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Flame-resistant modified segmented polyurethanes with 3-chloro-1,2-propanediol in the main chain—thermoanalytical studies

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Abstract

In this study, a series of segmented polyurethanes based on 4,4′-diphenylmethane diisocyanate (MDI), polyoxypropylenediol (POPD) and low-molecular chain extenders: 1,2-propanediol (PD) or 3-chloro-1,2-propanediol (CPD) has been obtained by one-step polyaddition. The thermal properties were investigated by thermogravimetric method in both isothermal and dynamic mode. The relation between the amount of 3-chloro-1,2-propanediol in the polyurethane's structure and the maximum temperature of first derivative of thermogravimetric analysis (TG) profile (DTG) has been described. For further characterisation of the thermal behaviour of modified polyurethanes under investigations thermogravimetric analysis coupled with Fourier-transform infra-red (FTIR) spectroscopy or mass spectrometry (MS) were used. The main decomposition products, including CO_2, amines and aliphatic ethers, were identified on-line. Comparison of the intensity of evolution of $[CH_2=NH_2]^+$ ion ($m/z = 30$), which can be associated with primary amines, has shown that there is a correlation between the amount of chlorine in PU structure and the intensity of amines' formation during the main decomposition step around 300 °C.
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1. Introduction

Segmented polyurethanes are a group of widely used materials as coatings, binder resins and high-performance elastomeric products [1,2]. They derive most of their useful properties from the incompatibility of soft and hard segments and subsequent microphase separation; besides, the hard-segment domains act as physical cross-links for the soft-segment matrix [3].

One of the few drawbacks of polymers with such complex morphology is their low thermal stability and flammability governed primarily by the heat liability of the urethane groups is dependent upon the substituents on these groups [4]. The highest degradation temperature (ca. 250 °C) is observed for urethane formed from alkyl isocyanate and alkyl alcohol, followed by an aryl isocyanate–alkyl alcohol combination (degrading at about 200 °C), an alkyl isocyanate and aryl alcohol (stable up to 180 °C), and an aryl–aryl combination whose temperature limit is in the 120 °C range.

Low thermal stability and flammability seriously limit the number of new applications, hence, an extensive research is performed to flame retard these polymers [5,6]. One of the approaches is to incorporate an 'additive' or 'reactive' flame retardant into polymer. The 'additive' flame retardant is physically mixed with the parent polymer either prior to, during or right after polymerisation—there is no chemical bonding between the flame retardant and parent polymer. The second group of flame retardants, the 'reactive' ones, will react with other monomer units by polymerisation, polycondensation or polyaddition reaction. Since they are chemically bonded to the polymer backbone, bleeding and volatilising out of the polymer are prevented, enhancing thus their action in comparison to the 'additive' ones [7].

The aim of this work was to investigate the degradation process of a series of novel modified segmented polyurethanes based on 4,4′-diphenylmethane diisocyanate (MDI), polyoxypropylenediol (POPD) and low-molecular chain extenders: 1,2-propanediol (PD) or 3-chloro-1,2-propanediol (CPD). These polymers containing 3-chloro-1,2-propanediol as a constitutional repeat unit in the main chain are inherently flame-retarded materials as described in detail elsewhere [8,9].

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2. Experimental

2.1. Materials

For synthesis of segmented polyurethanes, partially polymerised 4,4′-diphenylmethane diisocyanate (31% of free isocyanate groups in relation to the pure MDI) (Zachem Bydgoszcz, Poland), polyoxypropylenediol ($M = 750$) (Rokita S.A., Brzeg Dolny, Poland), 1,2-propanediol (POCh, Gliwice, Poland) or 3-chloro-1,2-propanediol (Aldrich, Steinheim, Germany), and 1-allyl-2-methylimidazole (catalyst) (Zachem) were used. Ethyl acetate (POCh) was purified by distillation and used as a solvent during polymerisation.

