

# Flexible Polyurethane Foam. I. Thermal Decomposition of a Polyether-based, Water-blown Commercial Type of Flexible Polyurethane Foam

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## SYNOPSIS

This study of the pyrolysis of a flexible polyurethane foam showed that the composition of the products depends on the conditions of the pyrolysis. If the volatiles are removed rapidly from the system, they will contain tolylene diisocyanate (TDI). However, under confined conditions, the TDI will be replaced by diamino toluene (DAT).

These results can be explained by assuming two decomposition routes to be operative; one leading to the regeneration of the two source materials, TDI and the polyol; the other to DAT and a double-bond-terminated polyether (the polyol with its terminal hydroxy groups replaced by double bonds). The TDI route is the faster, however: if the volatile TDI is confined to the pyrolysis zone, an equilibrium will be established between the urethane group and the TDI plus polyol. Such conditions will favor the slower, though irreversible, route leading to the formation of DAT.

On pyrolysis, the urea groups in the foam dissociates into TDI and DAT. These will recombine in the vapor phase to form an aerosol of polyurea. It is proposed that this aerosol is the "yellow smoke" reported in the literature.<sup>12,27</sup> © 1997 John Wiley & Sons, Inc.

## INTRODUCTION

Commercial flexible polyurethane foams are rather complex chemically and contain a variety of thermally labile groups. The more important of these are urethane (also called carbamate), urea, biuret, allophanate, isocyanurate, ether, and ester.<sup>2,3,7-9</sup> A large number of studies have been published on the thermal decomposition of polyurethanes, but only a few involved commercial types of flexible foams. Most of the studies were based on model compounds rather than on foams. The compounds used as models were either small molecules, such as biscarbamates obtained by reacting the diisocyanate with monohydric alcohols, or linear polymers obtained by reacting the diisocyanate with diols. Although the use of models frequently containing only one of the groups of interest avoids complications arising

out of the presence of several labile groups in the substance studied, the conclusions drawn may not necessarily reflect the behavior of the same group when present in a commercial type cross-linked polymer matrix. Interaction, which can occur among the primary decomposition products, will not be manifest in studies performed on models containing only one such group, nor will linear polymers serve to reveal possible effects of cross-linking.

This paper presents a study of the first, low temperature (up to 360°C) stage of decomposition of a commercial type of polyether-based flexible polyurethane foam. In this first stage, the foam collapses to a liquid,<sup>10,11</sup> losing one third of its weight as volatile decomposition products.<sup>12</sup>

## BRIEF REVIEW OF THE LITERATURE

Of the groups commonly part of the matrix of flexible polyurethane foams, biuret and allophanate are the thermally weakest links. Dissociation of both

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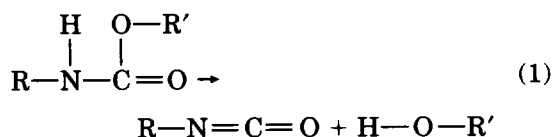
types generally takes place above about 110°C<sup>2</sup> and is completed by about 170°C.<sup>7</sup> On pyrolysis, both types of materials are stated to regenerate their precursors, isocyanate and urea, in the case of biuret, isocyanate, and urethane from allophanate.<sup>2,13</sup> Next in thermal stability are the urethanes, closely followed by ureas, with the isocyanurate group being the most stable of these nitrogen-containing derivatives.<sup>7,11,14,15</sup> The ether group is stated to be markedly more stable than any of these,<sup>10,16</sup> with the possible exception of the isocyanurate group, which is claimed to be stable up to 270°C.<sup>7</sup>

According to Saunders and Backus,<sup>14</sup> dissociation of the urethane group is one of the first reactions to be expected when polyurethanes are heated above 200°C. Fabris<sup>7</sup> states that urethanes of many commercially available isocyanates and primary and secondary alcohols start to decompose at 150–200°C, proceeding at a measurable rate between 200–250°C. Up to 200°C, random bond scission occurs at the urethane links, while unzipping of the polyether chain occurs in the range 250 to 320°C.<sup>7,16,17</sup> Benbow and Cullis<sup>10</sup> quote an even higher temperature, 375°C, for the breakdown of polypropoxylene chains.

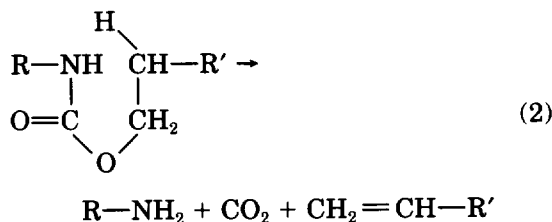
Batt and Appleyard<sup>18</sup> state that all foams begin to lose weight at about 185–195°C.

Although Orlov and Tarakanov<sup>19</sup> proposed a radical mechanism to be involved in the thermal decomposition of polyurethanes, the general consensus seems to be that the urethane linkage in polyurethanes decomposes by one or more of the following three mechanisms<sup>1,7,8,14,20,21</sup>:

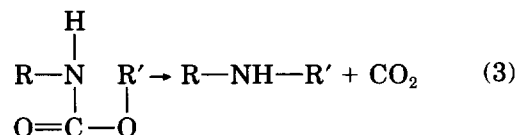
- 1) Depolymerization; that is, dissociation to the precursors, the isocyanate and the alcohol, the reverse of the following formation reaction:



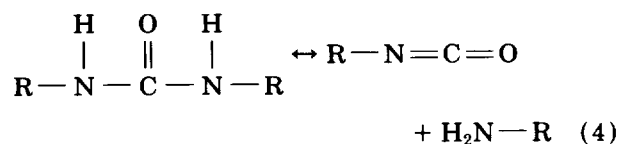
- 2) Dissociation to a primary amine, an olefin, and CO<sub>2</sub> via a putative six-membered ring transition state, as follows:



- 3) Extrusion of CO<sub>2</sub> leading to the replacement of the urethane link by a secondary amine group. A four-membered ring transition state was postulated.



Mukiya et al.<sup>22,23</sup> and Hoshino et al.<sup>24</sup> state that on heating, the ureas also dissociate reversibly into their precursors, the isocyanate and the amine, in a reaction that parallels reaction (1), above, for the urethanes, as follows:



The dissociations of both ureas and urethanes are accelerated by both acids and bases.<sup>22,23</sup>

Many workers have reported depolymerization [reaction (1)] to be either the predominant or at least a major degradation route for the urethane link in these polymers.<sup>7,12,17,20,22,25–32</sup>

The elucidation of decomposition mechanisms generally involves identifying and quantifying the primary decomposition products. In the case of reaction (1), these would be the two precursors used in the preparation of the polyurethane: the diisocyanate (tolylene diisocyanate is the diisocyanate generally used for flexible foams), and the polyol (or alcohol, in the case of nonpolymeric carbamates).

Polyol-type materials have been confirmed in residues of the first stage of decomposition of linear polyurethanes,<sup>17,25</sup> as well as of commercial foams.<sup>12</sup> Such residues, although very similar to, were, however, not quite identical to the source diol or polyol.

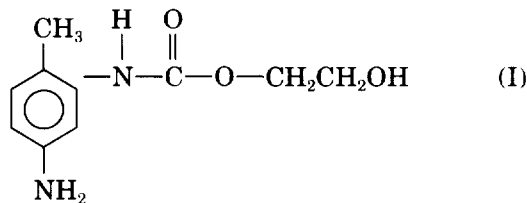
In spite of the many references claiming tolylene diisocyanate (TDI) to be a major decomposition product,<sup>12,17,20,22,26,27</sup> where quantification of this material was attempted, only a fraction of that potentially available was actually recovered. Woolley,<sup>12</sup> in a quantitative examination of the decomposition of commercial flexible foams at 200–300°C, reported the close to quantitative loss of the TDI-derived units from the foams (he examined both polyether and polyester-based foams). However, he succeeded in recovering only 1% of the TDI used in the preparation of the foam.<sup>27</sup> Ingham and Rapp<sup>17</sup> recovered only 2%.

Woolley<sup>12</sup> reported that virtually all of the nitrogen originally in the foam reappeared in the form of a yellow smoke, which is released on heating the foam. He suggested that the lack of recovery of the isocyanate is due to its condensation or polymerization to form this yellow smoke. This is a possibility as isocyanates undergo decarboxylation at about 300°C to form carbodiimides<sup>8,14,16,33,34</sup>; and diisocyanates could, therefore, be expected to form polycarbodiimides. However, in a later publication,<sup>27</sup> Woolley showed TDI to be stable up to 400°C. As a material stable to 400°C would not be expected to condense or polymerize at temperatures below 300°C, this makes Woolley's explanation for the minimal recovery of free diisocyanate somewhat less acceptable.

Thorne<sup>35</sup> found reaction (2) to predominate in the decomposition of *t*-alkyl *N*-arylcarbamates. The work of Frisch and coworkers<sup>15,25</sup> indicates this mechanism to be a major degradation pathway for linear polyurethanes based on tolylene and xylylene diisocyanates, as well as for some model bis-carbamates.

A decomposition that follows the route depicted by reaction (2) should produce a diamine and CO<sub>2</sub> as the major volatile products, leaving a nonvolatile residue of double-bond-terminated polyether chains in place of the polyol. With TDI as the source material, the diamine would be diaminotoluene (DAT). Anthony<sup>29</sup> mentions the formation of volatile aromatic amines. Specific mention of the presence of diaminotoluene among the decomposition products of TDI-based polyurethanes has been made by only a few workers.<sup>30,31,36,38</sup>

The presence of both hydroxy and amino groups in compound I (see Scheme I), identified among the decomposition products of a linear polymer prepared from TDI and ethylene glycol,<sup>19</sup> suggests that both reactions (1) and (2) are involved in the decomposition of this polymer. The involvement of both these reactions has also been proposed by Fabris.<sup>7</sup>



Decomposition according to the route depicted by reaction (3) should yield CO<sub>2</sub> as the only volatile material of the first low temperature stage of decomposition.

There is a basic difference between reactions (1) and (2), on the one hand, and reaction (3), on the other. The two former lead to the disruption of the urethane units, which link the polyether (or polyester) chains. This results not only in the disintegration of the polymer's chemical structure; inevitably, it destroys the physical structure of the foam, causing it to collapse to a liquid of a volume very much smaller than that originally occupied by the foam. Volatilization of the TDI and/or the DAT (both have boiling points below 300°C) should lead to a weight loss of about one third of the original weight of the foam. Reaction (3), on the other hand, involves the extrusion of CO<sub>2</sub> from the urethane groups, still leaving the two ends of the polyether (or polyester) chains linked. This mechanism, therefore, does not mandate the collapse of the foam's physical structure, as do reactions (1) and (2). The loss of the CO<sub>2</sub> represents only 15% of the weight of the foam; that is, about half of that of reactions (1) or (2). Furthermore, reaction (3) would be expected to leave all the nitrogen in the nonvolatile residue, which should produce a residue of nitrogen content higher than that of the original foam. Both reactions (1) and (2) should lead to residues containing little or no nitrogen.

The experimental findings reported in the literature<sup>12</sup> do not support a mechanism based on reaction (3). The foam structure collapses on heating, and this is accompanied by a loss of one third of the weight of the foam. The residue contains little or no nitrogen. Therefore, if reaction (3) is involved at all, it plays only a very minor role.

From the sparse information available in the literature on the composition of the residue, it would appear that reaction (1) predominates over reaction (2). Ingham and Rapp<sup>17</sup> obtained a material very similar to the starting diol of their linear polyurethane. Rumao and Frisch<sup>25</sup> recovered the starting diol, also from a linear polyurethane. Woolley<sup>12</sup> recovered a polyol from the thermal decomposition of a commercial flexible foam. However, he did not compare it with the source polyol.

To summarize, the labile groups that can be expected to break down during the first stage of decomposition—allophanate, biuret, urea and urethane—are all derived from the isocyanate used in the preparation of the foam. All these groups serve as links or are part of links or cross-links that connect the polyether (or polyester) chains.<sup>39</sup> All these units decompose thermally to regenerate their respective precursor groups— isocyanate, amine, and hydroxy. In the case of the urethane group, an alternative (or parallel) decomposition path may

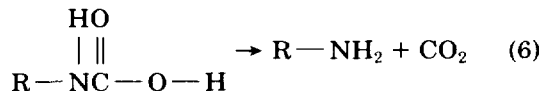
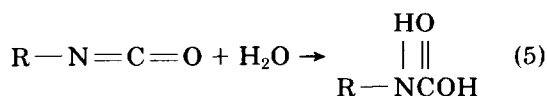
also exist involving the formation of an aromatic amine, a terminal olefinic group on the polyether chain, and CO<sub>2</sub>.

The relatively low thermal stability of the isocyanate-derived groups that link the polyether chains and their apparently straightforward decomposition path would have been expected to give a simple picture for the decomposition of these foams. However, judging by the conflicting claims in the literature, this does not appear to be so.

## DISCUSSION

### Composition of the Foam

The foam that was the subject of this study was of the water blown type. Isocyanate reacts with water at a rate similar to that of its reaction with the primary hydroxy groups of the polyol.<sup>2</sup> The product of the isocyanate-water reaction is a carbamic acid that is unstable and decomposes to an amine and CO<sub>2</sub>. It is the evolution of the latter that "blows" the foam.<sup>2,40</sup>



The amine thus formed also reacts with isocyanate to form a urea<sup>2,40</sup> in a reaction that is the reverse of that depicted in reaction (4), above.

The 157.8 g of formulation of this foam [147 g after loss of CH<sub>2</sub>Cl<sub>2</sub> and CO<sub>2</sub> (see experimental)] contains the following amounts of reactive components in millimoles (mM).

TDI:	293
Water:	214
Polyol F-3020:	33

The 214 mM of water will react with 107 mM of TDI to form 107 mM of DAT by the above depicted reaction sequence [reactions (5) and (6)]. This diamine will then react with a further portion of 107 mM of TDI to form 214 mM of urea groups [reverse of reaction (4)].

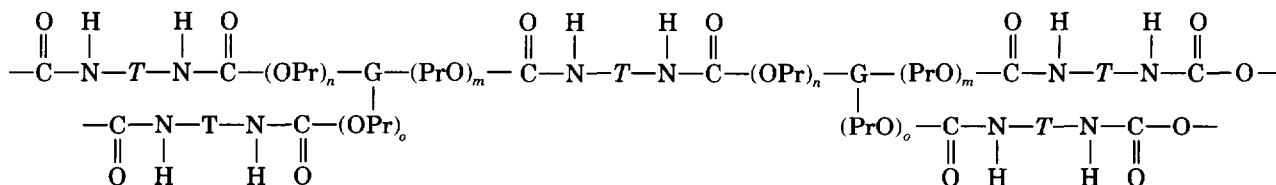
The 33 mM of the polyol (a triol; see Experimental) will react with 50 mM of TDI to form 100 mM of urethane groups.

