

Flammability and Thermal Stability of Isocyanate-Based Polymers

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Synopsis

A series of model polyurethanes and polyureas, a polyamide, and a polyimide were prepared by reacting 4,4'-diphenylmethane diisocyanate or polyisocyanates having similar polybenzyl structures with aliphatic or aromatic coreactants. Thermogravimetric analyses indicated that the flammability of the polymers was related to the formation of volatile flammable products during early stages of decomposition. Determinations of the heat evolved during differential thermal analyses and of the thermodynamic heats of combustion suggested that the extent and rate of reaction were among the important factors governing flame propagation. Flame-resistant polymers were prepared by use of structural elements which were thermally stable and nonvolatile or which formed nonflammable decomposition products.

INTRODUCTION

The first two papers of this series^{1,2} dealt with the thermal stability of common types of rigid urethane foams and with an analysis of the factors which affect their flammability. Both polyether and polyester urethane foams began to decompose rapidly at approximately 225°C. forming, after rupture of urethane bonds, products derived from the original reactants. The more volatile initial products, when flammable, contributed to flame propagation. Higher molecular weight products were degraded, at the same and higher temperatures, to carbonaceous char and to gaseous fragments, many of them flammable. Of the foam raw materials investigated, polyisocyanates prepared by phosgenation of aniline-formaldehyde condensates tended most to form solid chars rather than flammable gases.

The work reported here was an attempt to prepare less flammable model polymers from aromatic polyisocyanates by strengthening the primary bond structures and choosing reactants which were unlikely to decompose to volatile flammable products. Both flammability and volatile product formation were investigated. Measurements of the heat of combustion were also made to investigate the heat available to propagate combustion.

The molecular structures of the model polymers were chosen to illustrate a range of decomposition temperatures and probable mechanisms. Reactants used with polyisocyanates were both branched and linear, aliphatic

and aromatic. The linear polymers, in particular, were similar in elemental composition and structure but included polyurethanes, polyureas, a polyamide, and a polyimide and allowed a comparison of the contributions of these bonds and of aliphatic, phenylene, and xylylene reactant structures to polymer flammability. Molecular branching in the aromatic polyisocyanates and in aliphatic hydroxyl-terminated polyethers were also studied. Because the investigation dealt primarily with the relation between flammability and molecular structure, no flame-retardant additives were studied. Ring-chlorinated polyurethanes and polyureas were included, however, for comparison with identical unchlorinated polymers.

EXPERIMENTAL

Materials

Materials used in preparing the polymers described were obtained from commercial sources and were dried or otherwise purified as required before use. Isocyanates were: MDI (4,4'-diphenylmethane diisocyanate), MDI-2.7 (MONDUR MR, Mobay Chemical Company), and MDI-3.0 (similar polymeric isocyanate, average functionality 3.0). Coreactants were: triol 660 (Voranol CP-260, Dow Chemical Company); MOCA (methylenebis-*o*-chloroaniline); bis-(β -hydroxyethyl) ether of hydroquinone (Eastman Chemical Co.); pyromellitic acid (Hexagon Laboratories); and *p*-xylylene- α , α' -diol, *m*-xylylene- α , α' -diamine, tetrachloro-*p*-xylylene- α , α' -diol, tetrachloro-*m*-xylylene- α , α' -diamine (all from Diamond Alkali Co.).

Preparation of Experimental Polymers

Although the investigation concerned polymers formed from polyisocyanates and potentially applicable as foams, wide differences in reactivity and physical state of the reactants made preparation of all samples by standard urethane foam techniques impractical. For this reason, four methods of preparation were used.

Foams. Rigid foams were prepared from liquid polyisocyanates and hydroxyl-terminated resins by standard laboratory techniques. Only the inert blowing agent CFCl_3 was used, eliminating formation of bonds other than urethane.

Solid Polymers from Undiluted Systems. When the coreactant or polyisocyanate was solid at room temperature, the reactants were melted, then combined in equivalent amounts and cast into solid specimens. The use of resins dried at 80°C. under vacuum and of 30 psi dry air pressure during the casting stage eliminated bubble formation.³

Solution Methods. A number of the starting materials were not easily melted or were too reactive towards isocyanates to be used without dilution. The aromatic polymers, therefore, were prepared in solution, most often in dimethylformamide, dimethylacetamide, and/or dimethyl sulfoxide. The solvent, in each case, was dried by mixing with MDI to remove reactive

impurities, then distilled. Equivalent amounts of the polyisocyanate and coreactant were dissolved in equal volumes of solvent to give a concentration, after mixing, of 5–10 g./100 ml., shown by earlier workers^{4,5} to be satisfactory. The solutions of the individual reactants were used at room temperature unless warming was required to increase solubility. In each preparation, the solution of polyisocyanate was added to the coreactant solution with vigorous agitation, and the combined materials warmed with continuing agitation until reaction began. The temperature was then maintained at approximately 110°C. for 1–2 hr. until the infrared spectrum showed disappearance of the isocyanate group absorption at 2270–2240 cm^{-1} . The solution was cooled to room temperature and poured into water to precipitate the polymer. The solid product was filtered, washed with 50/50 water–acetone, again filtered, and dried under vacuum for 48 hr. at 80°C. The identity of the product was confirmed by infrared spectra.

