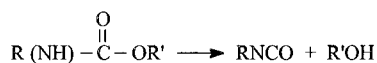
Results of TGA revealed that the degradation profiles of polyurethanes under investigation depend on the structure of macromolecules and can be described with different values of the thermal parameters, which are collected in Table III.

It can be seen that the initial decomposition temperature (IDT) ranges from 106 to 206°C, reaching its highest value for sample 7, containing 40% of chlorinated diol. Besides, the end temperatures of the first mass loss step are similarly correlated, indicating the stabilizing action

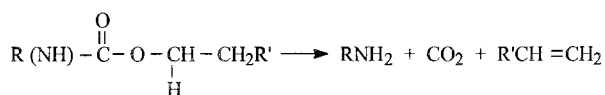
**Table III Results of the Thermogravimetric Analysis of Samples**

Sample	IDT (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{30\%}$ (°C)	$T_{50\%}$ (°C)	Char Residue (%)	$T_{\text{end}}$ of 1 <sup>st</sup> Step (°C)	DTG-max-temp. (°C)
1	143	186	251	265	278	20	176	267
2	106	154	265	285	304	24	148	300
3	134	208	255	267	300	27	166	274
4	113	159	265	289	313	26	203	295
5	183	204	258	271	340	31	231	270
6	188	245	266	279	360	34	205	265
7	192	206	263	279	370	34	219	276
8	178	240	263	274	339	32	190	269
9	115	139	250	263	300	31	160	270
10	189	199	265	275	313	33	215	275
11	186	246	265	273	321	32	193	274

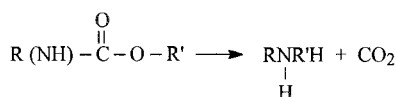
## I. Dissociation to isocyanate and alcohol



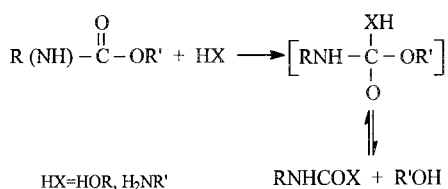
## II. Formation of primary amine and olefin



## III. Formation of secondary amine



## IV. Transesterification type bimolecular displacement



Scheme 1

of adequate amounts of halogen derivative on the propagation of initial decomposition. On the other hand, condensed-phase processes can be suitably described by means of a "static" parameter, that is, the amount of char residue formed on the thermal degradation. This was the highest for samples 6 and 7, containing 40% chloropropanediol. Although it is well known that the polymers based on aromatic and other cyclic structures produce high char yields on thermal degradation, there is no generalization about the structure (substituent) effect on the char yield of polymer. For instance, a —Cl group on the benzene ring may not affect the char yield (e.g., in polystyrene), or may increase the char (e.g., in epoxies), and in some cases (e.g., aromatic polyamides) the char yield may even be reduced. The influence of a substituent on char residue depends on its type and position, the polymer, and its mode of degradation.<sup>10</sup> Studies on the thermal decomposition of polyurethanes made it possible to find out the main degradation mechanisms, outlined in Scheme 1.<sup>11</sup> The propensity for a particular mechanism depends on the chemical nature of the groups adjacent to the urethane linkage and the environmental conditions.

There has been evidence found for each of the mechanisms outlined in Scheme 1. It may also be postulated that at a certain stage of thermal dissociation not only one degradation process occurs—such "mixed" mechanisms are often the rate-determining factors in cases of many solid state reactions.<sup>12</sup> They can be distinguished by kinetic analysis, assuming first a model-free determination of (apparent) activation energy.<sup>13</sup>

In order to gain a deeper look into the degradation mechanism, a coupling of TGA with FTIR was used. The information which can be gained is twofold: FTIR spectra of volatiles at given degradation temperatures may be obtained; secondly, Gram-Schmidt chromatograms showing intensity of gas products evolution are produced. Generally, evolved gas profiles, obtained by the Gram-Schmidt orthogonalization method, are of similar type (Fig. 1).