This leaves 29 mM of TDI, which can be expected to react with the only active hydrogens remaining in the system, those of the urea and urethane groups, the two major products of the primary reactions. The products of these two secondary reactions will be biurets and allophanates, respectively. However, as the reaction of isocyanate with urea is faster than its reaction with urethane and as the concentration of urea groups is double that of the urethanes, these secondary relatively slow reactions<sup>2</sup> will produce mostly biuret units.<sup>4,39,40</sup>

Side reactions of TDI may also be involved in the formation of the foam. Two of the more common of these are self condensations: trimerization to isocyanurate, and condensation of two isocyanate units to form a carbodiimide group. However, the extent of these reactions is probably small<sup>41</sup> as they require higher temperatures<sup>27</sup> or catalysis.<sup>5</sup> They would therefore be expected to play only minor roles, if any, in the formation of the foam.<sup>20</sup>

The major TDI-derived nitrogen-containing units in this foam can therefore be expected to be urea, urethane, and biuret. Assuming the polymer-forming reactions to be as simple as depicted (which may not be the case), the final polymer will contain the source TDI distributed among the three major groups as follows: urea, 53%; biuret, 30% (consisting 20% as urea and 10% as TDI); and urethane, 17%.

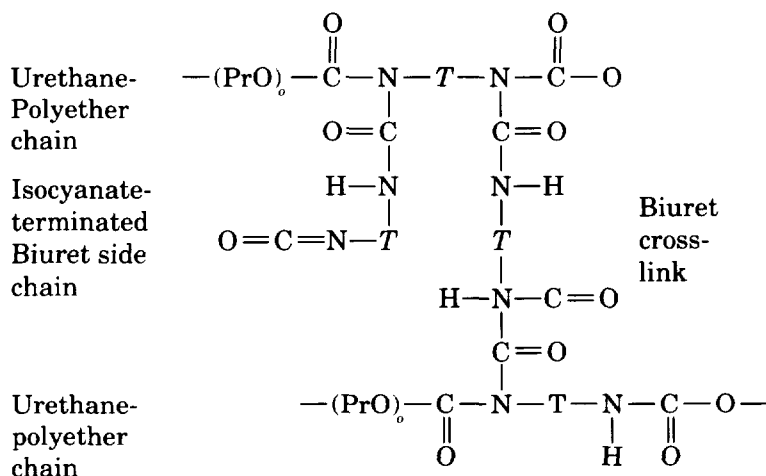
These three groups are incorporated into the polymer matrix in different ways. The urethane units, formed by reaction of the TDI with the hydroxy terminals of the polyether chains, link the latter to form the backbone and major component



*T* represents the tolylene moiety, the polyether part consisting of polypropoxy chains (PrO) linked at one end to glyceryl units G.

(the polyol represents two thirds of the weight of the formulation) of this polymer.

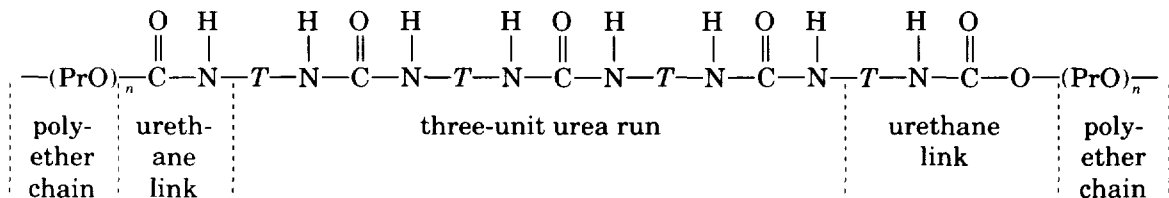
Biuret forms side chains on these urethane-polyether chains and can further cross-link this urethane-polyether network.<sup>39</sup>



*T* represents the tolylene moiety, the polyether part consisting of polypropoxy chains (PrO) linked at one end to glyceryl units G.

Based on the water/polyol ratio in its formulation, this foam would be expected to contain two urea units per urethane group. However, as urea units cannot be attached directly to the polyether chains, they are probably linked to them via urethane units. The simplest way to accommodate the extra urea

units would be as runs of several units, inserted between two urethane links. A urea/urethane ratio of two would require an average urea run length of four units. Urea runs could also form branches by being attached by one end to only one polyether chain, the other end being free.



*T* represents the tolylene moiety, the polyether part consisting of polypropoxy chains (PrO) linked at one end to glyceryl units G.

The urea units need not necessarily be incorporated into the urethane-polyether system. They could also form an oligomeric urea chain that exists as an independent polymeric structure within that of the urethane-polyether network<sup>39</sup> or even form a separate phase.

The extent of incorporation and distribution of the various units in the polymeric matrix will depend on the ratio of the reactants, as well as on the rates of four of these reactions: the TDI-polyol reaction

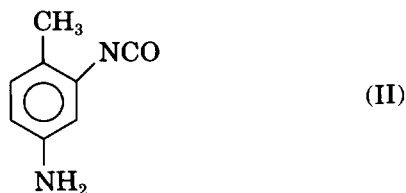
[the reverse of reaction (1)], the TDI-water reaction [reaction (5)], decomposition of the carbamic acid [reaction (6)], and the TDI-amine reaction [the reverse of reaction (4)]. The latter is the fastest of these,<sup>2,39</sup> while reaction (6) appears to be the slowest.<sup>2</sup> Reaction (6) probably controls the rate of formation of the urea groups.

The rate of the isocyanate-hydroxyl reaction is accelerated by the catalysts generally used in the

formulation of flexible foams. These catalysts, however, have little or no effect on the rate of the isocyanate-amine reaction.<sup>2,8,22,23,39</sup> So that if reaction (6) is slow and in the presence of such catalysts, the formation of urethane groups can be expected to be largely completed prior to the appearance of many urea groups. This is a situation that would favor the formation of an independent polyurea matrix.

### Expected Decomposition Products

As discussed above, it seems to be generally accepted that urea and biuret decompose by dissociating to regenerate their source components: isocyanate and amine from urea, isocyanate and urea from biuret,<sup>2,22-24</sup> with the urea from the biuret then decomposing further to isocyanate and amine. These two groups, urea and biuret (which together represent about 80% of the TDI used in preparation of the foam under examination), should therefore be released as free TDI and free DAT, with the TDI in slight excess (from the biuret). The formation of the mixed amine-isocyanate compound, aminoisocyanato toluene (Scheme II), would also seem a possibility.



TDI reacts very rapidly with amines;<sup>2,8</sup> in fact, according to Mukaiyama et al.,<sup>22,23</sup> the reaction between isocyanates and amines is instantaneous and quantitative, which implies that isocyanates and amines cannot coexist and that the TDI and the DAT distilling out of the pyrolysis zone will react very rapidly in the vapor phase to form a polyurea, most probably as an aerosol. We propose that this polyurea aerosol constitutes Woolley's yellow smoke and that the latter is not a condensate or polymer of TDI, as he proposed.<sup>12,27</sup> As the urea groups in the polymer represent 73% of the TDI-derived groups, it is not surprising that most of the nitrogen in the foam is lost in the form of this yellow smoke.<sup>12,27</sup>

The dissociation of the urea groups of the polymer and their subsequent reformation as an aerosol of polyurea is akin to the mechanism of volatilization

of  $\text{NH}_4\text{Cl}$ . In fact, a similar mechanism has been proposed to explain the fact that ethyl carbanilate (ethyl phenylurethane) can be distilled unchanged.<sup>20</sup>

As the TDI and the DAT are released from the urea portions in the polymer in stoichiometrically equivalent amounts and as the reaction between them is instantaneous and quantitative,<sup>22,23</sup> this means that the urea portion of the polymer will yield neither free TDI nor free DAT, which leaves only two potential sources of free TDI, biuret and urethane. The former can release an amount equivalent to 10% of the source TDI (see above). The amount of TDI the urethane units will release depends on their mode of decomposition. By reaction (1), the amount of TDI released will be equivalent to 17% of the source TDI. Adding this to the 10% of the TDI released by the biuret gives a total of 27% of the source TDI that could be released as free TDI. On the other hand, if decomposition is by reaction (2), the product will be DAT, in an amount also equivalent to 17% of the source TDI. Of this DAT, an amount equivalent to 10% of the source TDI will react with the 10% TDI released by the biuret units so that, in effect, of the DAT released, an amount equivalent to only 7% of the source TDI would remain as free DAT.

It can therefore be concluded that the first stage of the decomposition that is under study here should release one third of the weight of the foam as volatiles containing all or most of the nitrogen, leaving the polyol-derived two thirds as a nonvolatile residue. The exact makeup of these two products will depend on the route. If by reaction (1), then the residue will consist of the regenerated polyol, the volatiles being made up of a polyurea aerosol (the yellow smoke) and TDI. If by reaction (2), the residue will consist of polyether chains with terminal double bonds and volatiles made up mostly of the yellow smoke,  $\text{CO}_2$ , and some DAT. The amount of DAT released by reaction (2) will depend on the ratio of urea to urethane units in the polymer, which depends on the amount of water used in the formulation of the foam and probably also on the type and amount of catalyst.

## EXPERIMENTAL

### Polyurethane Flexible Foam Formulation

The foam was prepared at the Akzo Research Laboratory, Dobbs Ferry, New York, according to the following formulation:

**Foam Formulation**

Component	Source	Amount (g)
Polyol F-3020	Arco Chemical	100.0
CH <sub>2</sub> Cl <sub>2</sub>		1.5
Water		3.85
Dabco 33LV/Niax A-1 (3 : 1)		0.20
L620	Union Carbide	0.80
Dabco T-10	Air Products	0.42
Tolylene diisocyanate 2,4- : 2,6-, 80 : 20 (Mondur TD-80 Grade A)	Miles	51.06 (32.4%) <sup>a</sup>
TDI index		110
Cream time (sec)		7
Rise time (sec)		123
Density (lb/cu. ft)		1.60

Polyol F-3020 is a glycerol-ethylene oxide-propylene oxide polyether of average molecular weight 3000.

Dabco 33LV is 33% triethylenediamine in dipropylene glycol (Air Products).

Dabco T-10 is a tin-based catalyst in dioctyl phthalate.

NiAx A-1 is 70% 2,2'-Oxybis(N,N-dimethylethanamine in dipropylene glycol (OSI Specialities).

L620 is a silicone surfactant

<sup>a</sup> In the foam, this would be 34.7%, allowing for the loss of the CH<sub>2</sub>Cl<sub>2</sub> by vaporization and of the CO<sub>2</sub> produced by the TDI-water reaction. The nitrogen content of the foam was calculated to be 5.6%, taking into account the loss of CO<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub>. This value was confirmed by elemental analysis.

**Thermogravimetric Analysis**

These were run under a nitrogen flow of 100 mL/min, on a model high resolution TGA 2950 thermal analyzer (TA Instruments Inc., New Castle, Delaware), using the high resolution mode.

**Infrared Analysis**

Spectra were run on a Fourier transform infrared spectrometer (Nicolet 5MX, Madison, Wisconsin), with liquids between NaCl plates and solids in KBr pellets.

**Elemental Analysis**

These were performed on an NA 1500 Analyzer (Carlo Erba, Milan, Italy). The silver crucibles used were p/n 24005405.

**Pyrolysis**

Pyrolysis of the foam to the first decomposition stage (320–360°C) resulted in the formation of three

phases: a nonvolatile residue with both solid and liquid components, and volatiles. Five modes of pyrolysis were developed in order to prepare, separate, and examine the individual phases. Three of these techniques, which dealt with milligram quantities of foam, were used to examine the vapor phase, in conjunction with gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Two other techniques were used to examine the nonvolatile residue. One of these techniques, also involving milligram quantities, was used in combination with an elemental analyzer to determine the nitrogen contents of the residues. The second, applied to tens of milligrams of foam, was used preparatively to obtain sufficient residue to permit separation of the solid and liquid phases from one another for further examination by elemental analysis, infrared (IR) spectroscopy, and thermogravimetry (TGA). Of these five modes, one was a static mode where all the pyrolysis products remained in the pyrolysis zone throughout the pyrolysis period, while the others

were dynamic, the volatiles being swept out of the pyrolysis zone by a carrier gas.

#### Capillary Tube Pyrolysis: Confined Mode

This is a static mode in which the pyrolyses were run in sealed capillaries (melting point tubes 100 × 1 mm i.d.; Corning p/n 9530-2). After loading, these tubes with the foam (ca. 0.5 mg), they were flame-sealed under vacuum. The pyrolysis was performed by placing the tubes in a preheated oven for the desired period. After cooling, the top of the tube was cut off, and 10  $\mu$ L of solvent (generally acetone) was injected with a microsyringe. After mixing the contents, 0.5  $\mu$ L of the solution were withdrawn and injected into the GC-MS.

Part of the confined mode pyrolysis products were light brown insoluble solids. These are, of course, not represented on the chromatograms of the extracts.

#### Capillary Tube Pyrolysis: Open Mode

This is a dynamic mode in which the melting point tube, open at one end and containing the sample (ca. 0.5 mg), was pushed through the septum, open end first, into the heated injection port of a gas chromatograph, with the injection port acting as a pyrolysis chamber. The carrier gas (helium) transports the volatiles produced by the pyrolysis to the separating column. This work was performed on a Varian 3700 gas chromatograph. To accommodate the pyrolysis tube, the holes in the septum retainer nut and the injection port liner retainer were enlarged by drilling. For the same reason, the glass liner was reversed.

To set up the pyrolysis, an 18G hypodermic needle was used to force a hole through a septum. The loaded melting point tube (see below for a description of the loading technique) was then forced through the resulting hole, sealed end first (to prevent particles of septum from entering the tube), and the septum was positioned along the tube so that when mounted in the injection port, the open end of the tube is just inside the glass liner, with the sealed end being outside. The sample of foam is positioned inside the melting point tube so that when the latter is mounted in the injection port, the sample is outside the port, 10 mm away from the septum retainer nut. After mounting the tube, the system is sealed by tightening the septum retainer nut. One minute is allowed in this "ready" position for the helium to flush the air out of the tube (allowing a longer period made no difference to the resulting

pyrograms). To start the pyrolysis, the tube is pushed into the injection port until its sealed end protrudes 10 mm above the septum retainer nut. In this position, the foam is inside the zone of maximum temperature in the injection port. The temperature program of the gas chromatographic oven is then started, and, after one minute, the melting point tube is retracted to its initial position, that is, with the place where the foam had been now outside the port and 10 mm from the septum retainer nut. After pyrolysis, the residue in the tube generally appeared as a small, opaque, dark brown to black spot of solid surrounded by a halo of clear, pale brown, viscous liquid.