2.2. Preparation

Segmented polyurethanes were prepared by a one-step method, according to the general procedure: into a thermostated reactor first put isocyanate (MDI) and solvent (ethyl acetate); next, a mixture of diols (POPD and low-molecular chain extenders: PD or CPD) with catalyst was added dropwise under mixing within 30 min; temperature of the exothermal polyaddition did not exceed 60 °C. The obtained highly viscous polymer was placed into an open mould and dried for 7 days.

Detailed description of the synthesised samples is given in Tables 1 and 2. Isocyanate/sum of diols ratio was determined equivalently.

2.3. Technique

2.3.1. Thermogravimetric analysis

Thermogravimetric analysis (TG) was performed on a Netzsch TG 209 thermal analyser, operating in a dynamic mode at a heating rate of 10 K min^{-1} or in an isothermal mode for 150 min. The conditions were: sample weight, ca. 5 mg; atmosphere, argon; open α-Al$_2$O$_3$ pan.

2.3.2. Thermogravimetric analysis coupled with Fourier Transform infra-red spectroscopy

Thermogravimetric analysis coupled with Fourier transform infra-red spectroscopy (TG-FTIR) was carried out using a Mettler-Toledo TGA/SDTA 851 thermal analyser (heating rate = 20 K min^{-1}, sample weight ca. 2 mg, nitrogen flow = 50 cm^3 min^{-1}) and a JASCO 610 FTIR spectrometer.

2.3.3. Thermogravimetric analysis coupled with mass spectroscopy

Thermogravimetric analysis coupled with mass spectroscopy (TG-MS) was performed with a TA Instruments DTA-TGA 2960 SDT and a Balzers ThermoStar quadrupole mass spectrometer at a heating rate of 20 K min^{-1} under helium atmosphere (flow rate = 100 cm^3 min^{-1}). Sample mass was ca. 3 mg. The mass spectrometer was connected to the thermobalance via a capillary coupling. The ionising voltage of the cross-beam electron impact ionisation source was 70 eV.

The thermogravimetric analyser and spectrometer were suitably coupled to enable the passage of evolved products from the furnace to the gas cell over a short path, to minimise 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: (i) the particles follow the gas streamlines, thus minimizing condensation and (ii) the particles produce little scattering.

3. Results and discussion

Thermogravimetric results in dynamic mode show that polyurethanes under investigation are thermally stable up to 225 °C ($T_{10\%}$) and the decomposition proceeds in one step.

It is noteworthy that the char residue for samples 2–4 is lower than for sample 1 that shows that vapour-phase process prevail over condensed-phase reactions. As it will be seen later, vapour-phase reactions are investigated in detail by hyphenated thermal analysis–spectroscopic methods.

Results of thermogravimetric analysis under isothermal conditions, displayed in Fig. 1 for representative sample 3, show that there are no unexpected thermal effects that occur when a sample is subjected to elevated temperature for a given time; so we investigated the thermal processes by dynamic methods.

Table 1
Samples description

Sample	Diols content (%)		
	POPD	PD	CPD
1		60	0
2	40	40	20
3		20	40
4		0	60

Table 2
Results of thermogravimetric analysis of samples 1–4 at heating rate of 10 K min^{-1}

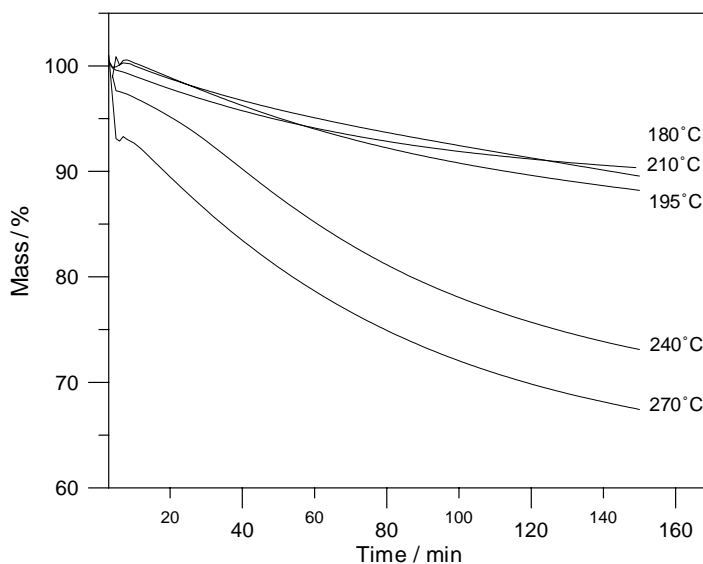| Sample	ID $T_{2\%}$ (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{30\%}$ (°C)	$T_{50\%}$ (°C)	Char residue (%)	DTG$_{max}$ (°C)
1	127.5	227.6	273.8	297.0	412.2	39.5	276.5
2	126.6	224.9	278.8	300.7	404.6	36.1	288.4
3	129.4	224.6	281.0	301.4	415.2	37.4	285.2
4	134.6	234.9	284.8	299.8	414.8	36.1	287.6

