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Investigation of the Thermal Degradation of
Alkylisocyanate Polymers by Direct Pyrolysis
Mass Spectroscopy

by

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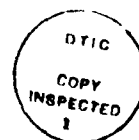
Investigation of the Thermal Degradation of
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INTRODUCTION:

Poly(alkyl isocyanates) are an important class of polymers exhibiting both thermotropic and lyotropic liquid crystalline behavior. Since the original preparation of these polymers (1,2), much attention has been directed at the syntheses of related homo and copolymers (3,4). In addition, their chemical behavior (5), liquid crystalline properties (3-12) and mechanical behavior (13,14) have been actively investigated. Thermal analysis of poly (alkyl isocyanates) has confirmed that they all undergo rapid decomposition at temperatures not too far above their melting points. Thus, the use of poly (alkylisocyanates) as thermotropic liquid crystals is limited. This is unfortunate because the positive characteristics of these polymers, such as high solubility in common solvents and ease of synthesis, would otherwise make them ideal examples of semi-rigid macromolecules amenable to physical studies. Therefore, it would be worthwhile to study the degradation mechanism to see if there are methods by which this class of polymers could be stabilized.

Previous studies have indicated that the thermal degradation products of poly (alkylisocyanates) are isocyanate monomers and their trimers, namely alkylisocyanurates (2,11). The aminolysis of these polymers



A-1

done by Iwakura et al., gave primarily trimers (5). The aminolyses were carried out in dimethyl formamide solutions using di-n-butylamine. However, little confirming information on this is available in the literature.

Though thermal degradation studies of polyisocyanates have been carried out with neat polymers as well as with solutions, no detailed reports have appeared in the literature on the identification of all the thermal decomposition products. Furthermore, the mechanism of decomposition of the isocyanurates (isocyanate trimers), generated in the primary degradation step, is not well understood.

Direct pyrolysis mass spectrometry (DP-MS) is clearly an appropriate tool for studying the mechanism of thermal degradation of poly (alkylisocyanates). DP-MS has been extensively used to identify the thermal fragments of various polymers (15-18). The general advantage of this technique is its ability to detect volatile species as they are formed. In addition, fragments of high mass, which are often diagnostic for the mechanism of the decomposition processes, can be detected; such fragments are often lost using other techniques.

In this paper, we report on the thermal and electron impact (EI) fragments obtained from DP-MS analyses of homopolymers synthesized from butylisocyanate, hexylisocyanate, undecylisocyanate and copolymers of undecylisocyanate. Based on the results, general mechanisms of the thermal decomposition of poly(alkyl isocyanates) are proposed.

EXPERIMENTAL

Materials

All the isocyanate monomers and solvents obtained from commercial sources were distilled from calcium hydride before use. The syntheses of undecylisocyanate and its (50:50) copolymers are reported elsewhere (19).

Homopolymerization was carried out in dimethyl formamide using sodium cyanide as the catalyst. Polymers were precipitated in methanol, filtered and washed several times with water and methanol. Finally all polymers were dried in a vacuum oven at 50-60°C for 3 days before analysis.

Thermogravimetry

Thermogravimetric analyses were carried out with a Dupont model 950 thermal analyzer in a nitrogen atmosphere at a heating rate of 20°C/min.

Mass Spectrometry

Direct pyrolysis mass spectroscopy (DP-MS) analyses were carried out with a Hewlett-Packard 5985 GC/MS mass spectrometer utilizing a technique described elsewhere (15). The heating rate was 25°C/min and the mass spectra were obtained at 18eV.

RESULTS AND DISCUSSION

Thermal Stability

The TGA results for homo and copolymers made from butylisocyanate, hexylisocyanate and undecylisocyanate are shown in Figure 1. Temperatures corresponding to the initial (5%) and complete (95%) decomposition are listed in Table I. The shapes of the TGA curves suggest that the polymers decompose in two different stages. The first stage corresponds to a minor weight loss (15-20%); The second stage, 10-50°C higher, completes the decomposition. In all polymers, the initial decomposition starts around 190°C while the complete decomposition temperature varied from 270 to 450°C.

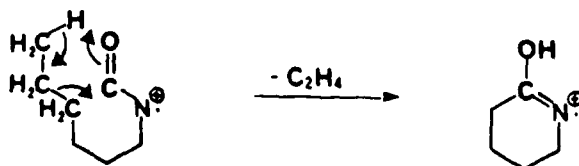
Mass Spectroscopy

For all polymers the total ion current (TIC) curves were plotted as a function of retention time. The maximum in the TIC curve corresponds to the maximum decomposition rate of the polymer. The electron impact (EI) mass spectra corresponding to different maxima of the TIC curves

were recorded at a reduced electron energy of 18eV to minimize EI fragmentation.

Poly (butyl isocyanate) The TIC curve obtained from DP-MS analysis shows two maxima (Figure 2) corresponding to retention times of 8.6 min (215°C) and 9.6 min (240°C). The electron impact mass spectrum recorded at these two temperatures are reproduced in Figure 3. Analysis of the spectra in Figure 3 revealed peaks at m/z of 43, 56, 98, 186, 200, 242 (principal peak), 268 and 297. The peak at m/z = 297 is due to the presence of the trimer of butyl isocyanate. The structural assignments for the key thermal and EI fragments of poly(butyl isocyanate) are summarized in Table II. Figure 3 indicates that the base peak observed at m/z = 242 can probably be attributed to an EI fragment originating from the isocyanurate. Both the TIC curve and TGA analysis show that complete decomposition of this polymer takes place at ~250°C.

Poly (hexyl isocyanate) Similar to poly (butyl isocyanate) the hexyl derivative's TIC curve (Figure 2) featured retention times at 9.1 and 9.7 min. Hence this polymer also decomposes in two different steps as suggested by the TGA curve. The absence of a peak at m/z = 127 indicates that very little hexylisocyanate is formed during decomposition. The mass spectral peaks and the possible thermal and EI fragments associated with them are given in Table II. The minor peak at m/z=99 is proposed to be due to the C₅H₉NO ion resulting from the following reaction of monomer.



The minor intensity and this peak combined with the fact that this peak is intense during mass spectral analysis of monomer (20) suggests that monomer is not escaping via this path during the pyrolysis of the polymer.