#### In-Line Pyrolysis-GC

In this mode, the pyrolysis is performed in a glass liner positioned inside the injection port of a Perkin Elmer Model 8310-B GC, with the liner outlet being connected to the analytical GC column. The glass liner is 120 mm long and has an o.d. of  $\frac{1}{4}$  in. The original glass liner, liner retainer, and spring were removed from the injection port, and the 120 mm glass liner was attached to the injection port outlet using a  $\frac{1}{4}$  in. graphite ferrule. The GC column was attached to the glass liner by means of a  $\frac{1}{4}$  to  $\frac{1}{16}$  in. Swagelok reducing union (ss-400-6-1) using graphite ferrules. In operation, the injection port is brought up to the desired pyrolysis temperature, and the glass liner is disconnected from it, while still remaining connected to the GC column. The foam (ca. 0.5 mg) is positioned inside the liner about 20 mm from its open end, and the liner is reattached to the injection port outlet so that the foam is outside the port. One minute is allowed for the carrier gas (He) to flush the system clear of air. The nut attaching the liner to the injection port is now loosened slightly, and the glass liner is slid further into the port so that the foam is positioned in its hot zone (20 mm from the inside of the oven door) and the nut is retightened. The oven door is closed, and the program started. The program includes an initial 5 min isothermal period at 45°C to trap the volatiles at the column entrance in order to get sharp GC peaks.

#### Glass Tube Pyrolysis

This was performed on 50–60 mg of foam placed inside a 120 mm long,  $\frac{1}{4}$  in. o.d. glass tube that was fitted with the aid of a graphite ferrule into the  $\frac{1}{4}$  in. injection port outlet of a Perkin Elmer Model 8310-B GC. (In this technique, the gas chromatograph is used not as such but as an oven conveniently



supplied with a source of inert gas.) The outlet end of the glass tube had been necked down to a capillary in order to prevent the back diffusion of air into the tube. Prior to attaching the tube to the injection port outlet, the foam is placed in it so that when attached, the foam will be situated in the oven about 20 mm from the inside of the oven door, with the tube sitting horizontally in the oven. In this mode, the injection port is not heated. With the carrier gas (He) flowing at 5 mL/min, one minute was allowed for the air to be flushed out of the glass tube. On closing the oven door, the GC oven heats up to the preset temperature (usually 340°C). After reaching the end of the desired pyrolysis period, the oven door was opened manually. The purpose of manually opening instead of using the automatic cooling cycle is to increase the cool down rate. The pyrolysis tube was allowed to cool to room temperature under helium flow. After pyrolysis, the tube contained two phases, a viscous, clear light brown liquid, and an opaque, dark brown to black solid. To separate them, the tube was positioned vertically over a small vial with the capillary tip of the tube inside the vial. This allowed the liquid to drip into the vial while the solid remained in the tube. This solid was then washed free of the liquid fraction by flushing the tube with ethanol. The tube containing the ethanol insoluble solid was then reattached to the GC injection port to evaporate the ethanol at 80°C under helium flow until a constant weight was achieved.

### Pyrolysis in Silver Crucibles

This technique was used to obtain pyrolysis residues and transfer them into an elemental analyzer for nitrogen determination. The pyrolysis was performed in the silver crucibles supplied for use with the elemental analyzer. The unit for holding the silver crucibles was built as follows, with all parts being constructed of stainless steel (ss). A  $\frac{3}{8}$  in. Swagelok union (ss-600-6, Swagelok Co., Solon, Ohio) was fitted with two  $\frac{3}{8}$  to  $\frac{1}{8}$  in. reducers (ss-200-R-6) (one at each end). A  $\frac{1}{8}$  to  $\frac{1}{16}$  in. reducer (ss-100-R-2) fitted with a 20 cm length of  $\frac{1}{16}$  in. ss tubing was attached to one of the  $\frac{1}{8}$  in. outlets. This assembly was connected to the  $\frac{1}{8}$  in. outlet of the injection port of a Perkin Elmer Model 8310-B GC by a short piece of  $\frac{1}{8}$  in. o.d ss tubing that was bent 90 degrees so that the  $\frac{3}{8}$  in. union, intended to hold the silver crucible, hangs vertically inside the GC oven. (In this technique, the gas chromatograph is used not as such, but as an oven conveniently supplied with a source of inert gas.) The  $\frac{1}{16}$  in. tube served as a back-dif-

fusion outlet intended to prevent air from entering the unit.

In operation, the silver crucible containing the foam is placed inside the  $\frac{3}{8}$  in. union. With the carrier gas (He) flowing at 5 mL/min, several minutes are allowed for the air to be flushed out of the unit. On closing the oven door, the GC oven will heat up to the preset temperature (usually 340°C) and, after completion of the preset isothermal period, the oven door is opened manually. When the assembly had cooled to room temperature (still under helium flow), it was disassembled, and the silver crucible was transferred directly to the elemental analyzer for determination of the nitrogen content of the residue.

The pyrolysis periods quoted in the body of this work are the periods actually at the given pyrolysis temperatures. These periods do not include the heat up and cool down times.

### Melting Point Tube Loading

Loading small pieces of foam (0.5–1 mg) into the melting point tubes under conditions that avoided contamination by finger contact was found to be quite difficult. The following is a description of the system finally adopted.

A loading funnel was prepared by cutting off the narrow section of a Pasteur pipette at a place in the neck so as to leave a hole just large enough for a melting point tube to pass through. The wide part of the pipette is then cut short to leave a length of about 10 mm above the neck. The open end of a melting point tube is pushed into the small hole of this funnel and positioned so that 1–2 mm protrudes into the funnel. A small piece of tape is used to hold the two together. With a pair of tweezers, a small piece (ca. 0.5 mg) is teased from a piece of foam and placed in the funnel. Holding the tube in the funnel (with forefinger and thumb), this piece of foam is coaxed into the mouth of the melting point tube with the aid of hypodermic needle or piece of wire. When the foam is in the tube, the latter is removed from the funnel, and the foam is worked down the tube with the aid of a straight piece of wire. For the confined pyrolysis mode, the foam is pushed to the bottom of the tube. For the open pyrolysis mode, the foam is positioned 40 mm from the open end of the tube. The melting point tube is then wiped down with a piece of acetone dampened tissue to remove skin exudates and tape glue.

### Gas Chromatographic Conditions

Gas chromatographic conditions were as follows.

A Varian 3700 (Palo Alto, California) was used with a column of 5 m  $\times$  0.53 mm HP-1. Temperatures were as follows: column, initial, 50°C; rate, 15°C/min; final, 280°C. Temperatures in the injection port were 320 and 360°C, and the temperature was 360°C in the FID detector. The flow rate of helium was 10 mL/min.

Another instrument, a Perkin Elmer 8310-B (Norwalk, Connecticut), was used with a column of 30 m  $\times$  0.53 mm Restek Rtx50. Temperatures were as follows: column, initial, 45°C, held 5 min; rate, 15°C/min; final, 330°C, held 10 min; injection port temperatures were 320 and 360°C; FID detector was 360°C. The flow rate of helium was 5 and 12 mL/min.

### Gas Chromatography–Mass Spectrometry

GC-MS conditions were as follows.

A Hewlett Packard HP 5971 (Avondale, Pennsylvania) was used with a column of 20 m  $\times$  0.25 mm Restek Rtx-20. Temperatures were as follows: column, initial, 70°C; rate, 15°C/min; final, 280°C. The injection port temperature was 280°C.

Peak Identification was by retention time comparison with authentic samples in the case of the dynamic modes. The acetone extracts obtained from static mode pyrolysis were injected into the GC-MS with peak identification by library search.

### Preparation of Smokes

#### *Foam Smoke*

0.7 g of foam, cut into small pieces, was placed inside a 500 mL beaker. A glass funnel, which just fit inside the beaker, was placed inverted over the foam at the bottom of the beaker, with the stem of the funnel pointing up. This assembly was placed on a hot plate set at maximum (350°C). After some time, the inside of the cone of the funnel became covered by a solid, dark brown layer. After removing the beaker from the hot plate and allowing the system to cool, the funnel was removed, and the coating on the inside of the cone was washed down with hexane and acetone to remove low molecular weight materials (TDI or DAT). After air drying, the coating was scraped off to yield a dark brown powder.

#### *TDI-DAT Smoke*

0.27 g DAT was placed in a 5 mL beaker, and 0.4 g TDI was placed in another similar beaker. Both beakers were placed in a 500 mL beaker, which was then covered with a watch glass and placed on a hot

plate set at maximum (350°C). After some time, the space in the large beaker was filled with a yellowish vapor, which gradually settled on the walls and the underside of the watch glass. After allowing the system to cool, the watch glass was flushed with hexane and methylene chloride to remove any TDI or DAT that may have condensed there, then allowed to air dry, and then the coating was scraped off to yield a yellow powder. This material was soluble in both DMF and DMSO, but insoluble in hexane, methylene chloride, and acetonitrile.

## RESULTS

To obtain the primary decomposition products and separate and identify them, we applied TGA, various combinations of pyrolysis with GC, GC-MS, IR spectroscopy, and elemental analysis.

### Thermogravimetry

The thermogram presented in Figure 1 shows the behavior of this foam in an atmosphere of nitrogen. The first-stage weight loss recorded by the instrument was 33.2%. If this weight loss consists solely of TDI [reaction (1)],<sup>12</sup> then it represents 95.7% of the TDI used in the foam (34.7%), in which case, the residue should consist mainly of the regenerated source polyol and therefore contain little or no nitrogen. To examine this, nitrogen analyses were run on the residues of foam pyrolyzed to various weight losses.

## EXAMINATION OF PYROLYSIS RESIDUES

### Elemental Analysis of the Residue

Woolley performed nitrogen analysis on residues of foams pyrolyzed under nitrogen at various temperatures in the range of 200 to 300°C. He reported the virtual complete loss of nitrogen from the foam when the weight loss reached about 35%.<sup>12</sup>

We performed similar experiments. However, instead of varying the temperature and holding the pyrolysis period constant, as Woolley had done,<sup>12</sup> we reversed the conditions by holding the temperature constant (340°) while varying the pyrolysis period. These pyrolyses were performed under helium flow in silver crucibles, which were then submitted with their contents for elemental analysis.

The results are given in Table I and Figure 2. In the latter, they are presented as nitrogen loss as a

Sample: POLYURETHANE FOAM  
 Size: 3.4880 mg  
 Method: HIGH RESOLUTION; 10°C/MIN  
 Comment: NITROGEN PURGE

TGA

File: A: NFR-HRTGA.01

Run Date: 16-Oct-93 06:05

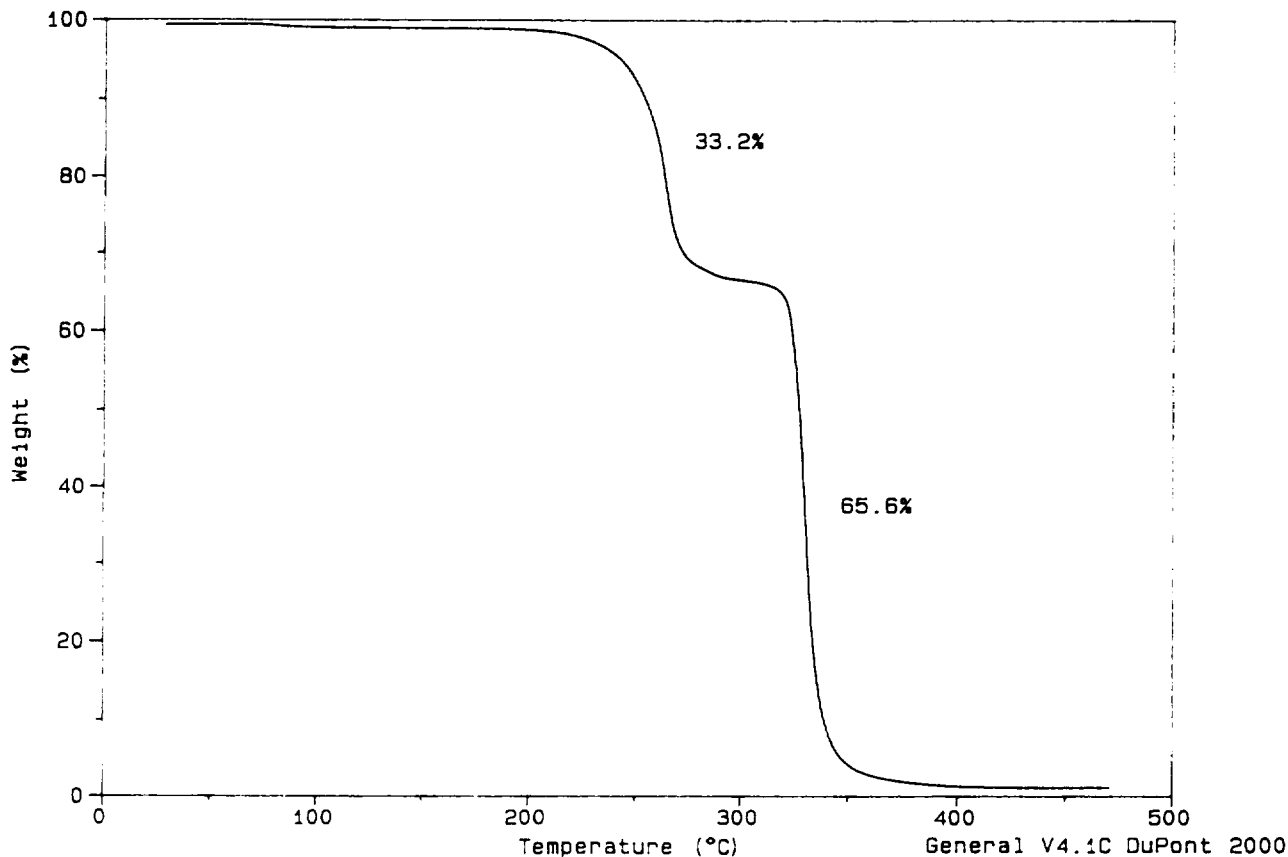


Figure 1 Thermogram of flexible polyurethane foam.

function of weight loss. The initial data points (squares, different data point styles have been used in Fig. 2 to differentiate between the segments of the curve), covering the weight loss up to 26.3%, yield a linear relation between the nitrogen and weight losses ( $r = 0.9998$ ). The curve flattens out above a weight loss of about 35%, reaching a maximum nitrogen loss of about 96%. The linear regression line of the last six points (crosses) of Table I extrapolates back to intersect that of the first five data points (squares) at a point representing a nitrogen loss of 95.6% at a weight loss of 33.7%, in good agreement with the TGA results given above, as well as with those of Woolley.<sup>12</sup>