They indicate on a two-step degradation process. The FTIR spectrum, taken at the maximum of the first peak (after 3 min), consists of several absorption bands (Fig. 2) which can be attributed to the absorption bands of saturated C—H (3000  $\text{cm}^{-1}$ ),  $\text{CO}_2$  (2400  $\text{cm}^{-1}$ ), C=O (1760  $\text{cm}^{-1}$ ), —OH bending (1400  $\text{cm}^{-1}$ ), and C—O stretching (1250 and 1070  $\text{cm}^{-1}$ ).

The second peak may be associated with an intensive evolution of  $\text{CO}_2$ , as shown in Figure 3.

These observations support mechanisms I and II from Scheme 1 and lead to the conclusion that there occurs a mixed decomposition mechanism which may be strongly influenced by external factors, such as geometry of structural elements and irregularities in the polymer chain. These factors, which often cannot be separated one from another, are of primary importance both for diffusion- and reaction-controlled processes.

From the DSC analysis, which was also widely used to characterize the thermal transitions of polyurethanes, one can find heat-flow versus temperature profiles of samples under investigation. They were of similar type, with a degradation endotherm commencing from ~ 160–180°C (Fig. 4).

DSC curves may be analyzed in regard to the gaseous combustible products formation since this process is always connected, depending on external conditions, with heat release or absorption. Such analysis is crucial for investigation of efficiency of some flame retardants which are known to function predominantly in the vapor phase, but certain problems arise with the proper

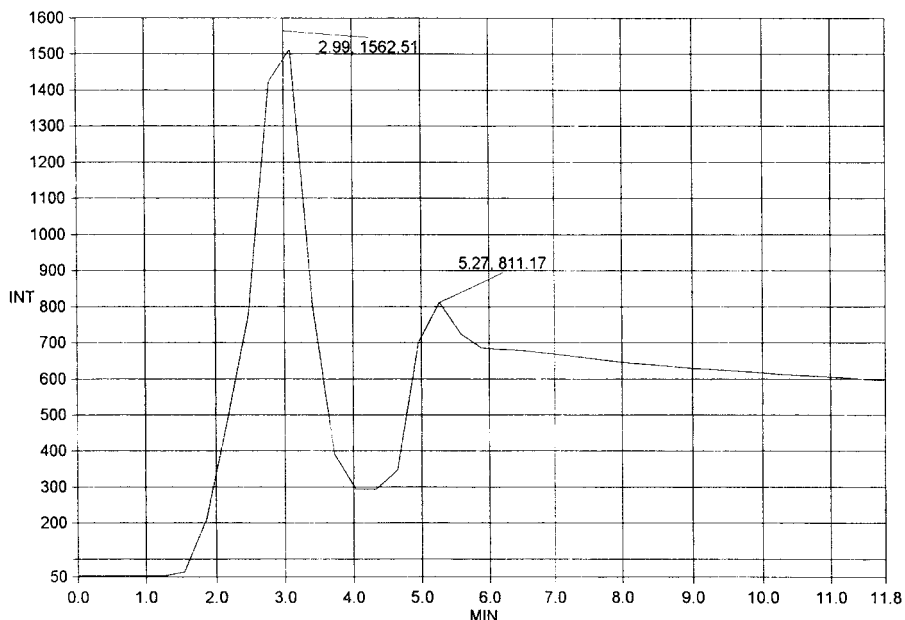


Figure 1 A Gram-Schmidt chromatogram of sample 6.

determination of heat of combustion ( $\Delta H_c$ ) and  $T_{onset}$  of the combustion process.

Taking into account results of oxygen index determination and thermogravimetric data one can find some correlations between them, thus enabling predictions of flammability on the basis of TGA only. OI values increase with an increase of IDT and temperature of 30% mass loss (Fig. 5); they are also correlated with the amount of char residue and DTG-max-temperature (Fig. 6).