Fig. 1. Thermogravimetric profiles of sample 3 under isothermal conditions.

Based on TG data, one can observe the relation between the amount of 3-chloro-1,2-propanediol in the polyurethane's structure and the maximum temperature of first derivative of TG profile (DTG), Fig. 2.

It can be seen that introduction of CPD into the polyurethane structure results generally in an increase of the DTG_{max} temperature; one can assume that CPD is preferentially located in hard segments—it is believed that the thermal decomposition starts at hard phase where urethane groups (which are the less stable linkages in polyurethane backbone) are mainly placed [10]. Analysis of the data presented in Fig. 2 indicates that addition of more than 20% of CPD does not increase the DTG_{max} temperature; it is probably connected with the structural features of the multiphase PU morphology. Soft segments form a flexible matrix between the hard domains that in turn provide physical cross-linking, a complex, phase-segregated morphology can be observed that varies with the temperature [11].

Next, in order to gain a deeper look into the mechanism of decomposition, thermogravimetric analysis coupled with Fourier-transform infra-red spectroscopy was used. This technique allows the on-line identification of the volatile products by providing continuous monitoring of the IR spectra. Stacked plot of the FTIR spectra of the decomposition products of sample 1 is presented in Fig. 3.

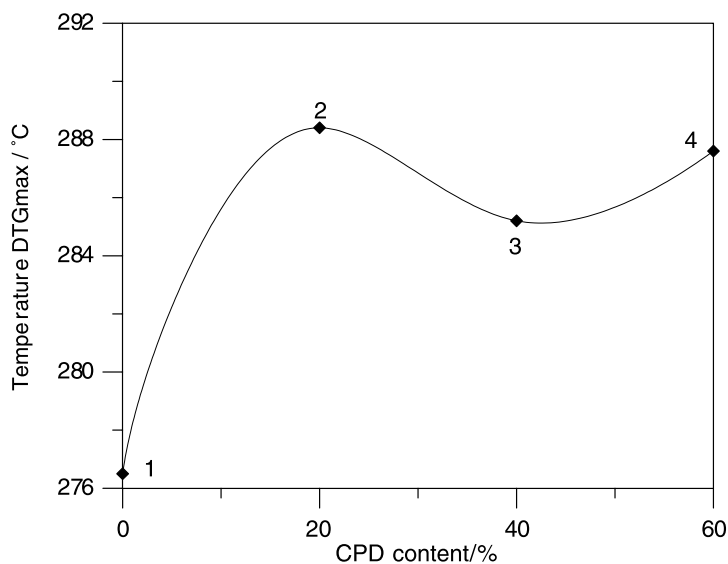At 270 °C one observes absorption bands of C–H stretching in CH_2 or CH_3 (2990 cm^{-1}), CO_2 bands (2352 and
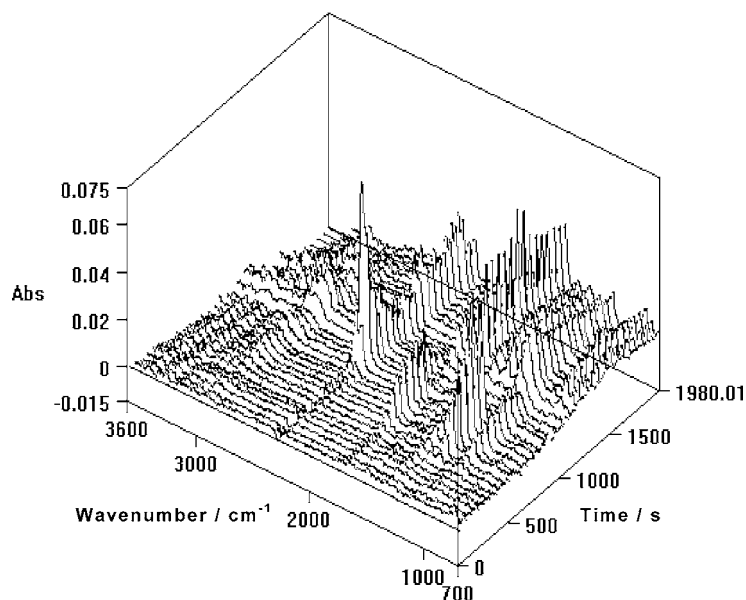