A linear relation between the nitrogen and weight losses indicates that the material lost had a constant nitrogen content, which suggests that it was either a single compound or a mixture of constant composition. The foam contains 5.6% nitrogen (see experimental). Using this value, the nitrogen content

of the volatiles, up to a weight loss of 26.3% (the linear range), was calculated to be 16.0%. This value is compatible with TDI, which contains 16.1% nitrogen. The loss of nitrogen via reaction (2) (loss of DAT and CO<sub>2</sub>) would produce a vapor containing 13.3% nitrogen. If these volatiles do consist mostly of TDI, then these results indicate that up to a weight loss of 26.3%, a total of 75% of the TDI used in the preparation of the foam (the source TDI) is evolved as free TDI. However, as mentioned above, the few reported attempts to recover the released TDI resulted in recoveries of 2% and less.<sup>12,17,27</sup>

#### Examination of the Liquid Fraction of the Residue

When similar pyrolyses were run in glass tubes, in all cases in which sufficient time was allowed to reach the end of the first decomposition stage, that is, a weight loss of about 34%, the residue consisted of a small dark brown to black solid spot surrounded

**Table I** Pyrolysis in Silver Crucibles for Various Periods at 340°C: Weight Losses of Foam and Nitrogen Contents of Residues

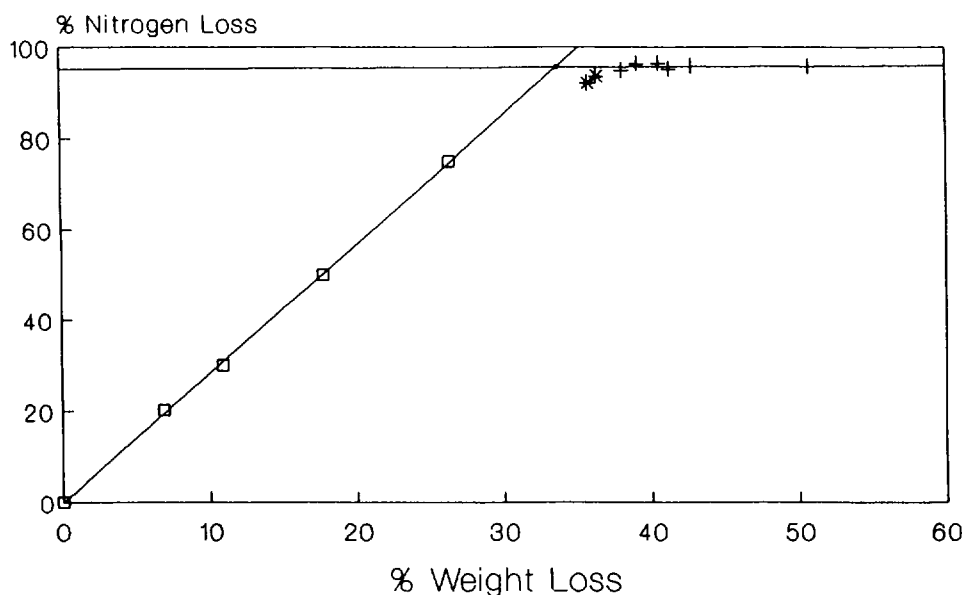
Weight of Pyrolyzed Foam (mg)	Pyrolysis Period (min)	Weight Loss (%)	Nitrogen in Residue (%)	Nitrogen Loss <sup>a</sup> (%)	Data Point Style Used in Figure 2
	0	0	5.6	0	square
3.4	0.5	6.9	4.8	20.2	square
4.0	1.0	10.9	4.4	30.0	square
4.1	1.5	17.7	3.4	50.0	square
4.6	2.0	26.3	1.9	75.0	square
4.6	2.5	35.8	0.70	92.0	star
3.1	3.0	36.4	0.56	93.6	star
3.8	3.5	38.1	0.47	94.8	cross
4.7	4.0	39.1	0.34	96.3	cross
2.1	4.0	40.6	0.34	96.4	cross
1.9	4.0	41.3	0.46	95.2	cross
3.3	4.5	42.8	0.40	95.9	cross
2.5	7.0	50.7	0.49	95.7	cross

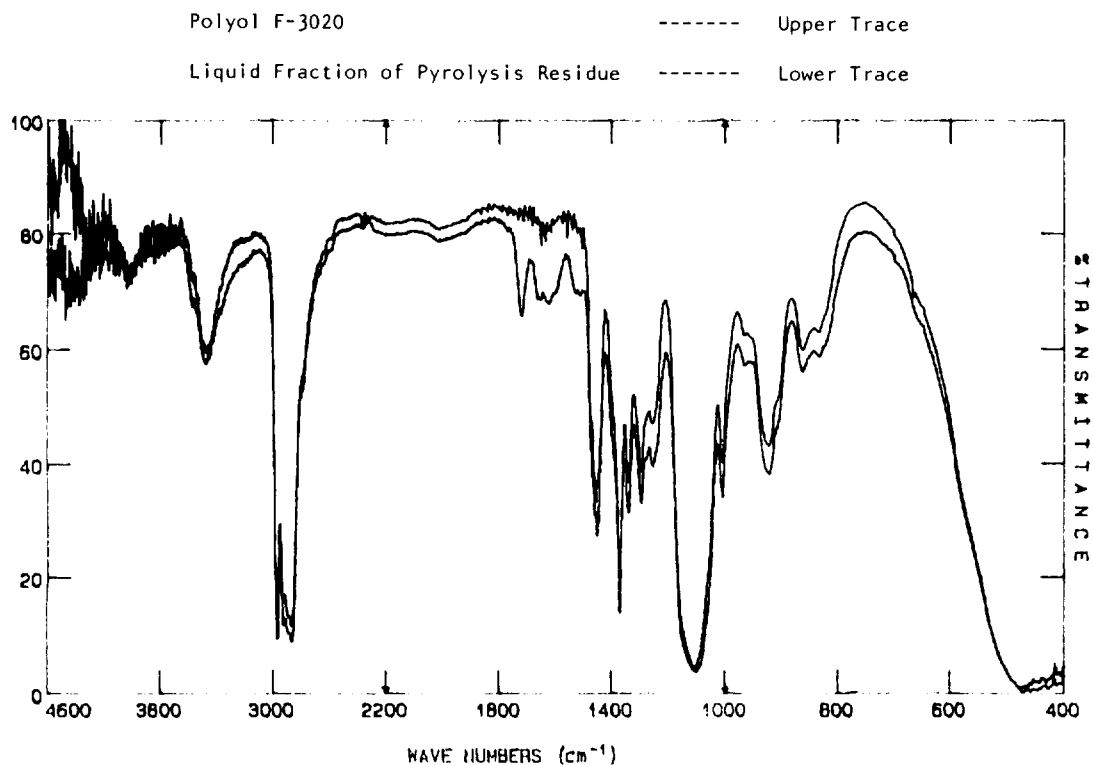
<sup>a</sup> Calculated from nitrogen content and weight of residue.

by a halo of a clear, dark yellow to light brown, viscous liquid. Elemental analysis of the liquid fractions of such pyrolysis residues showed nitrogen contents that ranged from 0.33 to 0.39%. These values represent 3.8–4.5% of the nitrogen originally in the foam, in good agreement with the 95.6% nitrogen loss value extrapolated on Figure 2 (although the black solid has a high nitrogen content, it represents only a small fraction of the weight of the foam).

This liquid is soluble in ethanol, as is the source polyol; the black solid residue is not.

The IR spectrum of the liquid fraction of the pyrolysis residue is given in Figure 3 superposed on that of the source polyol. These two spectra are identical, except for the 1750–1500  $\text{cm}^{-1}$  region, in which only the pyrolysis residue exhibits absorbances. Of the bands in this region, that at 1720  $\text{cm}^{-1}$  can be assigned to the carbonyl of urethane and/or

**Figure 2** Nitrogen loss versus weight loss.



**Figure 3** Infrared spectrum of liquid fraction of foam pyrolysis residue superposed on that of polyol F-3020: polyol F-3020, (-----, upper trace); liquid fraction of pyrolysis residue (-----, lower trace).

isocyanurate; the bands in the  $1670\text{--}1620\text{ cm}^{-1}$  region are characteristic of urea carbonyls, but vinyl ethers also have a band in the lower range of this region, as does the benzene ring; the shoulder at  $1520\text{ cm}^{-1}$  is also in a region characteristic for the benzene ring.<sup>42</sup> The relative weakness of these absorptions, taken together with the almost perfect overlap of the rest of the two spectra and, in particular, that of the hydroxy bands at  $3470\text{ cm}^{-1}$ , indicates that this liquid fraction of the pyrolysis residue consists mainly of the regenerated source polyol. This points to reaction (1) as the major decomposition route for the urethane link; because, had reaction (2) been involved to any marked extent, the hydroxy band at  $3470\text{ cm}^{-1}$  would have been reduced relative to the other absorption bands, as the hydroxy groups of the polyol would have been replaced by double bonds. However, although the material appears to be mostly regenerated polyol, some residual urethane, urea, and, possibly, isocyanurate groups are still present. These could be units still attached to some of the polyether chains, or they could represent dissolved material. In either case,

their concentration is small, with 0.39% nitrogen being equivalent to 2.4% TDI.

Further support for the close similarity between the source polyol and the liquid phase of the pyrolysis residue of the foam was obtained by TGA. Figure 4 presents the superposed thermal derivatograms (derivatives of the weight loss versus temperature thermograms) of three TGA runs: those of the foam, the source polyol, and the liquid phase of the pyrolysis residue. The derivatogram of the foam was derived from a TGA curve similar to that given in Figure 1 and appears here as two peaks. The first, the smaller of the two, centered near  $300^\circ\text{C}$ , represents the 33.2% weight loss of the first stage, involving most of the nitrogen-containing moieties. The larger of the two peaks represents the second stage of the decomposition, the loss (by volatilization and/or decomposition) of the polyol regenerated during the first decomposition stage. It will be seen that this larger peak closely overlaps the (single) peak of the source polyol, as well as that of the liquid phase of the pyrolysis residue. The good matching of these overlaps stresses the similarity between the

Sample: NFR  
 Size: 7.0740 mg  
 Method: TGA-25°-900°C  
 Comment: N2PURGE 100CC/MIN

TGA

File: A:NFR-TGA.01  
 Operator: KLARIS  
 Run Date: 6-Jul-93 01:48

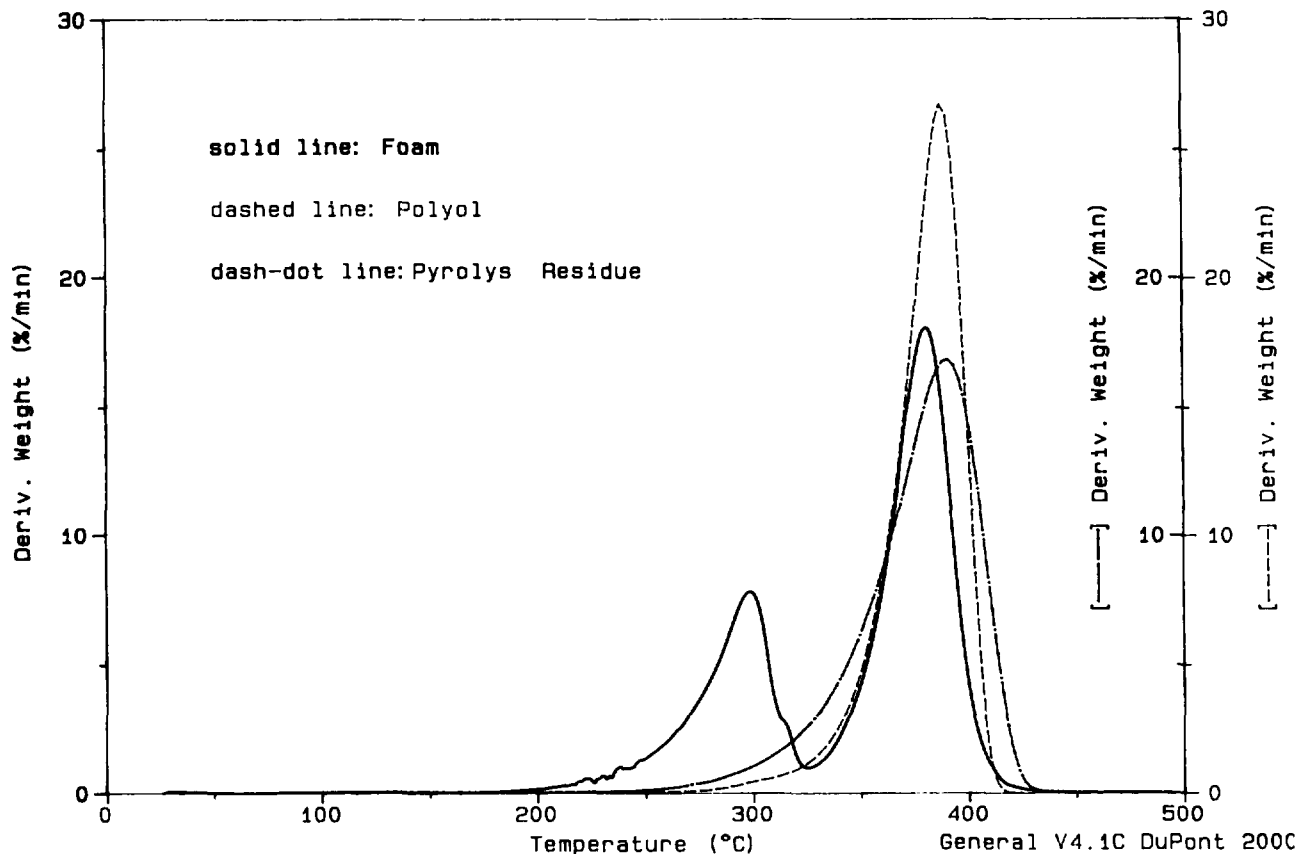


Figure 4 Thermal derivatograms of the foam, polyol F-3020, and the liquid fraction of the foam pyrolyzate.

liquid phase of the pyrolysis residue and the source polyol.