An analytical description of the relationships which are presented in Figures 5 and 6 is the following:  $OI = 0.528 [IDT (^\circ C)] - 75.647$ ;  $0.616 [T_{30\%} (^\circ C)] - 145.830$ ;  $1.582 [Char\ residue (\%)]$

$- 28.139$ ;  $0.786 [DTG-max-temp. (^\circ C)] - 191.731$ . This applied for polyurethanes based on TDI, 3-chloro-1,2-propanediol, and/or propanediol, investigated by TGA under definite experimental conditions.

CONCLUSIONS

It has been shown that for a series of polyurethanes containing chloropropanediol it is possible to apply TGA for evaluation of flammability. The process of thermal dissociation, followed by TGA/FTIR, seems to proceed through a complex path-

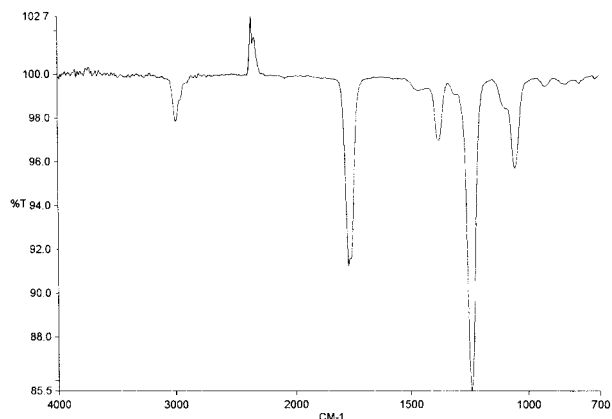


Figure 2 FTIR spectrum of sample 6 after 3.0 min.

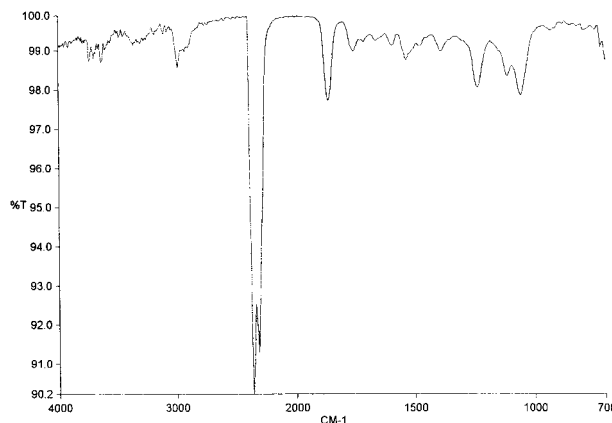


Figure 3 FTIR spectrum of sample 6 after 5.3 min.