Poly (undecyl isocyanate) The TIC curve (Figure 2) for poly (undecyl isocyanate) shows a peak at a retention time of 9.4 min. and a shoulder at 10.0 min. The TIC curve also suggests that the decomposition of this polymer is complete at $\sim 325^{\circ}\text{C}$. In contrast, the TGA analysis shows that complete decomposition is delayed until $\sim 450^{\circ}\text{C}$. This difference is attributed to the high vacuum conditions employed in the DP-MS analysis. The principal peak appearing at $m/z = 99$ (temperature = 245°C) is assigned to an EI fragment obtained from the isocyanurate. The mass spectrum recorded at 300°C showed the EI fragment from undecyl isocyanurate (principal peak at $m/z = 428$) as the major component and the isocyanurate (peak at $m/z = 591$) as a minor product.

Poly (undecylisocyanate-co-butyl isocyanate) The (TIC curve (Figure (4)), shows that the thermal decomposition process is taking place between $190\text{-}270^{\circ}\text{C}$, while the TGA curve indicates decomposition between $190\text{-}380^{\circ}\text{C}$. Again the difference can be attributed to the vacuum conditions employed in the GC-MS analysis; that is, the high boiling volatile materials produced by fragmentation of the polymer are removed at lower temperature than in the TGA analysis. The TIC curve clearly shows a peak with three sharp maxima appearing at retention times of 8.1, 9.0 and 10.2 min. The EI mass spectra corresponding to the TIC maxima are shown in Figure 5; the structural assignments of the peaks are given in Table III. The mass spectral peaks observed at m/z 242, 340 and 438 are EI fragments of the corresponding trimers.

Poly (undecylisocyanate-co-hexyl isocyanate) Proposed structures corresponding to the peaks observed from the DP-MS analysis are included in

Table III. The thermal volatilization profile of this polymer is quite similar to that observed for poly (undecylisocyanate-co-butyl isocyanate); the principal peaks appear to be the EI fragments from the isocyanurates. To find their relative volatilities, the TIC and single-ion intensity curves are plotted as a function of the pyrolysis temperature for this copolymer in Figure 6. The single-ion intensity curves indicate that the volatile products observed and identified at the lower decomposition temperatures of isocyanurates correspond to the EI fragments of $m/z = 298$ and 368 . At the higher temperatures, isocyanurate corresponding to EI fragment $m/z = 438$ was detected. This implies that the isocyanurate obtained from undecyl isocyanate is thermally more stable than those containing hexyl isocyanate. (See Table III for structures.)

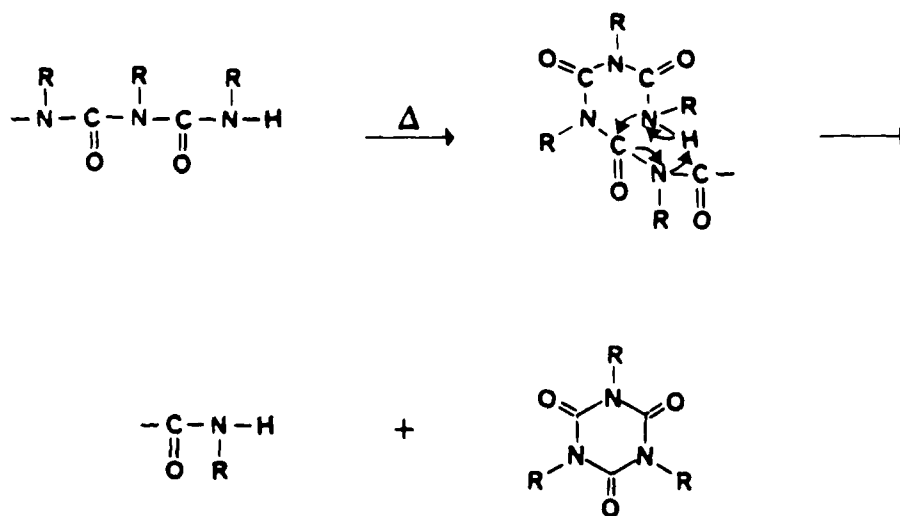
THERMAL DECOMPOSITION MECHANISM

The mass spectra of alkyl isocyanate homopolymers indicate that small amounts of monomer are formed in poly (butyl isocyanate) and poly- (hexyl isocyanate) decomposition. The occurrence of peaks corresponding to isocyanurates and their EI fragments implies that these products are formed directly from the polymer and not from the trimerization of the isocyanate monomers produced by the decomposition. As further evidence for this assertion, mass spectra of octylisocyanate monomer, held in tube at 275°C , were taken. No evidence of trimer was found; thus, if monomer were produced from the polymer, we would expect to have found strong monomer peaks.

While admittedly a different situation the aminolysis of poly (butyl isocyanate), reported by Iwakura et al (7) resulted in mainly cyclic trimers and only trace amounts of monomer. Depolymerization of polyisocyanates was assumed to be initiated by the abstraction of the protons at the end of the chain by the basic amine. Once the anion is

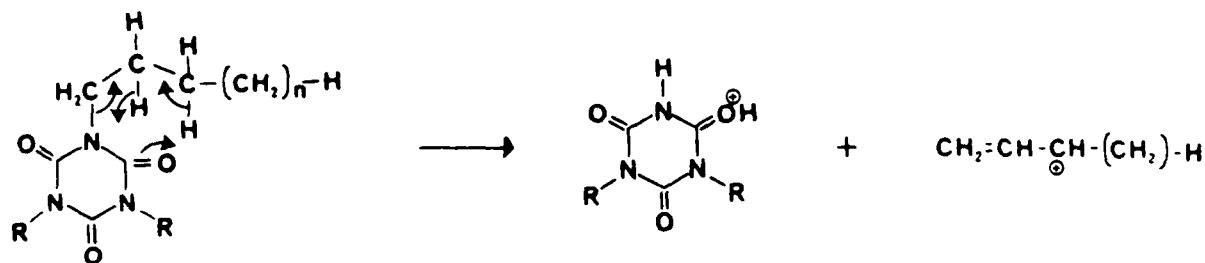
produced by proton abstraction, the depolymerization occurs spontaneously. The trimers are then directly formed from the above anion by an intramolecular attack of the generated nitrogen anion at the third carbonyl carbon down the chain. This reaction is irreversible and appeared to be favored by the electron-donating property of alkyl groups attached to the nitrogen atom.