#### Examination of the Solid Fraction of the Residue

Table II summarizes the results of pyrolyses run in glass tubes. Figure 5 (data from Table II) presents the relation between the black, solid, ethanol insoluble fraction of the pyrolysis residue (as a percentage of the weight of the foam) and the total weight loss. The initial part, covering a weight loss up to about 30%, represents residues that still contain undecomposed or partially decomposed foam. As the foam is insoluble in ethanol, such foam residuals will add to the weight of the residue insolubles. The two arms of this plot appear to be linear. The extrapolated lines of these two arms intersect at a point representing a weight loss of 28.7% at an ethanol insoluble

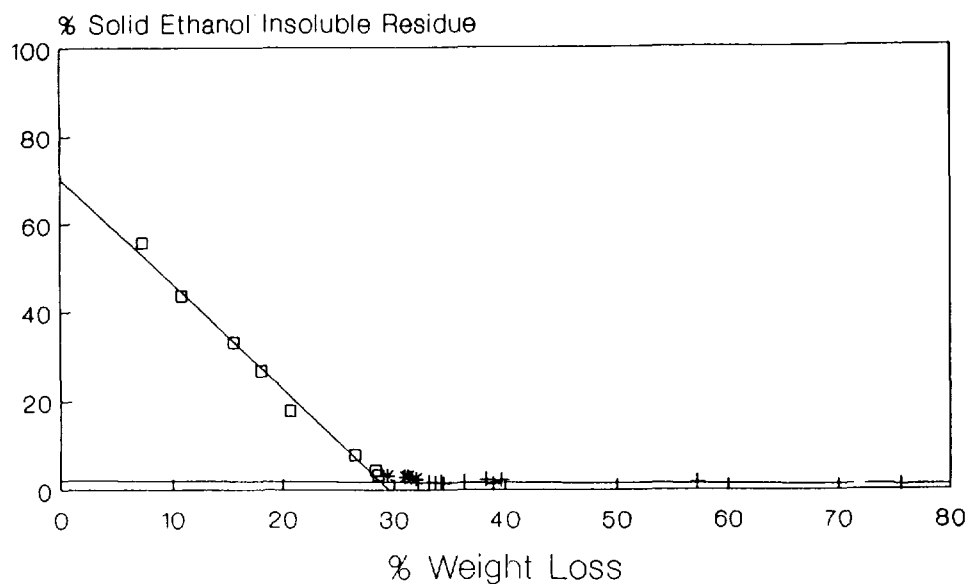
solid residue of 2%. This appears to be the point beyond which undecomposed foam is no longer present. Extending the pyrolysis period causes the solid fraction to lose weight roughly parallel with the total weight loss, dropping to 1% at a total weight loss of 75%.

Extrapolating the initial branch of this plot back to zero weight loss yields a value of 70% for the ethanol insolubles. Should this extrapolation represent the true state of events, with the relation remaining linear all the way back to zero weight loss, this would mean that 30% of the weight of the foam will become soluble in ethanol prior to any material vaporizing off. This could be explained as follows. The urea groups (representing 73% of the nitrogen containing groups in the polymer) are thermally more stable than the urethanes.<sup>7,11,14,15</sup> The latter should therefore be the first to decompose. Although the urethane groups represent only 17% of the ni-

**Table II Weight Loss, Residual Solids and Nitrogen Contents of Foam Pyrolyzed at 340°C for Various Periods**

Weight of Pyrolyzed Foam (mg)	Pyrolysis Period (min)	Total Weight Loss (%)	Solid Black Residue		Data Point Style Used in Figures 5 and 6
			Weight (%) <sup>a</sup>	Nitrogen Content (%)	
78	0.05	7.3	55.6	7.9	square
63	0.3	10.8	43.5	8.3	square
50	0.5	15.5	33.1	8.2	square
52	0.5	18.0	26.6		
48	0.7	20.6	17.9	8.2	square
60	1.3	26.4	7.9	9.2	square
55	1.5	28.3	4.4	10.2	square
67	2.0	28.5	3.4	12.0	square
89	3.0	29.4	3.3	15.4	square
118	4.0	31.0	3.0	14.1	cross
122	4.0	31.3	3.1	15.5	cross
96	4.0	32.0	2.5	14.3	cross
57	2.5	32.2	1.7	12.4	cross
68	3.5	33.2	1.8	12.7	cross
57	4.0	33.8	1.6	12.9	cross
78	5.0	34.3	1.7	13.8	cross
65	4.5	34.5	1.5	12.5	cross
77	6.0	36.7	1.8	13.7	cross
74	4.0	38.3	2.4		
74	8.0	39.0	1.4	13.4	cross
70	12.0	39.7	2.3	12.7	cross
69	15.0	57.2	1.7	11.6	cross
65	20.0	75.6	1.1	11.1	cross

<sup>a</sup> As a percentage of the foam.

**Figure 5** Pyrolysis solids versus weight loss.

trogen-containing groups in the polymer (see above, under discussion), these groups are attached directly to the polyether chains, which make up 65% of the weight of the foam. The initial dissociation of the urethane links, by breaking the cross-links, could release a relatively large amount of ethanol soluble polyether (or polyol) without producing much volatile material at this initial stage. However, although the first five data points on Figure 5 yield a line with an  $r$  value of 0.995, this linearity may be an artifact; the plot could actually curve up to the 100% mark on the y-axis.

Figure 6 (data also from Table II) plots the relation between the nitrogen contents of the solid fractions of the pyrolysis residues and the amount of these solids as residuals of the foam. Following the data points (squares) from the high (right) end of the "% pyrolysis solids" axis of this figure back towards the lower (left) end, there is only a very small increase in the nitrogen content down to about 10% of residual solids. This branch of this bifurcated curve covers the region where the residual solids still contain undecomposed foam. Continuing back beyond this point, there is a sudden rise in nitrogen content of the solids, the curve forming a cusp with a maximum at 15.5% nitrogen in a solid representing 3.1% of the foam. Going back from the maximum of the cusp towards the origin, it can be seen that the nitrogen content of these residual solids drops rather sharply down to about 11% in a solid representing 1% of the weight of the foam. This part of the curve uses crosses as data points. The point of

the cusp represents an total weight loss of 29.4%, which is very close to the value of 28.7% for the intersection point on Figure 5. The high nitrogen content at the cusp may represent the stage where the black material is at (more probably, near) its maximum concentration before it begins to decompose, as indicated by the fall in its nitrogen content.

Figure 7 gives the IR spectrum of one of these residual, black, ethanol insoluble solids. The bands can be assigned as follows.<sup>42</sup> The one at  $3370\text{ cm}^{-1}$  probably represents 1,3-disubstituted urea; the band at  $2140\text{ cm}^{-1}$ , carbodiimide; the shoulder at  $1720\text{ cm}^{-1}$ , isocyanurate; the broad absorption at  $1640\text{ cm}^{-1}$ , urea; and that at  $1110\text{ cm}^{-1}$  may be due to residual ether groups. However, the weakness of the C—H absorptions in the  $3000\text{--}2800\text{ cm}^{-1}$  region suggests the source of these C—H absorptions to be mostly aromatic. This is supported by the H/C ratios of these materials (elemental analysis) which ranged from 1.0 to 1.2, characteristic of aromatics. This implies that very few aliphatic ether groups are present.

The carbodiimide in these materials probably arises from the condensation of isocyanate groups.<sup>1-6,43</sup> Carbodiimides are readily hydrated to ureas.<sup>1-6</sup> Should this reaction be reversible, it could also explain the presence of carbodiimide. However, in a review on carbodiimides,<sup>43</sup> the possibility of dehydrating ureas to carbodiimides is not mentioned. The dark color of these solids suggests a highly conjugated system. Their insolubility points to cross-linking.

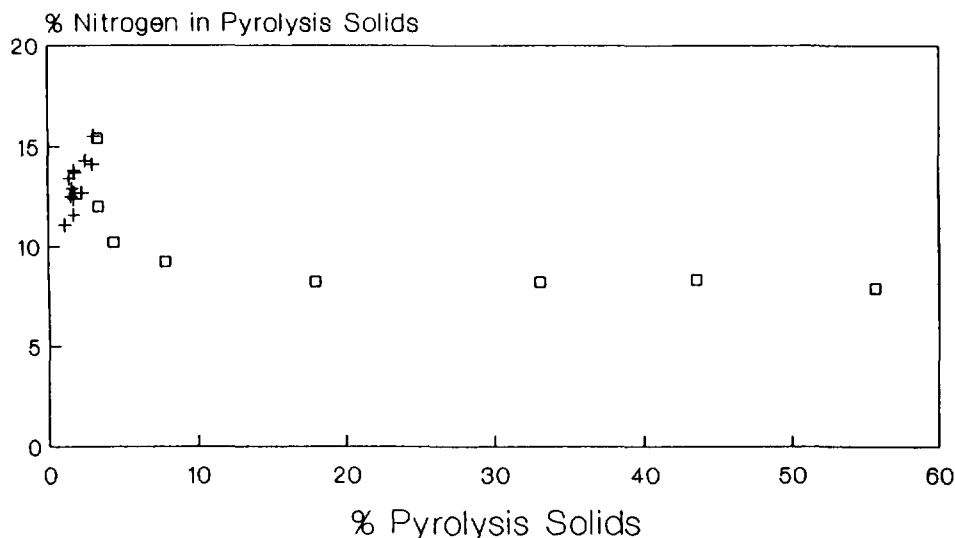


Figure 6 % N in pyrolysis solids versus % pyrolysis solids.



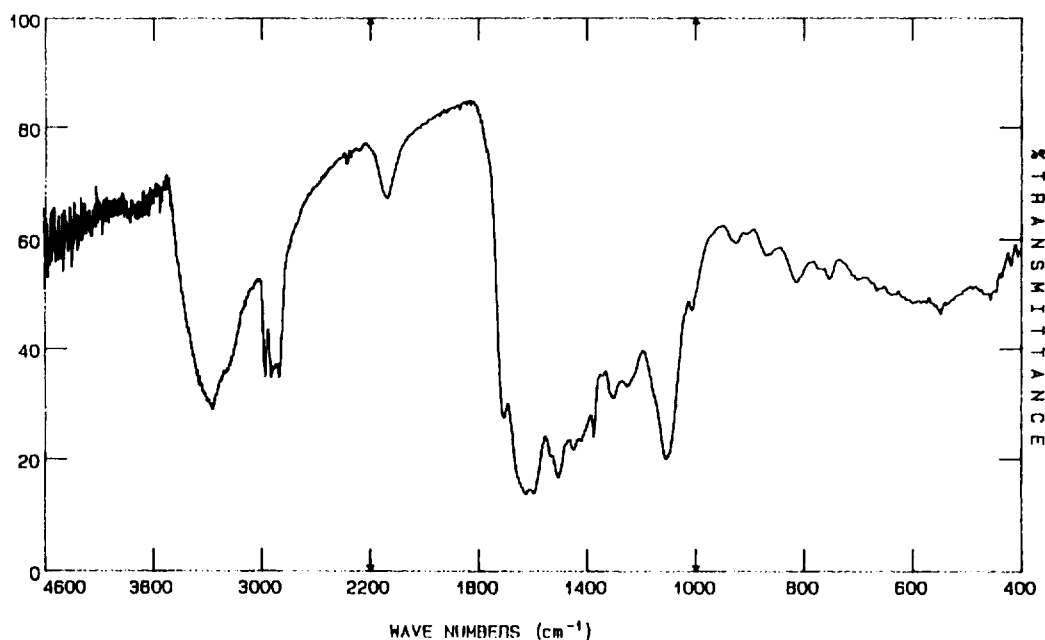


Figure 7 Infrared spectrum of solid fraction of foam pyrolysis residue.

## EXAMINATION OF THE PYROLYSIS VOLATILES

### Pyrolysis-Gas Chromatography (Py-GC)

This technique has been applied before to polyurethanes, but in temperature ranges well above that of the first-stage decomposition.<sup>44-46</sup> The high temperatures employed lead to secondary reactions yielding a large number of products. The tendency for such secondary reactions to occur is markedly reduced at the temperatures which we employed.

Three techniques, detailed in the experimental section, were employed.

### Confined Mode Pyrolysis

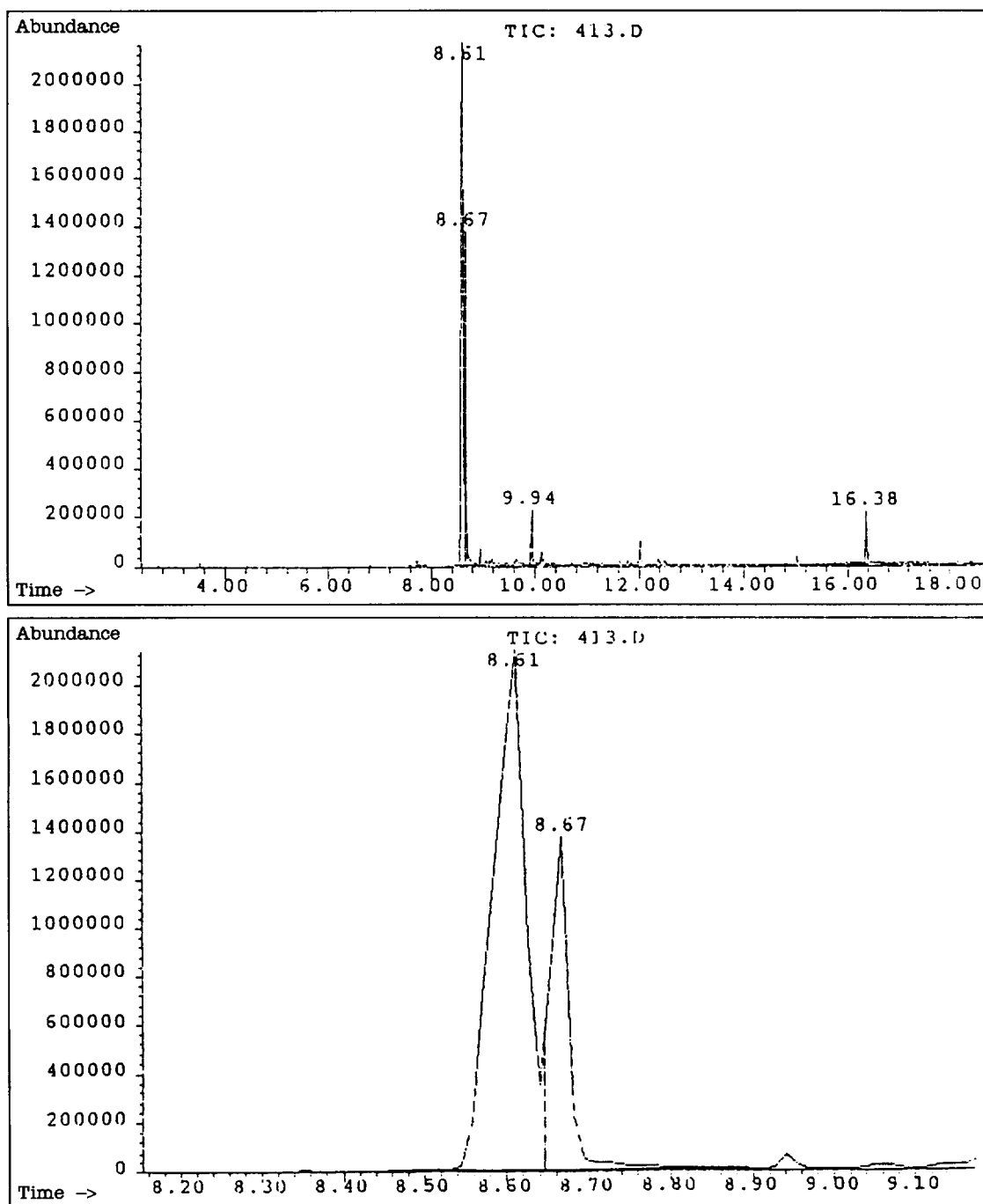
This is really not a true Py-GC technique and could be termed pyrolysis plus gas chromatography. It involves pyrolyzing the foam in a sealed (under vacuum) melting point capillary, solvent-extracting the product, and injecting it into a gas chromatograph. Figure 8 presents the gas chromatogram of the acetone extract (acetone peak not shown) of a foam pyrolyzed for 10 min at 320°C. The two partially resolved peaks at 8.61 and 8.67 min, which represents 88% of the total peak area, are shown more clearly in the lower part of this figure on an expanded scale. They represent the 2,4- and 2,6-isomers of

diaminotoluene (DAT), as identified by their mass spectra given in Figures 9 and 10. The area ratio of these two peaks is 2.6 : 1. This is somewhat different from what would have been expected from the 4 : 1 tolylene diisocyanate isomer ratio generally present in technical quality material, such as that used for the preparation of the foam under study. The difference may be due to inaccurate integration resulting from the incomplete separation.