Fig. 2. DTG_{max} vs. CPD amount for samples 1–4.

Fig. 3. Stacked plot of FTIR spectra taken during the decomposition of sample 1.

2311 cm^{-1}), C=O stretching in carbonyl group (1766 cm^{-1}), C–H def. in CH$_2$ or CH$_3$ (1379 cm^{-1}), C–O stretching in esters (1239 cm^{-1}) and C–O stretching in aliphatic esters. Intensity of CO$_2$ emission reaches its maximum at 289 °C; above 300 °C evolution of amines (N–H stretching: 3361, 3400, and 3479 cm^{-1} and N–H def.: 1621, 1513, and 819 cm^{-1}) and aliphatic ethers (1104 cm^{-1}) can be observed in Figs. 4 and 5.

Chambers et al. performed investigations of the thermal properties of ^{13}C labelled MDI-based polyurethane and found that HCN and all the other nitriles, generated during high temperature decomposition, originate in the thermal fission of the aromatic ring, the nitrile-carbon being the 2-, 4-, or 6-carbon of MDI [12].

Evolution of volatile decomposition products of sample 2 diminishes as it can be seen in Fig. 6.

CO$_2$ evolution that can be regarded as a measure of the rate of decomposition displays maximal intensity at 237 °C [13]. Again, above 300 °C characteristic absorption bands of amines are present, but their intensity is lower than in case of sample 1. Similar trend was observed for other samples of modified segmented PU.