For the alkyl isocyanates used in the present study, the polymerization was quenched with methanol, capping the polymers with -NH groups. When these polymers are heated to high temperatures, trimers (isocyanurates), are the major decomposition products. The formation of cyclic trimers indicates that an intramolecular exchange process is responsible for the first stage of thermal decomposition of (alkyl isocyanate) polymers. This process is most likely occurring through a back-biting reaction due to macromolecular chains with NH end-groups:

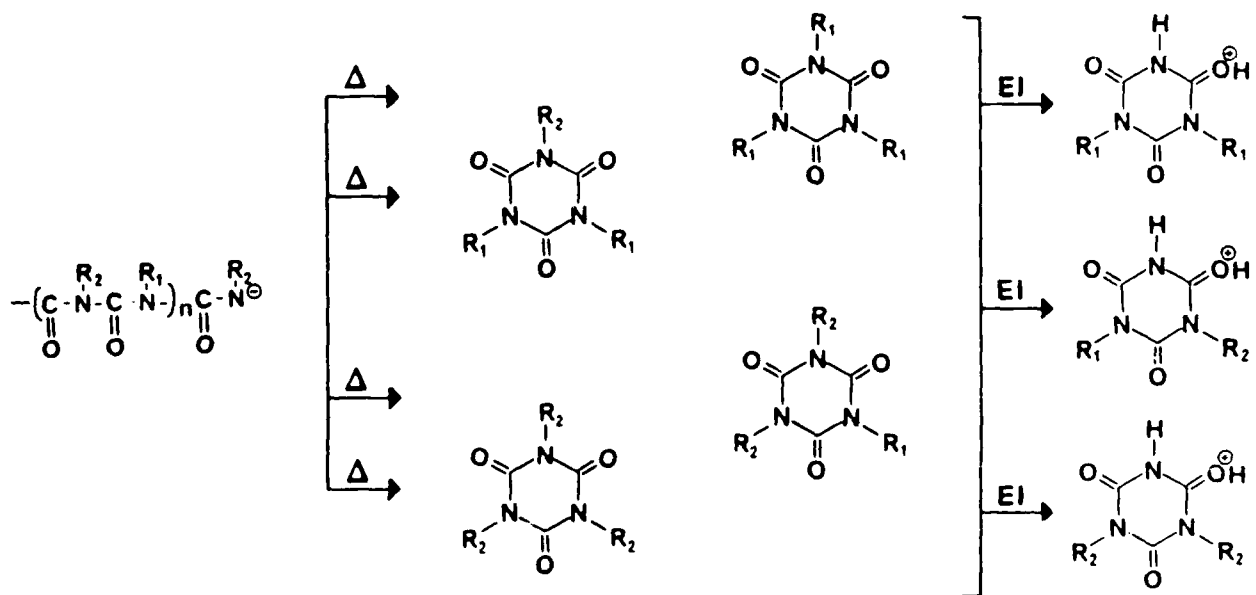


Similar observations leading to the formation of cyclic trimers are made by direct pyrolysis mass spectrometry for aliphatic polysulfides containing SH end-groups (21). Because the cyclic trimers (isocyanurates) are

much more thermally stable than the monomers (isocyanates), it appears that most of the decomposition fragments might have originated from the isocyanurates only. All EI mass spectra of these alkyl isocyanate homopolymers showed peaks corresponding to the fragments obtained from the respective isocyanate trimers. The formation of these fragments can be accounted for by the following mechanism:



Both of the copolymers of undecyl isocyanate (with butyl isocyanate and hexyl isocyanate) undergo decomposition exclusively via the formation of cyclic trimers. In these polymers there was no evidence for the formation of individual monomers from the decomposition. In general, the mechanism of decomposition can be represented as follows:



Because the thermal stability of these isocyanurates depends on the length of the alkyl substituent, isocyanurates containing shorter chains will exhibit lower thermal stability. Therefore, the isocyanurates with the shorter alkyl chain will appear first. This conclusion is in close agreement with the observation of volatile products identified from the EI mass spectra of these copolymers taken at the temperatures corresponding to the maxima in the TIC curves.

CONCLUSION

Thermal degradation mechanisms of alkyl isocyanate homo and copolymers were studied using TGA and DP-MS analyses. Both analyses showed that these polymers begin decomposing at $\sim 190^{\circ}\text{C}$ under inert or vacuum pyrolysis conditions. While the two analyses traced the complete decomposition of the polymers, DP-MS indicated a lower decomposition completion temperature than the TGA. This apparent lower temperature may result from the high vacuum conditions employed in the DP-MS analysis. DP-MS analysis showed the formation of trace quantities of monomer from poly (butyl isocyanate) only and none from the other polymers. In addition, all the polymers produced trimers of the isocyanate monomers (isocyanurates) as their principal decomposition product. It appears, therefore, that intramolecular cyclization is the dominant mechanism of decomposition of these alkyl isocyanates polymers. This observation is in substantial agreement with the work of Iwakura et al. (7) conducted on the solution decomposition of polymers.

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Table I

Thermogravimetric Analysis of Alkyl Isocyanates Polymers
in N₂ Atmosphere

<u>Polymer</u>	<u>Code</u>	<u>Temperature, °C, corresponding to</u>	
		<u>initial inflection^a</u>	<u>final drop^a</u>
1. Poly (butyl isocyanate)	PBUI	185	270
2. Poly (hexyl isocyanate)	PHYI	190	310
3. Poly (undecyl isocyanate)	PUNI	205	450
4. Poly (undecylisocyanate-co-butyl isocyanate) (50:50)	PUNBUI	190	370
5. Poly (undecylisocyanate-co-hexyl isocyanate) (50:50)	PUNHYI	195	380

^a These temperatures will correspond roughly to the peaks in the differential (DTGA) response

Table II

Assignments of Mass Spectral Peaks: Alkyl Isocyanate Polymers

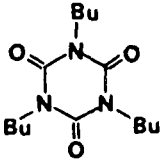
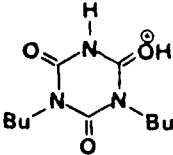
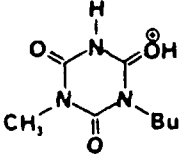
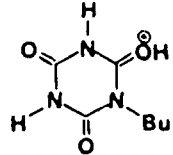
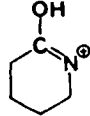
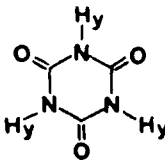
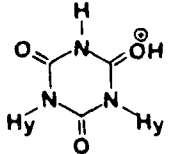
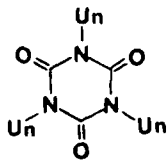
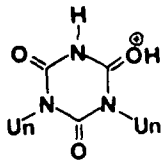
<u>Polymer</u>	<u>Structure</u>	<u>m/z</u>	<u>Structure</u>	<u>m/z</u>
Poly (butyl isocyanate)			$\text{CH}_3\text{CH}_2\text{CH}_2^+$	43
			$\text{CH}_3\text{CHCH}=\text{CH}_2, + \text{CH}_2\text{NCO}$	56
			+	
			$+\text{CH}_2\text{CH}_2\text{NCO}$	70
			$+\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NCO}$	98
		297	$(\text{M}^+) - \text{CH}_2\text{CH}_3$	268 ^b
				242
	$\text{Bu} = -(\text{CH}_2)_3\text{CH}_3$			200
				186
				99
				