The small peak at 9.94 min was not reliably identified. That at 16.38 min was identified by the mass spectrometer library search as dioctyl phthalate. The source of this peak is the Dabco T-10 catalyst used in the formulation which, according to the manufacturer's data sheet, contains this phthalate ester. (As this material is not a product of the pyrolysis of the polyurethane, its area can be subtracted, raising the area of the diaminotoluene peaks to 92% of the peaks on the chromatogram.)

No higher boiling materials appeared on the chromatogram, which is not unexpected, as the polyol used in the formulation of this foam is stable under the pyrolysis conditions employed; nor does it have sufficient vapor pressure to pass through the column under the chromatographic conditions applied.

TDI was not detected among the pyrolysis volatiles.



**Figure 8** Chromatogram of acetone extract of confined mode foam pyrolysis.

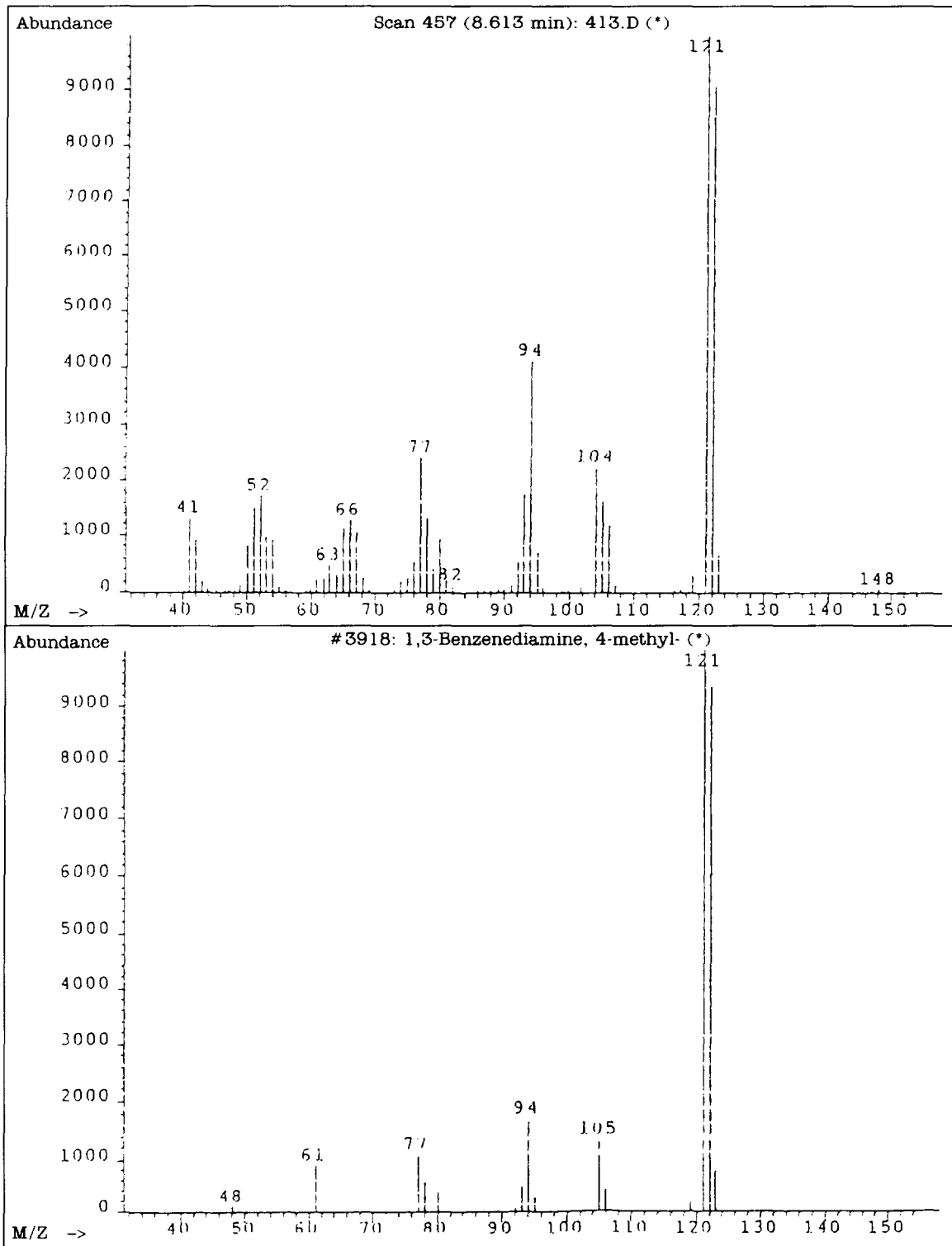


Figure 9 Mass spectrum of component of retention time of 8.613 min of Figure 8.

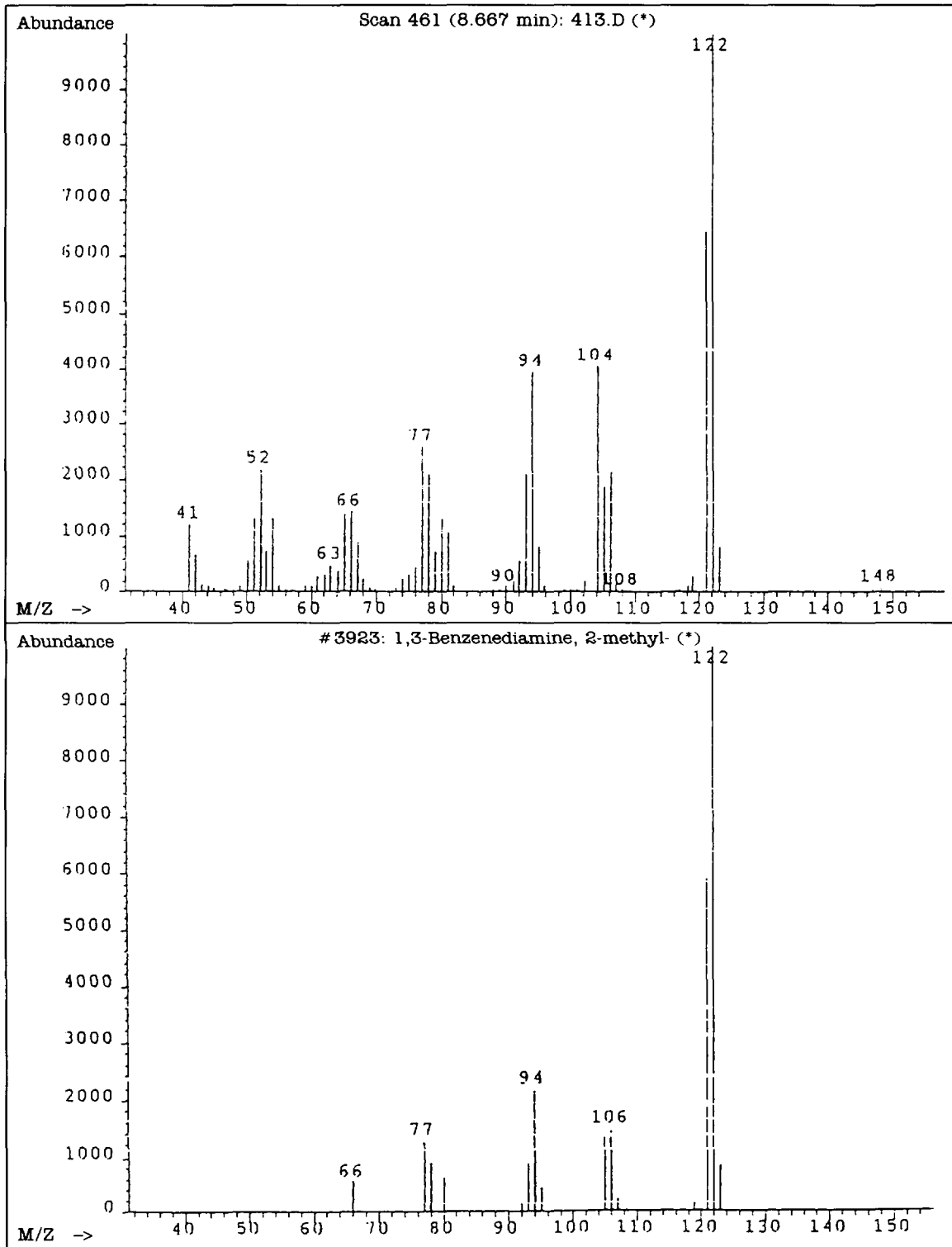


Figure 10 Mass spectrum of component of retention time (8.667 min) of Figure 8.

Using an internal standard (benzonitrile) in the extracting solvent, the DAT in the pyrolyzate was established to represent 6.9% of the weight of the foam, which is equivalent to 28% of the TDI used in the preparation of the foam.

That the source of the DAT in the pyrolyzate was not from free DAT present in the foam prior to the pyrolysis was shown by acetone extracting the foam. No DAT was detected in the extract. Pyrolysis of a foam that had been vacuum-dried at 105° overnight (0.4% weight loss) gave a qualitatively identical chromatogram, the major peak being identified as DAT; this showed the DAT not to be a product of a hydrolytic pyrolysis involving moisture adsorbed on the foam.

### Open Tube Mode Pyrolysis

Confined mode pyrolysis involves time periods of minutes, and, as time increases, so do the opportunities for secondary interactions, such as decomposition of the first-stage products or interactions between them. To reduce the chances of this, an open tube pyrolysis technique was developed.

This mode employs an open-ended melting point capillary, with the open end being pushed through the septum of the injection port of a gas chromatograph, and the injection port acting as a pyrolysis chamber. The foam is positioned in the capillary so that when the latter is pushed further into the injection port, the foam will be in the hot zone. After the specified pyrolysis period, the capillary is partially retracted, effectively withdrawing the pyrolysis residue from the hot zone without interfering with the chromatographic run (see experimental section for details).

Under open tube pyrolysis conditions, the volatile products are swept by the carrier gas onto the gas chromatographic column as they emerge from the melting point capillary. Once on the column, they are at a much lower temperature and become separated from one another; as a result, the chances of their interacting with each other or with the residue are greatly reduced. Fast secondary reaction can, however, still occur in this mode.

Open mode pyrolyses of foams were run on both air-equilibrated and vacuum-dried foams at 320°C, as well as at 360°. The pyrograms were qualitatively very similar to each other as well as to the chromatograms of the confined mode of these two foams. Each had a single major peak, identified as DAT, as well as a number of very small peaks. (open mode pyrolyses were performed on a Varian gas chromatograph fitted with a short column, which did not

separate the diamine isomers, so they emerged as a single peak. Identification was by retention time comparison with an authentic sample of DAT. No peak with the retention time of TDI was present on the pyrogram.)

The production of DAT should be accompanied by the formation of CO<sub>2</sub>. To check this point, a piece of foam was pyrolyzed under vacuum in a septum-capped vial by standing it on a hot plate set at maximum (350°C). After collapse of the foam structure, the vial was allowed to cool to room temperature, nitrogen was injected to bring the pressure in the vial up to ambient, and a sample of the gases in the vial was then injected into the GC-MS. CO<sub>2</sub> was identified as a major component of these gases.

Identification of the major component of the first-stage decomposition volatiles as DAT and the total absence of TDI in these volatiles tends to support reaction (2) rather than reaction (1) as the major decomposition mechanism for the urethane link.

### In-line Pyrolysis-Gas Chromatography

In this mode, the injection port of the gas chromatograph is also used as a pyrolysis chamber, the foam being pyrolyzed directly in the carrier gas stream inside the injection port liner. The volatile products will therefore be swept out of the hot zone into the separating column as they are formed (for details, see the experimental section). In this "in-line" mode (for lack of a more appropriate term), there is even less time for secondary interactions to occur than in the "open capillary" mode, in which the volatile products first have to diffuse or expand out of the capillary tube before they can enter the carrier gas stream to be swept out of the pyrolysis zone and onto the GC column.

The chromatogram resulting from the pyrolysis of 0.8 mg of foam at 340° is shown in Figure 11. The peak of retention time 13.583 min is that of TDI, identified by retention time comparison with an authentic sample. (Under these conditions, DAT had a retention time of 15.1 min, a time difference more than sufficient to confirm that the material of retention time 13.58 min was not DAT.)