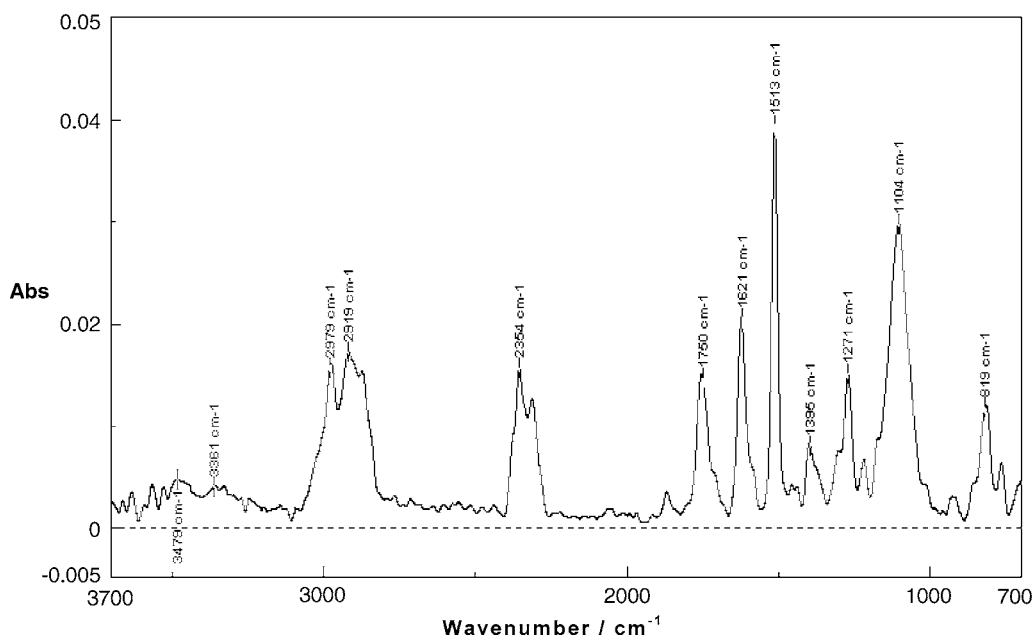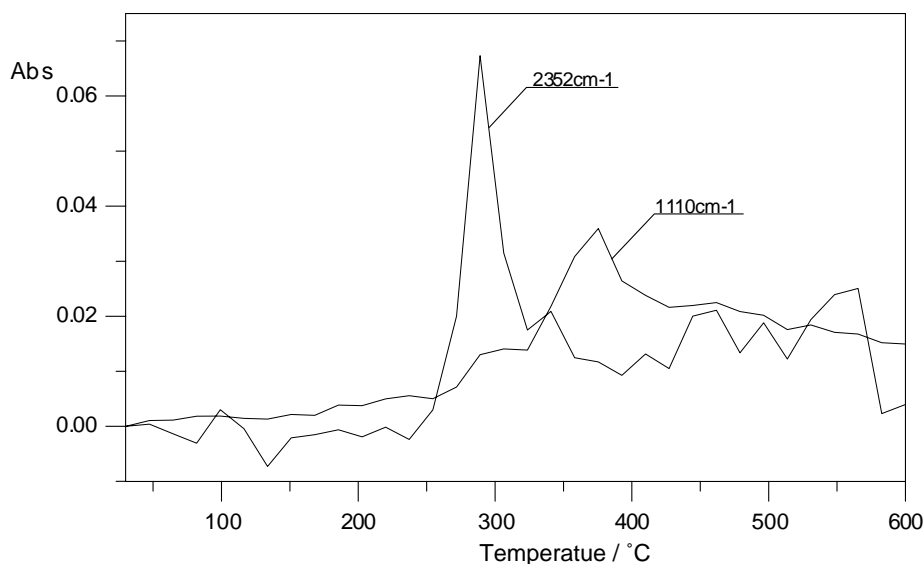

Fig. 4. FTIR spectrum of sample 1 at 375 °C.

Fig. 5. Intensity changes of 2352 and 1110 cm^{-1} bands during thermal treatment of sample 1.

The obtained results have been confirmed by thermogravimetric analysis coupled with mass spectroscopy. The main decomposition fragments detected were: CH_2 ($m/z = 14$), CH_3 ($m/z = 15$), O ($m/z = 16$), OH ($m/z = 17$), H_2O ($m/z = 18$), H_3O ($m/z = 19$), C_2H_2 ($m/z = 26$), HCN ($m/z = 27$), C_2H_4 (or CH=NH) ($m/z = 28$), aldehydes ($m/z = 29, 43, 57$), amines ($m/z = 30, 44, 58$), ethers ($m/z = 31, 45$), Cl ($m/z = 35, 37$) and CO_2 ($m/z = 44$), as it can be seen in mass spectrum of selected volatile products at 310 °C for sample 4 (Fig. 7).

Generally, the PU decomposition mechanism can be described as it is shown in Scheme 1.

Comparison of the intensity of evolution of $[CH_2=NH_2]^+$ ion ($m/z = 30$) during degradation of samples 1–4, which can be associated with primary amines, presented in Fig. 8, shows that there is a correlation between the amount of chlorine in TPU and the intensity of amines' formation (mechanism II in Scheme 1) during the main decomposition step around 300 °C.