Poly (hexyl isocyanate) ^a			$+\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NCO}$	112
		381	$(\text{M}^+) - \text{CH}_2\text{CH}_3$	352
			$(\text{M}^+) - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	324
				298 ^b
	$\text{Hy} = -(\text{CH}_2)_5\text{CH}_3$			

Table II (continued)

<u>Polymer</u>	<u>Structure</u>	<u>m/z</u>	<u>Structure</u>	<u>m/z</u>	
Poly (undecyl- isocyanate)	$\text{CH}_2=\text{CH}_2$	28	$\text{CH}_3\text{CH}_2\text{CH}_2^+$	43	
	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	56	$\text{CH}_3\text{CH}_2\text{CH}_2^+$	57	
			$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$	70	
			$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$	85	
			$\text{CH}_3(\text{CH}_2)_6^+$	99 ^b	
		$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}_2$	112		
		$\text{CH}_3(\text{CH}_2)_6\text{CH}=\text{CH}_2$	126		
			591		438
		$\text{Un} = -(\text{CH}_2)_{10}\text{CH}_3$			

a Minor peaks at 281, 256, 242, 228, 214

b Principal peak

Table III

Assignments of Mass Spectral Peaks: Undecyl Isocyanate Copolymers

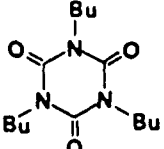
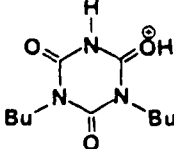
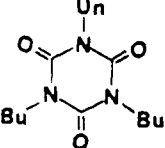
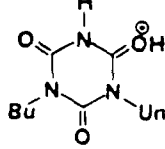
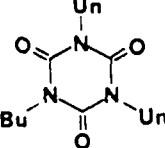
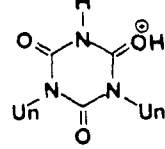
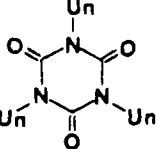
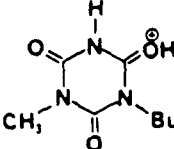
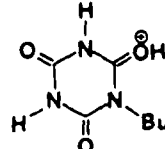
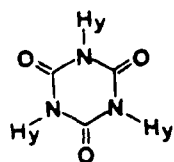
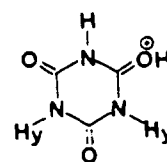
<u>Copolymer</u>	<u>Structure</u>	<u>m/z</u>	<u>Structure</u>	<u>m/z</u>
Poly (undecyl-isocyanate-co-butyl isocyanate)	$\text{CH}_2=\text{CH}_2$	28	$\text{CH}_3\text{CH}_2\text{CH}_2^+$	43
	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	56	$\text{CH}_3\text{CH}_2\text{CHF}_2\text{CH}_2^+$	57
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	70		
	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}_2$	98	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{CH}_2^+$	99
	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	100		
	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}_2$	112		
		297		242
		395		340
		493		438
		591		200
				186

Table III (continued)

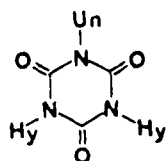
Co-Polymer	Structure	m/z	Structure	m/z
Poly (undecyl-isocyanate-co-hexyl isocyanate)	$\text{CH}_2=\text{CH}_2$	28	$\text{CH}_3\text{CH}_2\text{CH}_2^+$	43
	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	56	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+$	57
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	70	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2^+$	85
	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}_2$	98	$\text{CH}_3(\text{CH}_2)_5\text{CH}_2^+$	99
	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}_2$	112		



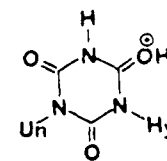
381



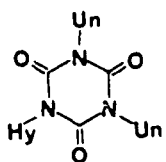
298



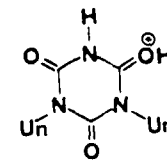
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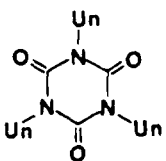
368



521



438



591

Bu= $-(\text{CH}_2)_3 \text{CH}_3$

Hu= $-(\text{CH}_2)_5 \text{CH}_3$

Un= $-(\text{CH}_2)_{10} \text{CH}_3$

Figure Captions

- Figure 1: TGA curves of alkyl isocyanates polymers
- Figure 2: Total ion current (TIC) for alkyl isocyanates homopolymers as a function of the pyrolysis temperature
- Figure 3: Mass spectra of the thermal degradation of poly (butyl isocyanate) at a probe temperature of 215°C.
- Figure 4: Total ion current (TIC) for copolymers of undecyl isocyanate as a function of pyrolysis temperature
- Figure 5: Mass spectra of thermal degradation of poly (undecylisocyanate-co-butyl isocyanate) at a probe temperature of A 203°C B 225°C and C 255°C
- Figure 6: Total ion current (TIC) and single-ion intensity of m/z 298, 368 and 438 as a function of pyrolysis temperature for poly (undecyl isocyanate-co-hexyl isocyanate)