The large, very broad peak at 23.040 min has not been identified. The broadness of this peak is uncharacteristic for this type of chromatographic column. A compound with this retention time would have been expected to produce a peak at most slightly broader than that of the TDI peak. This was confirmed by injecting, under the same conditions, dotriacontane (C-32), which produced a narrow peak of retention time (22.3 min). The similarity

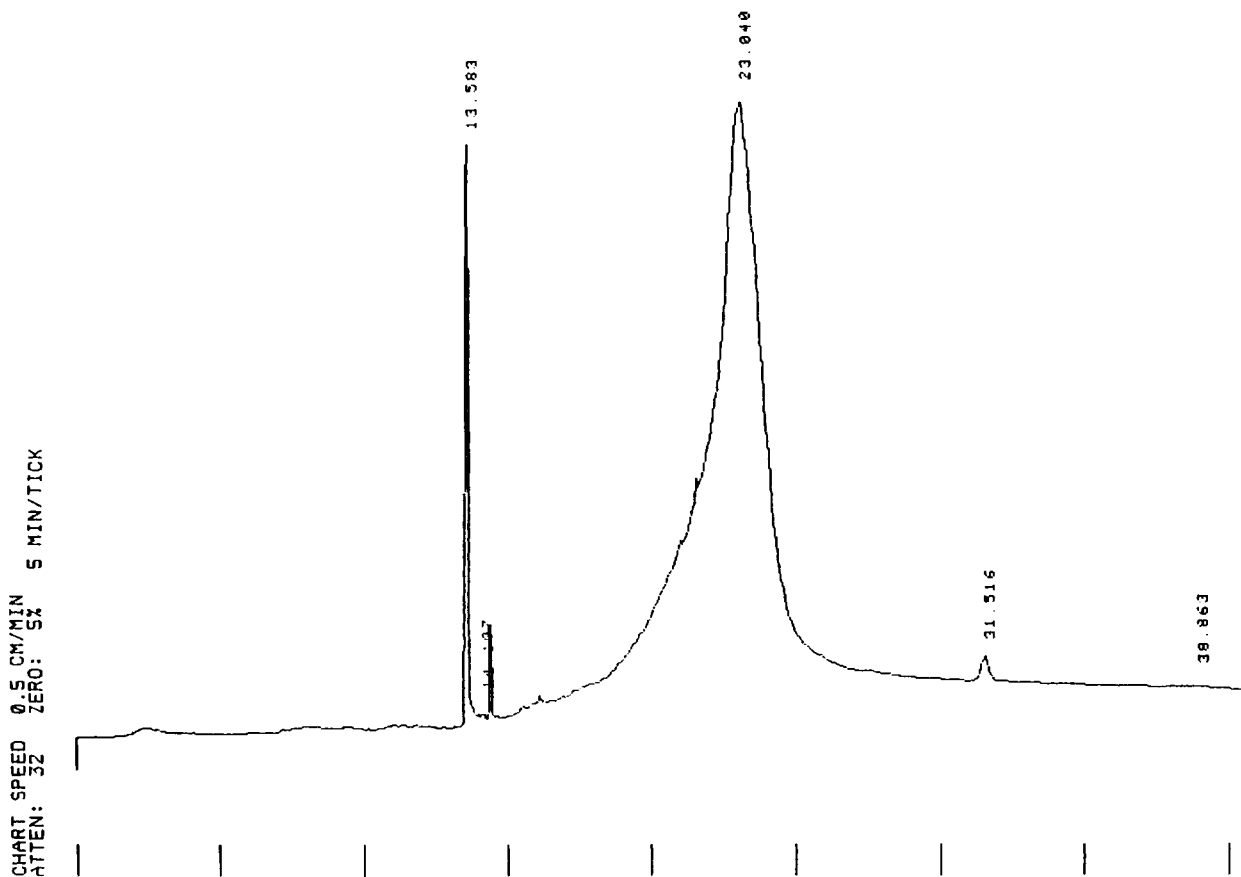


Figure 11 Pyrogram of foam by in-line Py-GC.

of retention times suggests that the broad peak represents a material of molecular weight similar to that of dotriacontane (450). It is feasible that the broadness of the peak represents a mixture of compounds of similar vapor pressures. However, we prefer another explanation, which is discussed below.

Injection of the source polyol under these conditions did not give rise to any peaks, indicating that the source of the broad peak does not lie in the polyol fraction of the foam.

The external standard technique was used to calibrate the detector response of the gas chromatograph for the TDI peak. It was found that over the range of the weights of foam examined, 0.2–1.9 mg, the TDI recovery was related inversely to sample size. The following relation was found to apply at a flow rate of 12 mL/min:

% TDI recovered

$$= 3.8 \times (\text{mg foam})^{-1} + 3.1, \quad r = 0.997 \quad (7)$$

(see Fig. 12 and Table III).

Such an inverse relation suggests that the TDI is involved in a reaction, the extent of which depends on its residence time in the pyrolysis zone. The residence time can be split into two stages, time spent in the melt of the decomposing sample, and time spent in the pyrolysis zone but outside the sample matrix. The former, being diffusion controlled, depends on the surface to volume ratio of the sample; the latter depends on the flow rate of the carrier gas. As the surface to volume ratio is inversely related to sample size, this would explain the decreasing recovery of TDI with increasing sample size. The larger the sample, the longer it will take the volatile products to diffuse out; therefore, the greater the chances of secondary reactions.

The effect of carrier gas flow rate on the TDI recovery is demonstrated in Table IV. For comparative purposes, the recoveries found were normalized by determining the values predicted by eq. (7) for a flow rate of 12 mL/min. As expected, increasing the flow rate increased the recovery. Reducing the flow rate reduces it. The difference between 12 and 20

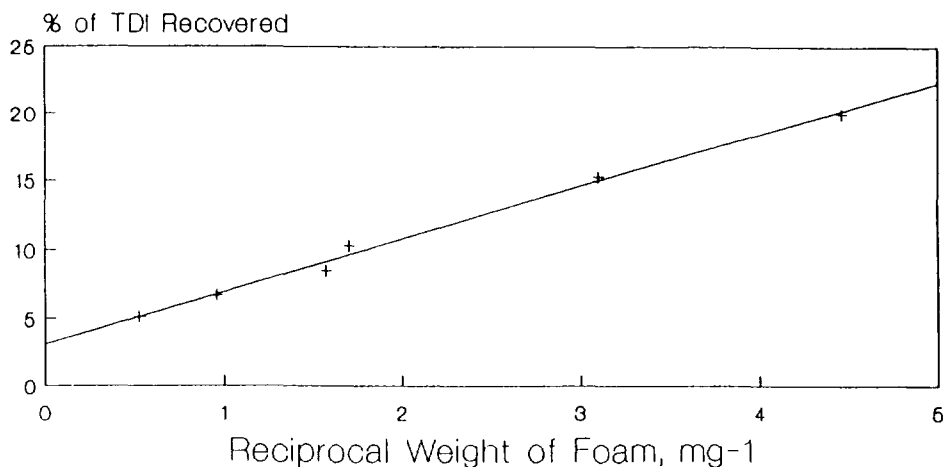


Figure 12 % TDI recovery as a function of reciprocal foam weight.

mL./min is not large. This is not unexpected as, at high flow rates, diffusion out of the sample will become the limiting factor. The extent of the effect of flow rate will therefore diminish as the flow rate increases. At the low flow rate, the drop in TDI recovery was striking.

These results lend strong support to the conjecture that the TDI released undergoes a secondary reaction in the pyrolysis zone.

### Smokes

As discussed above, according to the literature,<sup>22-24</sup> urea groups dissociate on heating to yield amine and isocyanate groups. Isocyanates react rapidly with amines at ambient temperatures to form ureas.<sup>22,23</sup> Therefore, if a polyurea is pyrolyzed on cooling the resulting vapors, it would be anticipated that they condense to reform the polyurea, probably as an aerosol. This has been proposed above to be the basis

of the mechanism for the formation of the yellow smoke.

In order to examine this hypothesis, we mixed the vapors of TDI and DAT (see the experimental section for details). The result was a yellow aerosol, which condensed on the cold parts of the apparatus. On scraping it off, it yielded a dark yellow powder soluble in DMF and DMSO. We also collected the smoke given off by a piece of foam undergoing pyrolysis. This smoke was much darker in color. Figure 13 gives the superposed spectra of these two smokes. These spectra are very similar. The following assignments can be made<sup>42</sup> for the common absorbances (wave numbers in  $\text{cm}^{-1}$ ):  $-3320$ , 1,3-disubstituted urea;  $2270$ , isocyanate;  $1650$  and  $1600$ , urea  $\text{C}=\text{O}$ ;  $1540$ , amide II;  $1220$ , polyurea; and  $870$  and  $810$ , 1,2,4-trisubstituted benzene. The major difference between these two spectra appear in the  $\text{C}-\text{H}$  region ( $2900 \text{ cm}^{-1}$ ), where the foam-derived smoke exhibits very small absorbances, and at  $1090 \text{ cm}^{-1}$ , where the foam-derived smoke has an absorbance that can be assigned to aliphatic ether. In other words, the foam-derived smoke appears to contain some polyol fragments. It is unlikely that these additional absorptions are due to volatile fragments of the polyol. Both smokes were solvent-washed, which would have removed any residual polyol, TDI, or DAT. Further confirmation for this was obtained by dissolving the foam-derived smoke in DMF and precipitating it with methanol. Neither the putative ether band nor the absorptions due to  $\text{C}-\text{H}$  were detectably diminished.

The method of preparation of this TDI-DAT smoke was rather crude as there was no control of the amounts of the two materials entering the vapor phase. A second preparation of this smoke gave a

Table III Recovery of TDI as a Function of Amount of Foam Pyrolyzed

Weight of Pyrolyzed Foam		TDI Recovered (%)
mg	mg <sup>-1</sup>	
1.918	0.52	5.1
1.042	0.96	6.7
0.636	1.57	8.5
0.589	1.70	10.3
0.325	3.08	15.3
0.224	4.46	20.0

**Table IV** Effect of Carrier Gas Flow Rate on TDI Recovery

Weight of Pyrolyzed Foam (mg)	Carrier Gas Flow Rate (mL/min)	TDI Recovery (%)	
		Found	Calculated for a Carrier Gas Flow Rate of 12 mL/min <sup>a</sup>
0.465	6	3.1	11.3
0.577	20	10.9	9.7

<sup>a</sup> Calculated from eq. 7.

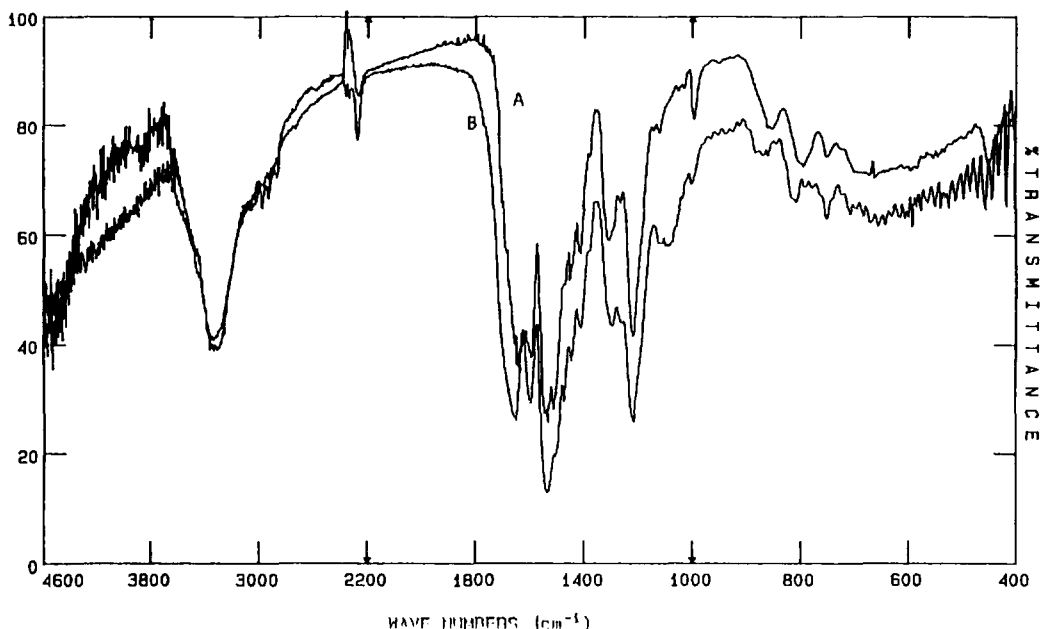
material, the spectrum of which showed a very strong isocyanate band at  $2260\text{ cm}^{-1}$  (Fig. 14). Otherwise, the spectrum was identical to that of the first preparation. This second batch was apparently prepared under conditions of excess TDI vapor, which would be expected to lead to the formation of isocyanate-terminated chains. Support for this was obtained by showing (1) that the band was not due to the presence of free TDI, as it could not be washed out with methylene chloride (in which TDI is soluble); and (2) that it was removed when a solution of this smoke in DMSO was mixed with a solution of DAT in DMSO, and the polymer was then precipitated with acetone.

Table V gives the elemental composition of these smokes as well as that reported by Woolley<sup>12</sup> for his yellow smoke.

It will be seen from Table V that the TDI-DAT smoke is very close in elemental composition to that

calculated for a polyurea based on TDI and DAT. Woolley's results for his smoke are also fairly close; the lower nitrogen content and increased hydrogen probably reflect the presence of some polyol fragments. The markedly lowered nitrogen and carbon content of our foam-derived smoke is probably due to oxidation (the oxygen content derived by difference is very high). Our smokes were prepared in air, whereas Woolley prepared his smoke under nitrogen. Although the TDI-DAT smoke was also prepared in air, this all aromatic material would be far less sensitive to oxidation than a material containing aliphatic ether fragments.

Injecting a DMF solution of this TDI-DAT smoke into the gas chromatograph produced a broad peak (Fig. 15) very similar both in shape and retention time (23.42 minutes) to that on the "in line" pyrogram (23.04 min. on Fig. 11). However, relative to the amount of material injected, this peak was small



**Figure 13** Infrared spectra of smokes: (A) TDI-DAT smoke; (B) foam pyrolysis smoke.



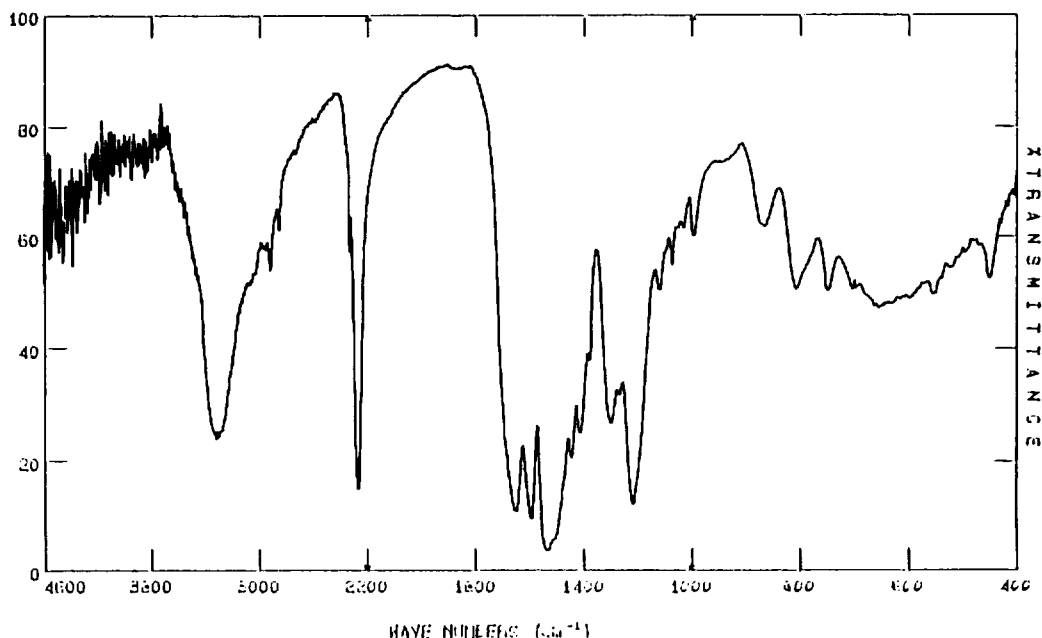


Figure 14 Infrared spectra of TDI-DAT smoke with excess TDI.

and therefore probably represents only a fraction of the TDI-DAT smoke.