Grassie and Zulfigar have suggested that based on the fact that weight loss under nitrogen never catches up with that under vacuum it may be assumed that not only are certain degradation products, which are volatile at degradation temperatures, inhibited by the nitrogen from diffusing out of the polymer but that during their retention in the degrading polymer they may undergo secondary reactions which generate non-volatile products [14]. Another evidence for diffusion control that was observed could be the appearance
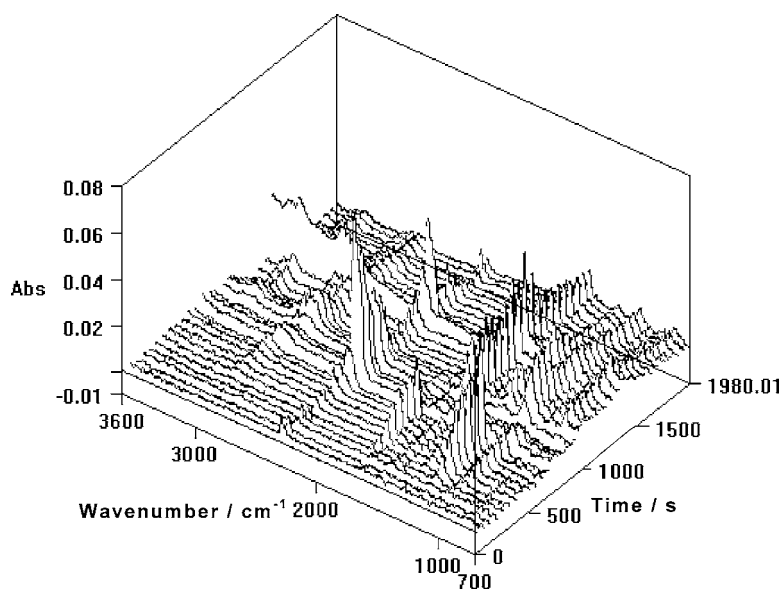

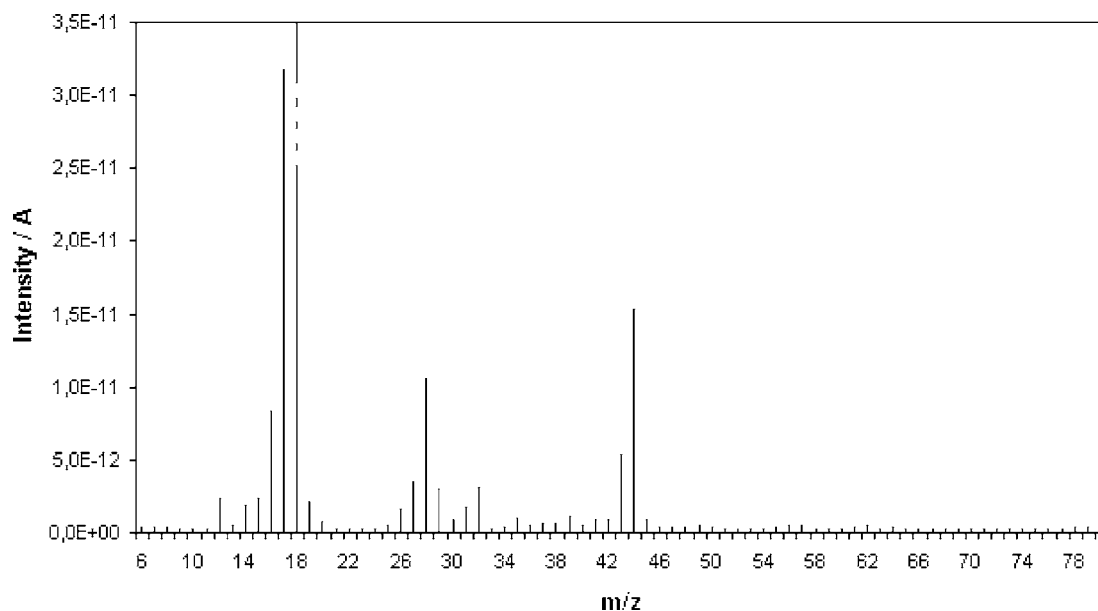Fig. 6. Stacked plot of FTIR spectra taken during the decomposition of sample 2.
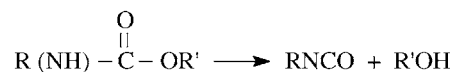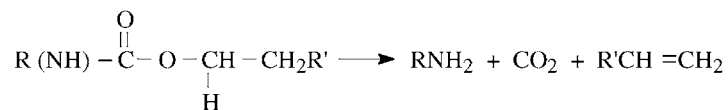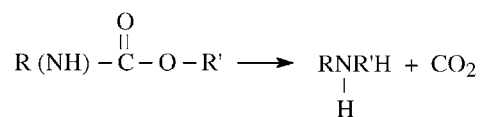
Fig. 7. MS spectrum of sample 4 at 310 °C.