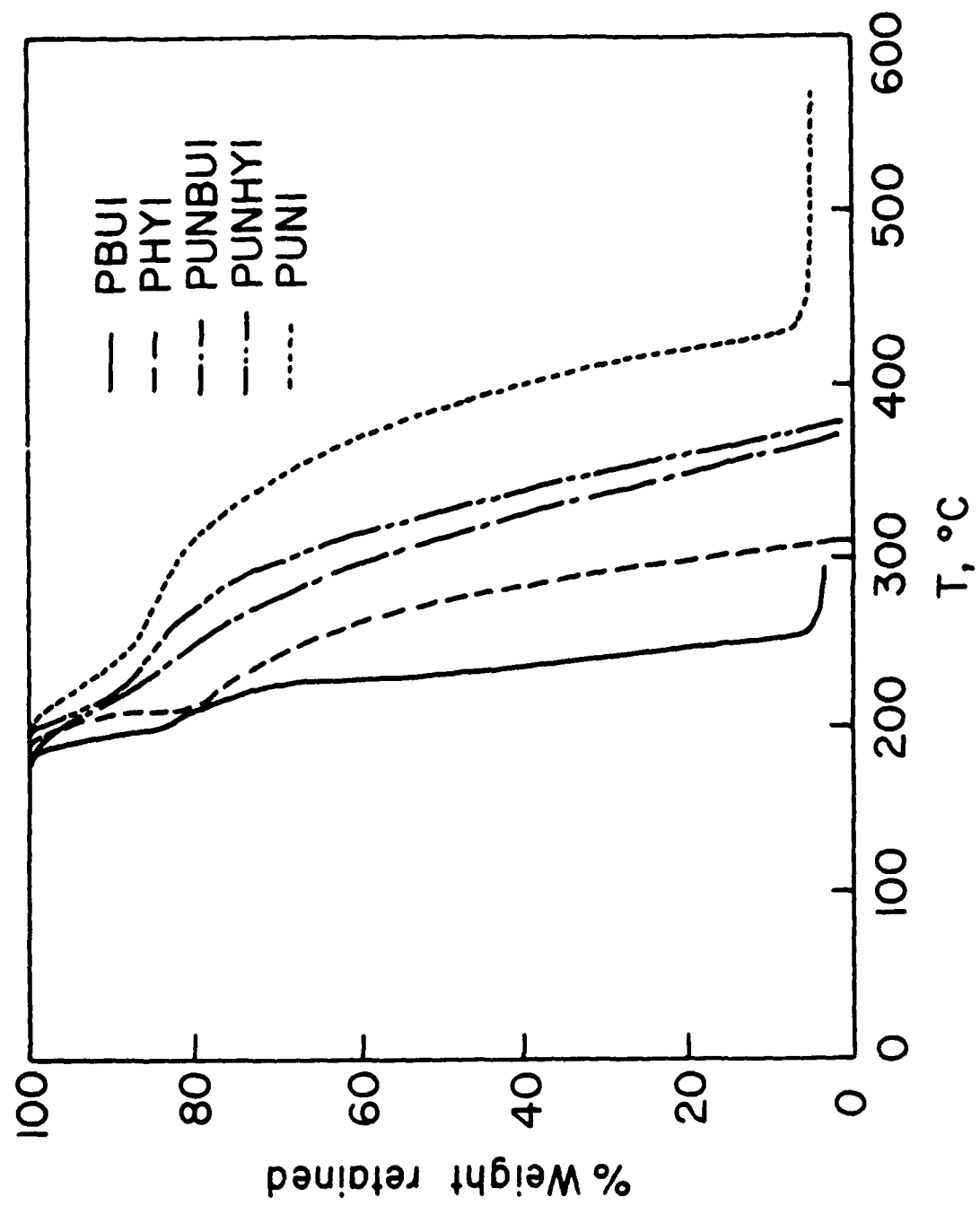


Fig 2

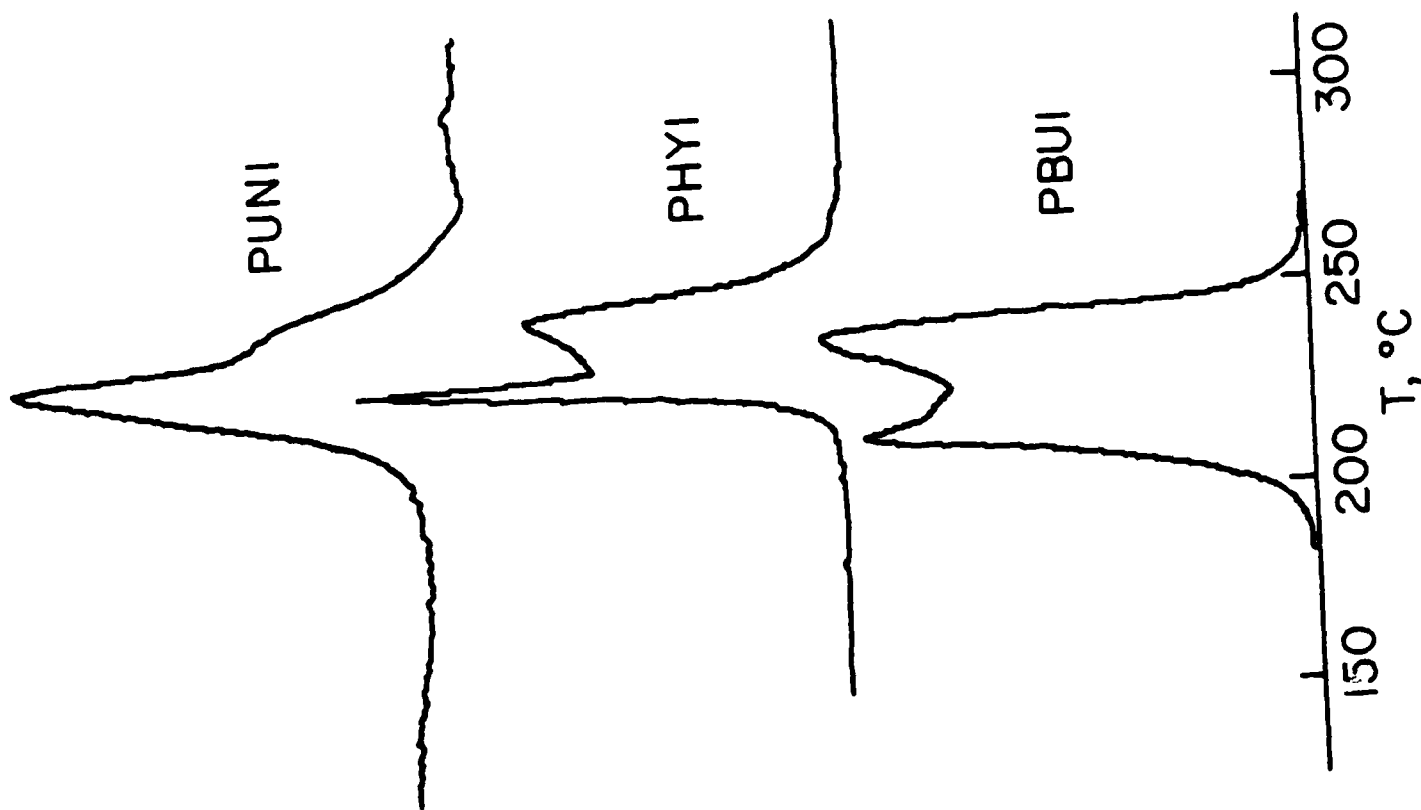