## PROPOSED MECHANISMS

### Decomposition the Urethane Group

The results of this study lead to what appear to be conflicting conclusions. The spectrum of the liquid phase of the residue shows it to be the regenerated polyol, which points to reaction (1). So does the nitrogen content calculated for the pyrolysis volatiles, 16.0%, which, being almost identical to the 16.1% nitrogen in TDI, strongly suggests these volatiles to be made up largely of the latter. This was confirmed by in-line pyrolysis, which showed TDI to be the major volatile product, therefore, also pointing to

reaction (1). On the other hand, pyrolyses performed in capillaries yielded DAT as the major volatile, which points to reaction (2) as the major route. In-line pyrolysis not only showed TDI to be a primary decomposition product, it also showed that the TDI is involved in a secondary reaction. The confined pyrolysis in the capillaries showed DAT to be the major volatile end product of this secondary reaction.

We suggest a mechanism that can reconcile these results. It is proposed that the decomposition of the urethane group follows both reactions (1) and (2), but that the former has a much higher rate. Under conditions in which the TDI produced can escape, it will be the major volatile product, with the residue consisting of the regenerated polyol. However, when the TDI is confined to the pyrolysis zone, reaction (1) being reversible,<sup>47</sup> an equilibrium will be established between the urethane group, on the one hand, and the isocyanate of the TDI and the hydroxy of the regenerated polyol, on the other. The existence of such an equilibrium would favor reaction (2), which, although slower, is irreversible. Therefore, under confined conditions, given sufficient time, all the TDI potentially available from the urethane group via reaction (1) will eventually be released as DAT via reaction (2).

This proposal is supported by the finding that under confined mode pyrolysis, the DAT recovered was equivalent to 28% of the source TDI. This is remarkably close to the 27% calculated above as the

Table V Elemental Composition of Smokes

Smoke	Percent			
	C	H	N	O <sup>a</sup>
Woolley's Yellow Smoke <sup>7</sup>	64.2	5.7	17.0	13.1
Foam smoke	59.7	5.9	14.5	19.9
TDI-DAT smoke <sup>b</sup>	63.2	5.9	18.4	12.5
TDI-DAT polyurea (calculated)	64.9	5.4	18.9	10.8

<sup>a</sup> By difference.

<sup>b</sup> From the first preparation, having only a very small isocyanate band.

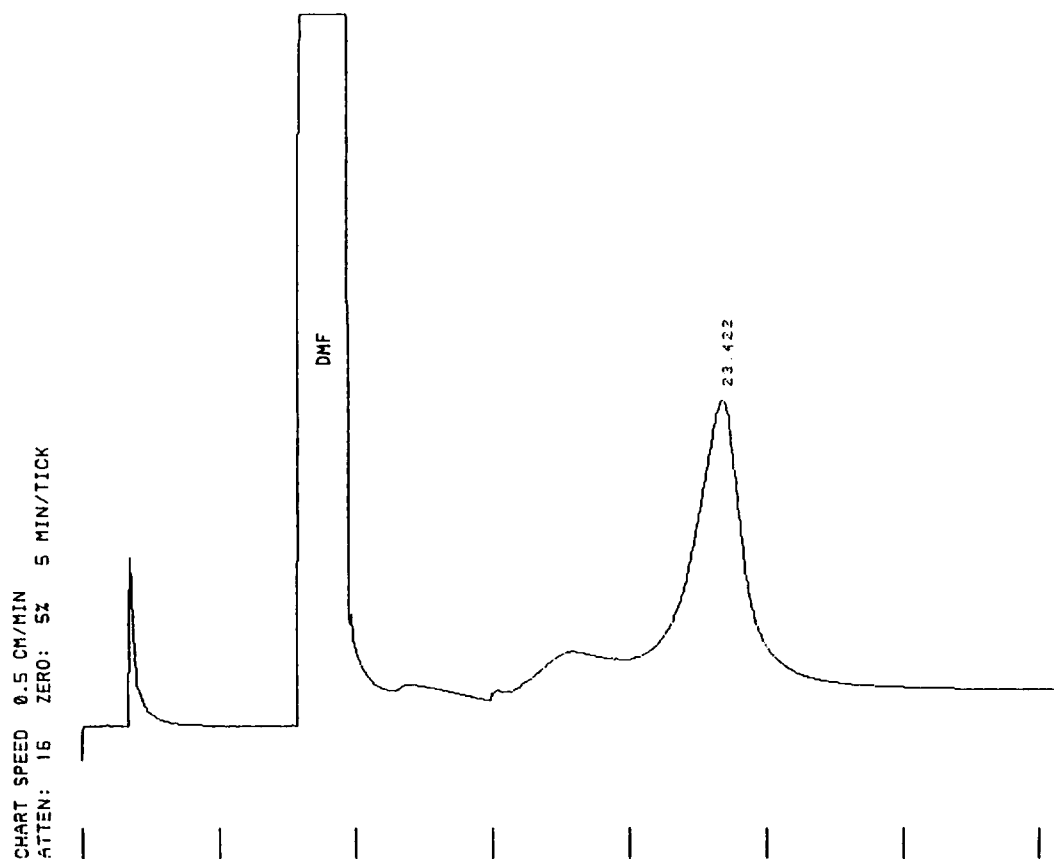


Figure 15 Chromatogram of TDI-DAT smoke in DMF solution.

maximum amount of source TDI potentially available from the biuret and urethane groups. However, if the potentially available TDI is 27% of the source TDI, according to the above calculations, this is so only if this material is released as TDI. Released as DAT, only 7% should be available, the difference of 20% forming a polyurea. The confined mode recovery of 28% of the TDI as DAT may therefore indicate that the foam contains less biuret and/or more urethane groups than the above calculations indicated.

The highest recovery of TDI in the in-line work above was 20% (for the smallest sample, 0.224 mg). Although less than the calculated value of 27%, it is near enough to contribute some support to the proposal. Further reduction in sample size would be expected to raise this value [unfortunately, eq. (7) cannot be used to extrapolate the recovery to zero sample weight].

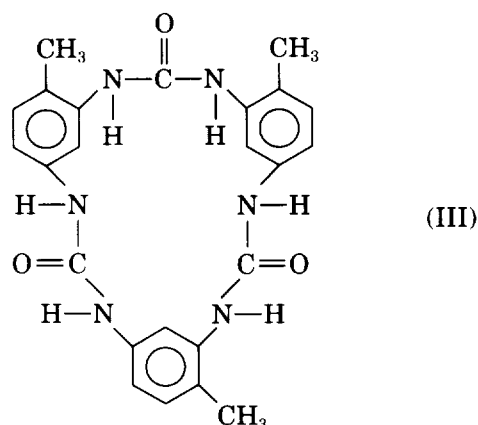
This is a simple explanation based solely on mechanisms proposed in the literature. It can also reconcile some of the conflicting reports in the literature.

### Decomposition of the Urea Group

As discussed above, this group can dissociate reversibly to yield the source components, the amine and the isocyanate; in this case, DAT and TDI. As proposed above, these relatively low boiling materials recombine in the vapor phase to form an aerosol of polyurea, the yellow smoke.

Regarding the broad peak in Figures 11 and 15, it is tentatively suggested that this material is a cyclic urea trimer. Dissociation of a polyurea based on TDI and DAT units may occur not only via the regeneration of the two source components, TDI and DAT, it could also result in the formation of aminoisocyanato toluene (see Scheme II, above), the empirical monomer of this polyurea.

The cyclic trimer of this material (see Scheme III) would have a molecular weight of 444, very close to that estimated above (by analogy to the retention time of dotriacontane) for a material of retention time of the broad peak on the pyrograms of Figures 11 and 15.



The reaction between TDI and DAT can produce cyclic ureas only of an even number of urea units. The amino-isocyanato toluene is not limited in this respect. An oligomeric urea of molecular weight in the region of 450 can therefore be formed only from the amino-isocyanato toluene.

If, as proposed, the broad peak represents a trimeric urea, its formation would involve at least two steps: dissociation of the urea segments in the foam, followed by reassociation in the vapor phase, most probably in the form of an aerosol of solid particles. Although solids cannot be transported along a gas chromatographic column, such a material could move along the column by a series of dissociation-reassociation steps, the dissociation step producing volatiles which move down the column. This is similar to the mechanism involved in the volatilization of ammonium chloride. Such a mechanism could account for the broadness of the 23 min peaks in Figures 11 and 15.

The black ethanol insoluble solid may be derived from polyurea sections that are cross-linked by biuret units.

For the foam, we are indebted to Ms. Barbara Williams, Akzo Research Laboratories, Dobbs Ferry, New York. The help of the following IMI persons is gratefully acknowledged: Ms. Irena Kaufmann (IR spectroscopy), Ms. Yael Winter (elemental analysis), Ms. Klaris Oren (TGA), Ms. Suzi Aloni (GC-MS), Mr. David Direktor (literature search), and especially Ms. Ina Keidar for many helpful discussions. One of us, M. R., wishes to express special gratitude to Professor Edward D. Weil of the Polymer Research Institute, Polytechnic University, Brooklyn, New York, for many helpful discussions. Part of this study was done on M. R.'s sabbatical at the Polytechnic University's Polymer Research Institute.

## REFERENCES

1. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology. Part I. Chemistry*, Wiley-Interscience, New York, 1963, p. 106.
2. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology. Part I. Chemistry*, Wiley-Interscience, New York, 1963, p. 221.
3. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology. Part I. Chemistry*, Wiley-Interscience, New York, 1963, p. 226.
4. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology. Part I. Chemistry*, Wiley-Interscience, New York, 1963, p. 72.
5. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology. Part I. Chemistry*, Wiley-Interscience, New York, 1963, p. 94.
6. J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology. Part I. Chemistry*, Wiley-Interscience, New York, 1963, p. 97.
7. H. J. Fabris, *Adv. Urethane Sci. Technol.*, **4**, 89-111 (1976).
8. J. H. Saunders, *Rubber Chem. Technol.*, **32**, 337-45 (1959).
9. E. R. Larsen and E. L. Ecker, *J. Fire Sci.*, **6**, 363-79 (1988).
10. A. W. Benbow and C. F. Cullis, *Combust. and Flame*, **24**, 217-30 (1975).
11. F. E. Rogers and T. J. Ohlemiller, *J. Macromol. Sci., Chem.*, **A15**, 169-85 (1981).
12. W. D. Woolley, *Brit. Polym. J.*, **4**, 27-43 (1972).
13. I. C. Kogon, *J. Org. Chem.*, **23**, 1594 (1958).
14. J. H. Saunders and J. K. Backus, *Rubber Chem. Technol.*, **39**, 461-80 (1966).
15. M. L. Matuszak and K. C. Frisch, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 637-48 (1973).
16. S. L. Madorsky and S. Straus, *J. Polym. Sci.*, **36**, 183-94 (1959).
17. J. D. Ingham and N. S. Rapp, *J. Polym. Sci. A*, **2**, 4941-64 (1964).
18. A. M. Batt and P. Appleyard, *J. Fire Sci.*, **7**, 338-363 (1989).
19. V. A. Orlov and O. G. Tarakanov, *Plasticheskie Massy*, **5**, 12-15 (1965); *CA*, **63**, 4463f (1965).
20. E. Dyer and G. C. Wright, *J. Am. Chem. Soc.*, **81**, 2138-43 (1959).
21. E. Dyer and R. E. Read, *J. Org. Chem.*, **26**, 4388 (1961).
22. T. Mukaiyama and Y. Hoshino, *J. Am. Chem. Soc.*, **78**, 1946-8 (1956).
23. T. Mukaiyama and M. Iwanami, *J. Am. Chem. Soc.*, **79**, 73-6 (1957).
24. T. Hoshino, T. Mukaiyama, and H. Hoshino, *J. Am. Chem. Soc.*, **74**, 3097 (1952).
25. L. P. Rumao and K. C. Frisch, *J. Polym. Sci. A-1*, **10**, 1499-1509 (1972).
26. J. Chambers, J. Jiricny, and C. B. Reese, *Fire and Mater.*, **5**, 133-41 (1981).

27. W. D. Woolley, *J. Fire and Flam. Comb. Toxic.*, **1**, 259-67 (1974).
28. F. W. Abbate, W. J. Farrissey, and A. A. R. Sayigh, *J. Appl. Polym. Sci.*, **16**, 1213 (1972).
29. G. M. Anthony, *Makromol. Chem., Macromol. Symp.*, **74**, 117 (1993).
30. V. K. Belyakov, A. A. Berlin, I. I. Bukin, and V. A. Orlov, *Vysokomol. Soed.*, **A10**, 599 (1968).
31. V. K. Belyakov, A. A. Berlin, I. I. Bukin, and V. A. Orlov, *Polym. Sci. USSR*, **10**, 700 (1968).
32. H. H. G. Jellinek and K. Takada, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2709 (1975).
33. E. Dyer and G. E. Newborn, *J. Am. Chem. Soc.*, **80**, 5495-8 (1958).
34. R. Stolle, *Ber.*, **41**, 1125 (1908); *CA*, **2**, 2232 (1908).
35. M. P. Thorne, *Can. J. Chem.*, **45**, 2537-46 (1967).
36. H. C. Beachell and C. P. Ngoc-Son, *J. Polym. Sci.*, **7**, 2217 (1963).
37. V. A. Orlov and O. G. Tarakanov, *Plasticheskie Massy*, **6**, 11-13 (1965); *CA*, **63**, 8550h (1965).
38. V. A. Orlov and O. G. Tarakanov, *Vysokomol. Soedin.*, **6**, 1157 (1964); *CA*, **61**, 10825b (1964).
39. S. L. Axelrod, C. W. Hamilton, and K. C. Frisch, *Ind. Eng. Chem.*, **53**, 889 (1961).
40. H. Ulrich, *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol. 23, 1983, pp. 576-608.
41. A. J. Papa, *Ind. Eng. Chem.*, **9**(4), 478-496 (1970).
42. M. St. C. Flett, *Characteristic Frequencies of Chemical Groups in the Infra-Red*, Elsevier, New York, 1963.
43. H. G. Khorana, *Chem. Rev.*, **53**, 145-166 (1953).
44. T. Takeuchi, S. Tsuge, and T. Okumoto, *J. Gas Chromatogr.*, **6**, 542-7 (1968).
45. D. T. Burns, E. W. Johnson, and R. F. Mills, *J. Chromatogr.*, **105**, 43-8 (1975).
46. J. K. Haaken and M. Millingen, *J. Chromatogr.*, **283**, 371-4 (1984).
47. V. L. K. Valli and H. Alper, *J. Org. Chem.*, **60**, 257-8 (1995).

Received February 26, 1996

Accepted May 28, 1996