I. Dissociation to isocyanate and alcohol

$$R\,(NH) - \overset{\overset{O}{\|}}{C} - OR' \longrightarrow RNCO + R'OH$$

II. Formation of primary amine and olefin

$$R\,(NH) - \overset{\overset{O}{\|}}{C} - O - \underset{\underset{H}{|}}{CH} - CH_2R' \longrightarrow RNH_2 + CO_2 + R'CH = CH_2$$

III. Formation of secondary amine

$$R\,(NH) - \overset{\overset{O}{\|}}{C} - O - R' \longrightarrow \underset{\underset{H}{|}}{RNR'H} + CO_2$$

IV. Transesterification type bimolecular displacement

$$R\,(NH) - \overset{\overset{O}{\|}}{C} - OR' + HX \longrightarrow \left[RNH - \overset{\overset{XH}{|}}{\underset{\underset{O}{|}}{C}} - OR' \right]$$

$$\Downarrow$$

$$HX = HOR, H_2NR' \qquad RNHCOX + R'OH$$
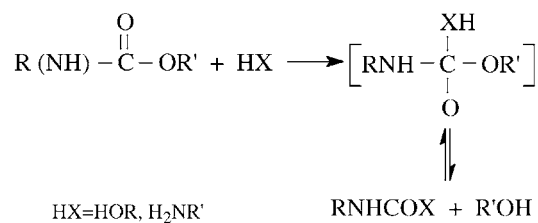
Scheme 1. PU decomposition mechanism.

of certain products above 250 °C which are not formed at lower temperatures. This was confirmed by observing the effect of the thickness of the degrading polymer film on the characteristics of the reaction of carbon dioxide formation under identical temperature conditions.