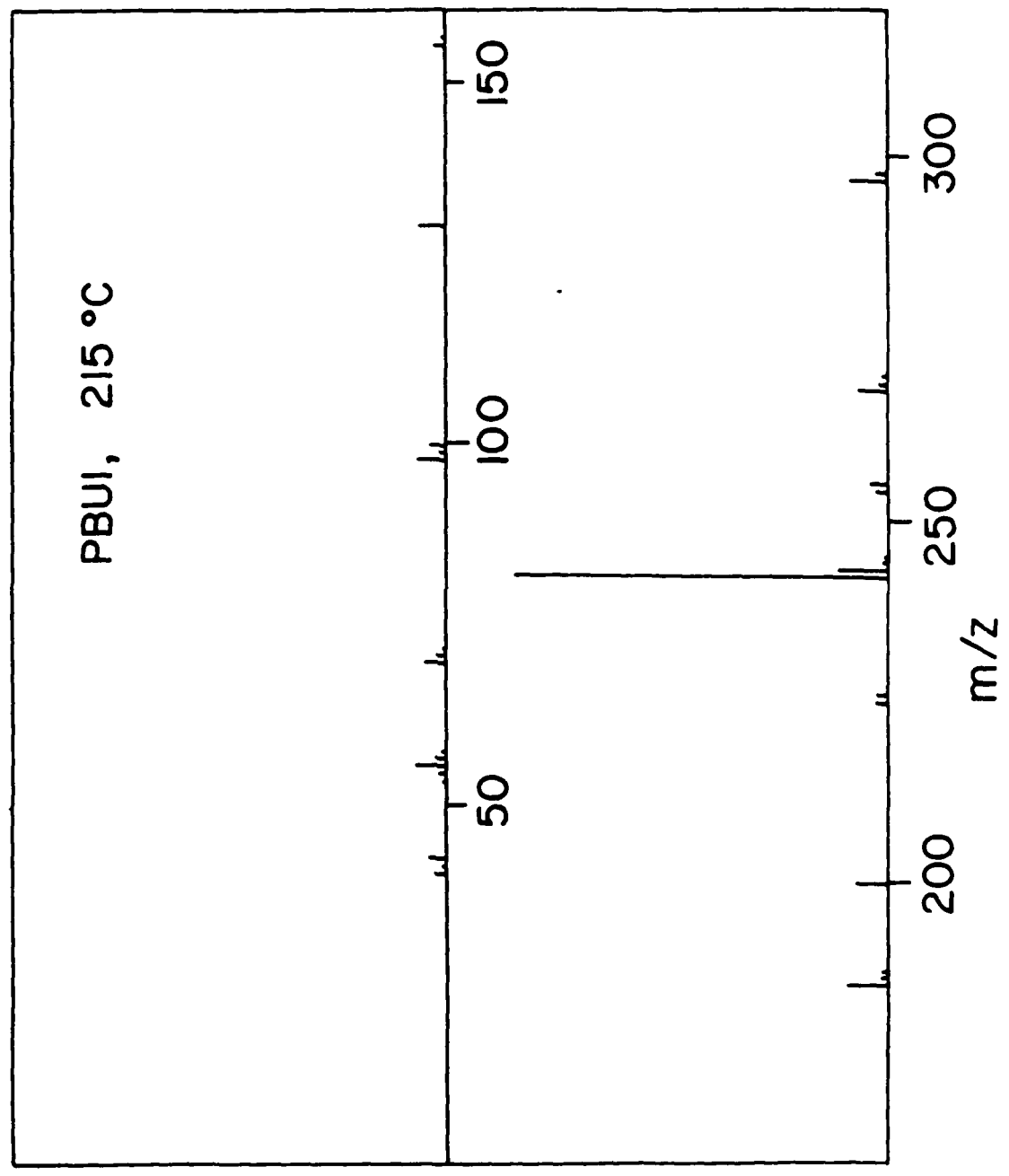
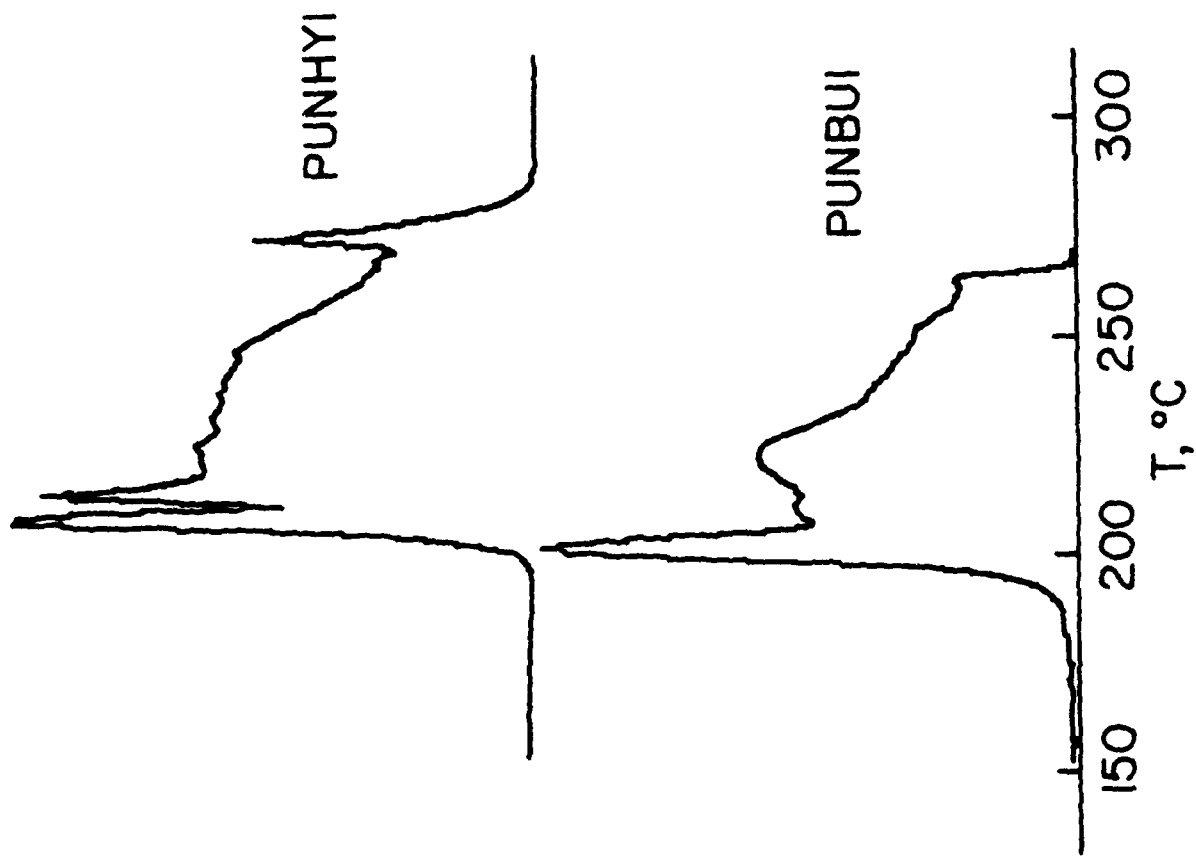