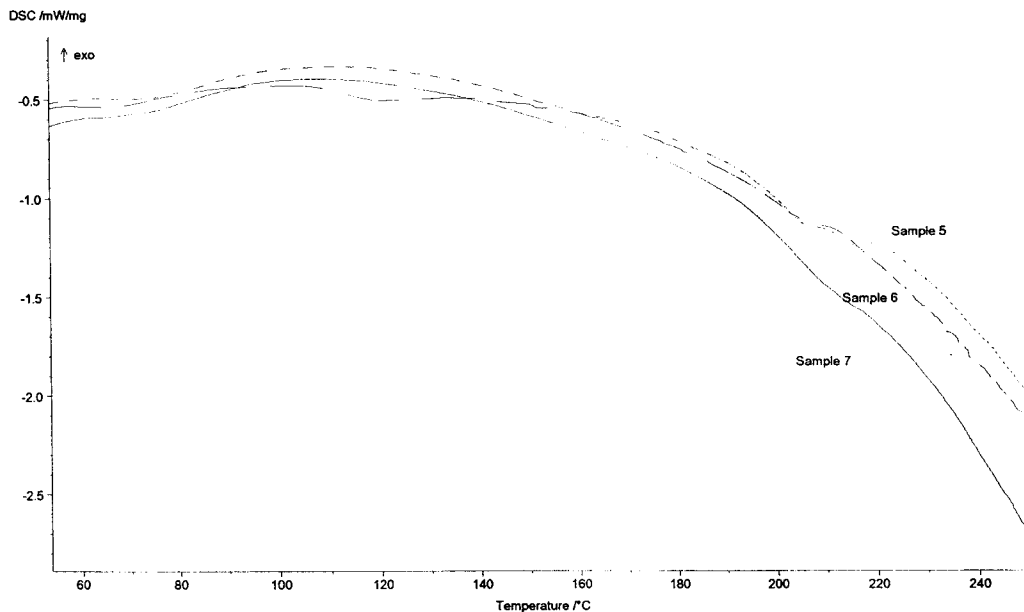


Figure 4 DSC curves at 10 K/min of samples 5–7.

way, including dissociation to isocyanate and alcohol, as well as formation of primary amine and olefin. It can be assumed that above the degradation temperature some molecular rearrangements occur, as displayed through Gram–Schmidt and FTIR profiles. Introduction of chlorinated diol caused an increase of the thermal stability and slightly changed the DSC profiles, suggesting dif-

ferent hard and soft segments distribution in comparison to diol-based polyurethanes. This may be of particular interest in the processing of RIM systems that have undergone premature phase separation. By breaking the urethane bonds in those precipitated hard segment domains, the soft segments may then be incorporated to increase the molecular weight and form a highly interconnected morphology with better flame resistancy.

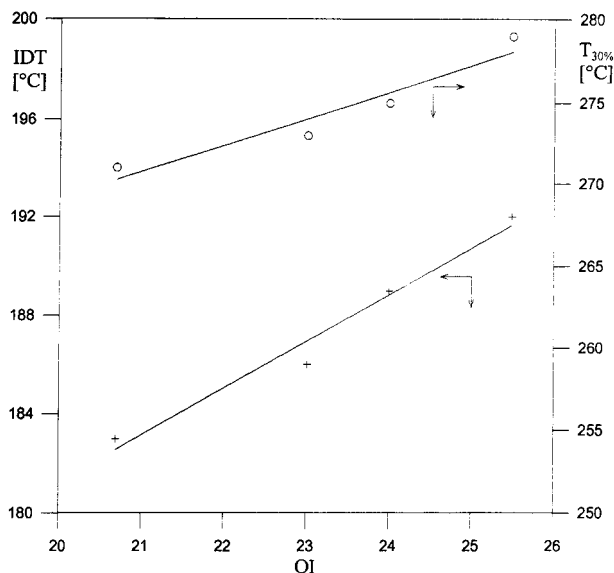


Figure 5 OI versus IDT and  $T_{30\%}$ .

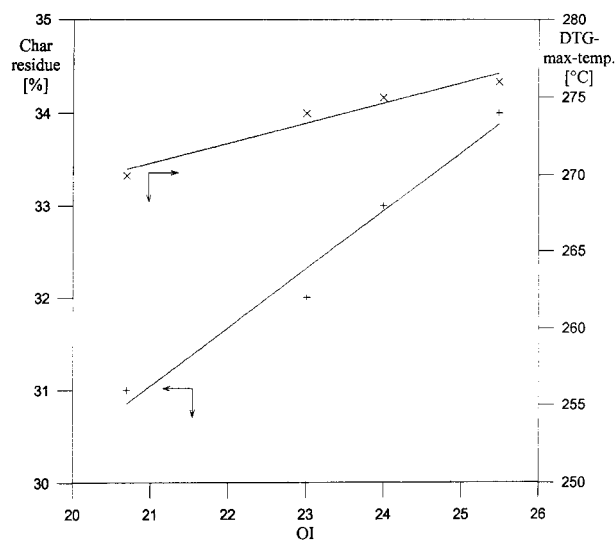


Figure 6 OI versus DTG-max-temp. and char residue.

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