Based on the results obtained, one can suggest (for segmented polyurethanes based on 4,4′-diphenylmethane diisocyanate, polyoxypropylenediol and low-molecular chain extenders: 1,2-propanediol or 3-chlor-1,2-propanediol) the following mechanism to be operating during the thermal
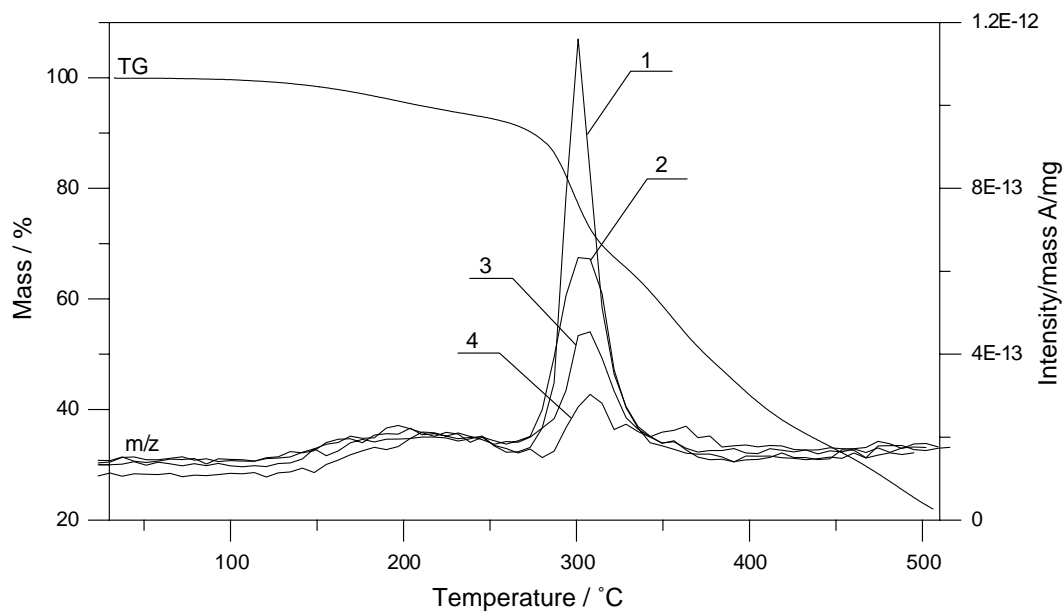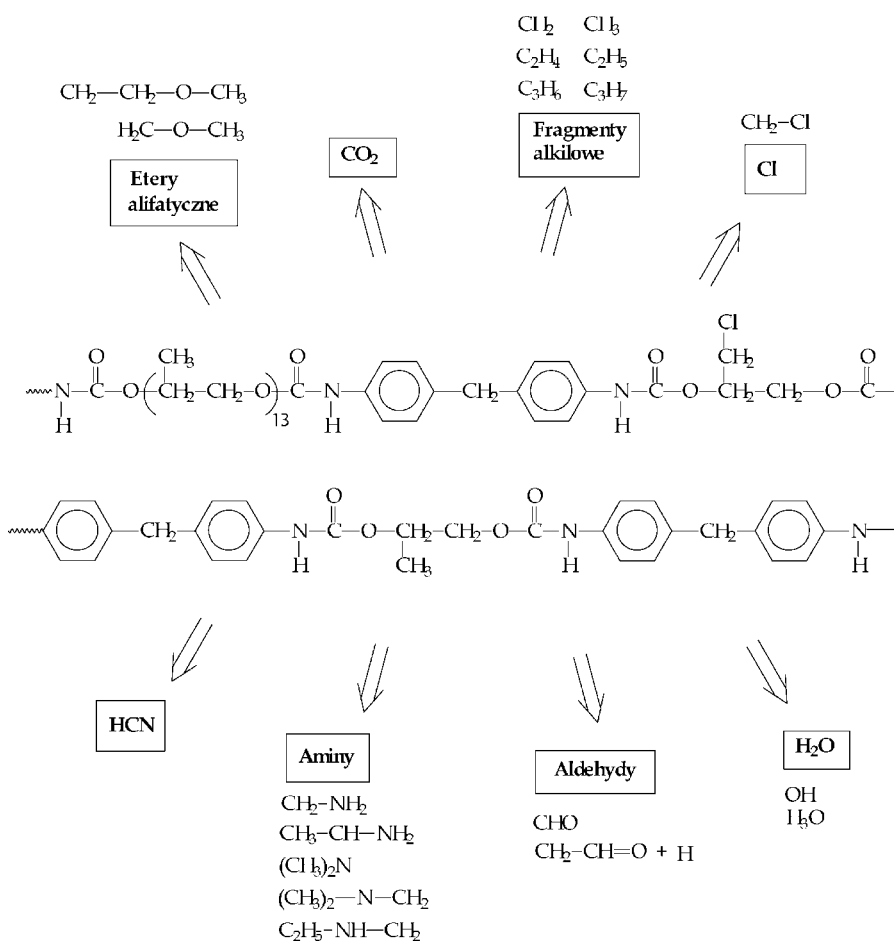
Fig. 8. Representative TG curve and intensity evolution profiles of $m/z = 30$ fragments during decomposition of samples 1–4.

decomposition:

4. Conclusions

Main features of the thermal decomposition of a series of novel polyurethanes containing 3-chloro-1,2-propanediol as a constitutional repeating unit in the main chain which are inherently flame-retarded polymers have been investigated by means of hyphenated methods (TG-FTIR, TG-MS)—it has been found that the main decomposition products are CO_2, amines and HCN.

Correlation between the amount of chlorine in TPU and the intensity of amines' formation during the main decomposition step around 300 °C has been presented. Based on the results obtained thermal decomposition route was suggested.

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