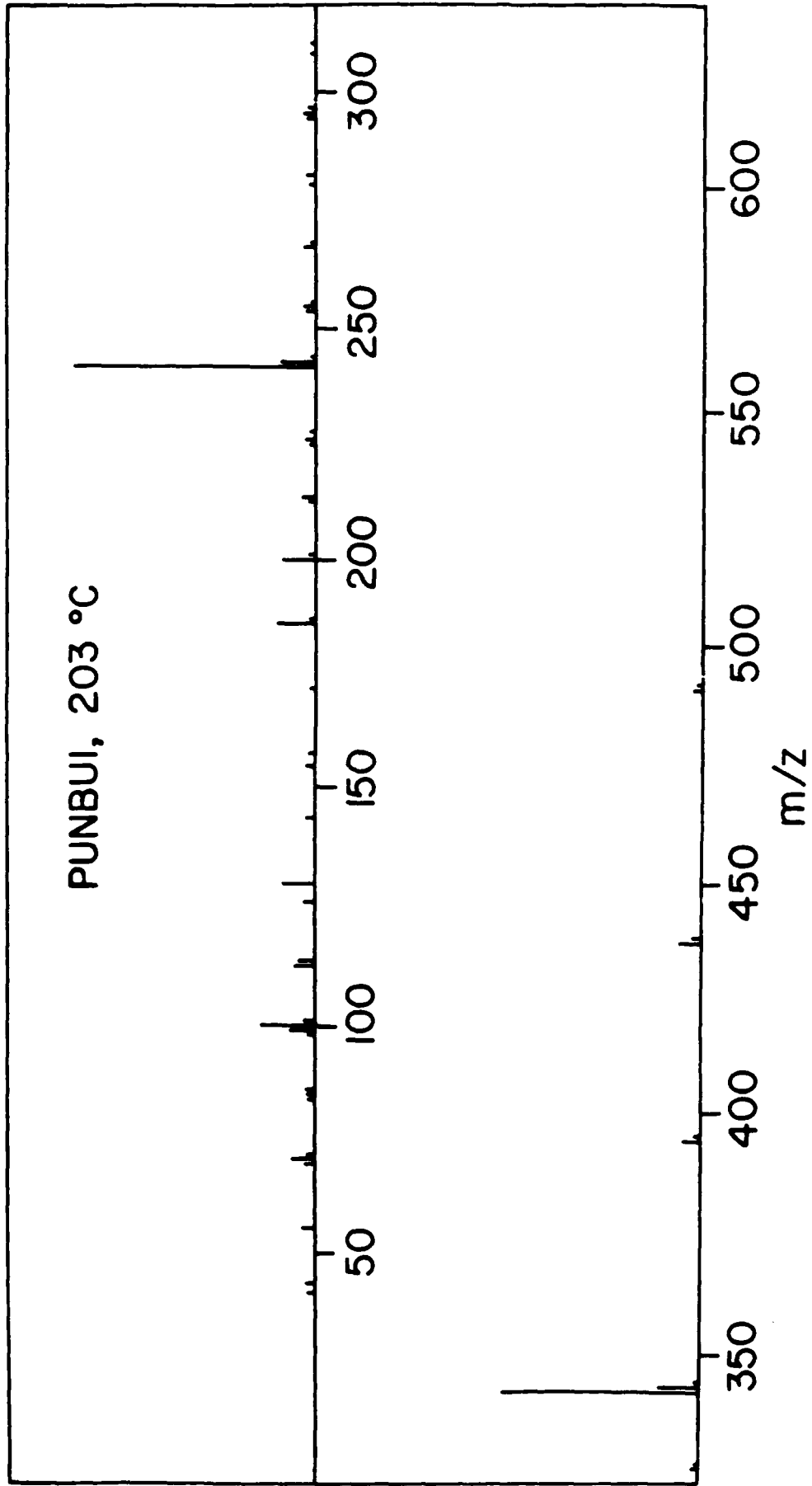
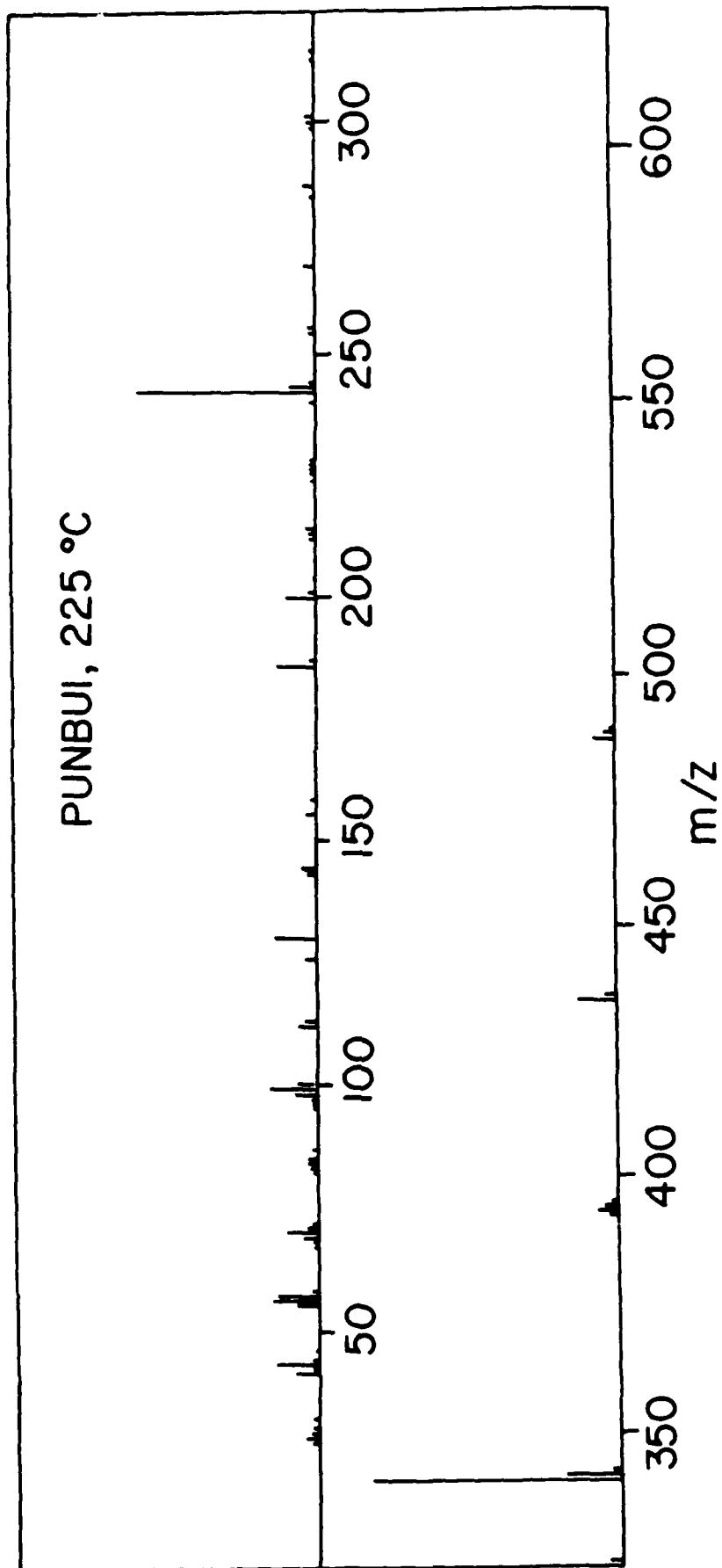


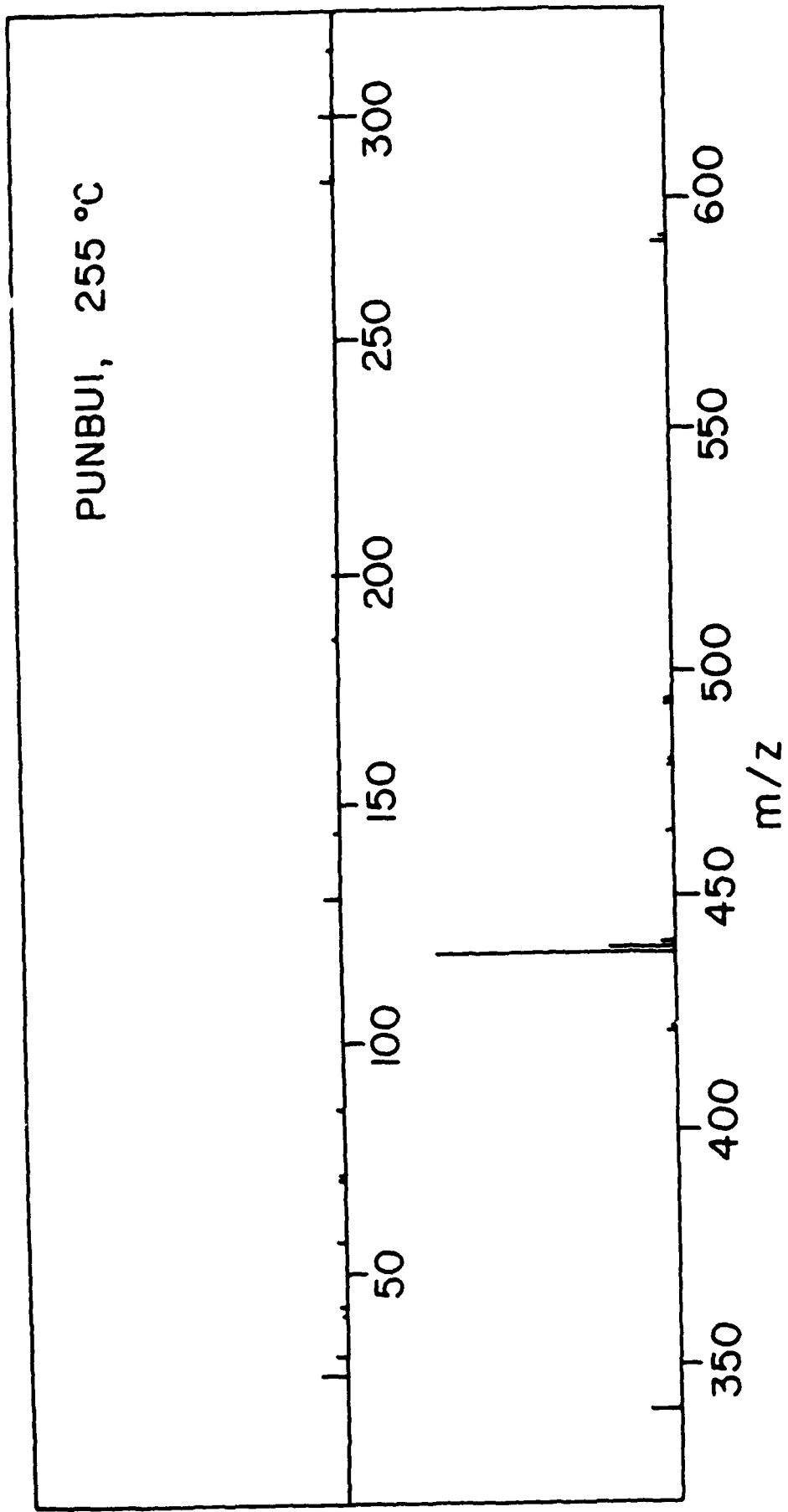
Fig 3











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