Preparation of Polyimide. The polyimide investigated was prepared by forming the polyamide acid from 1 mole of tetracarboxylic acid and 1 mole by diisocyanate by using the solution procedure outlined above. Within 24 hr. after drying, the polyamide acid was converted to the corresponding polyimide by heating at 300°C. The conversion was confirmed by comparison of the infrared spectrum with published data.⁶ Properties of typical linear polymers prepared from MDI are summarized in Table I.

TABLE I
Properties of Typical Model Polymers

MDI coreactant	Preparatory solvent	Solubility		PMT, °C.	Intrinsic viscosity
		Hot DMSO	Hot DMA		
Propylene glycol	None	+	+	165	0.20 ^a
Dipropylene glycol	None	+	+	120	0.20 ^a
Ph(OC ₂ H ₅ OH) ₂	DMA	+	+	245	0.15 ^b
MOCA	Acetone	+	+	260	Insol.
Hydroquinone	DMSO/MIBK	+	+	>300	0.24 ^{a,b}
<i>p</i> -Xylenediol	DMSO	+	+	265	0.14 ^a
<i>p</i> -Phenylenediamine	DMSO/MIBK	–	–	>300	0.24 ^b
<i>m</i> -Xylenediamine	DMSO	+	–	285	0.20 ^a
Terephthalic acid	DMSO/DMA	+	+	280	0.17 ^b
Pyromellitic acid	DMA	–	–	>300	0.06 ^b
Cl ₄ <i>p</i> -Xylenediol	DMA	+	+	>300	0.10 ^b
Cl ₄ <i>m</i> -Xylenediamine	DMF	+	–	>300	0.11 ^{a,b}

^a In DMSO.

^b In concentrated H₂SO₄.

Test Methods

TGA and DTA Measurements. The following two instruments used for TGA and DTA measurements gave results which were similar but characteristic of the instrument design. With the Robert L. Stone Model

12 BC 2 analyzer, Model GS 2 DTA furnace, and Model JAC record-controller, samples were tested at a heating rate of 10°C./min., with TGA samples finely ground and mixed with silica. DTA samples were tested without dilution. With the DuPont Model 900 differential thermal analyzer and Model 950 thermogravimetric analyzer, samples were tested at a heating rate of 15°C./min. without dilution.

A continuous flow of air or an inert gas was maintained during all measurements.

Flammability. The flammability of the polymers was determined by a horizontal strip test similar to ASTM D-635. Specimens $2\frac{1}{2} \times \frac{1}{2} \times \frac{1}{8}$ in. were cast or molded from powder at 200°C. and 10,000 psi for up to 3 min., and were held horizontally by a clamp at one end. A Bunsen burner having a 1-in. blue cone flame was applied to the free end of the strip for 30 sec. The time for the flame to extinguish and the distance burned were recorded and the sample rated. A rating of nonburning indicated no flame continued after removal of the burner and the sample did not melt and drip; self-extinguishing denoted the flame continued after removal of the burner, but was extinguished before traveling 2 in.; a rating of burning indicated the flame traveled more than 2 in.

Heating of Combustion. Heats of combustion of the experimental polymers were determined by three methods.

(1) Values were calculated from tabulated bond energies⁷ assuming complete conversion of the polymer to liquid water, CO₂, and elemental nitrogen and chlorine.

(2) Determinations in an oxygen bomb calorimeter were made according to ASTM D-2015-62T.

(3) The heat generated during total conversion of polymers to volatile products was obtained by integration of the area under DTA curves. Calibration of the instrument was based on the heat of fusion of tin metal.

RESULTS

TGA Measurements

The TGA curves of Figures 1-8 illustrate the comparative thermal stability of the polymers tested. Figure 1 gives the TGA curves of rigid urethane foams prepared from the polymeric isocyanate MDI-2.7 with propylene glycol and dipropylene glycol. These curves and those of Figures 2, 3, and 4 were obtained by using the Robert L. Stone equipment and finely ground samples thoroughly mixed with silica. The curves for the simple glycol based foams in air showed weight loss beginning at approximately 225°C. and a major loss of weight between 250 and 300°C. A second major stage of weight loss appeared at approximately 400-550°C. and accounted for the remaining sample weight. The two-stage degradation process and temperatures of weight loss were similar to those previously reported for other rigid polyether urethane foams.¹ The first stage of weight loss was caused by rupture of the primary bonds forming the poly-

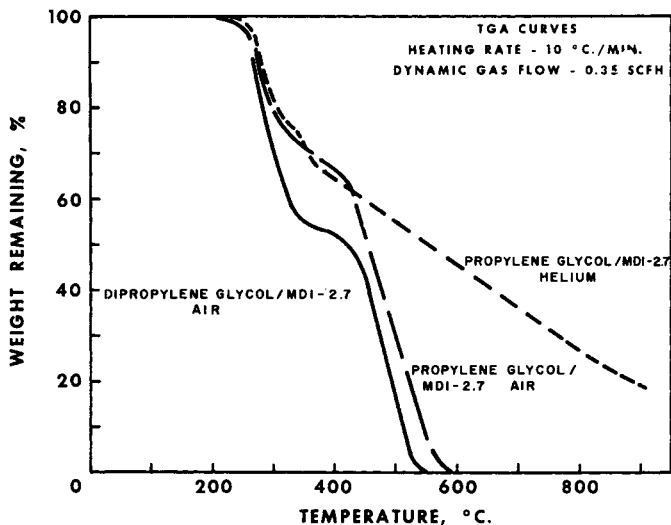


Fig. 1. TGA curves for rigid foams prepared from propylene glycol and dipropylene glycol with MDI-2.7.

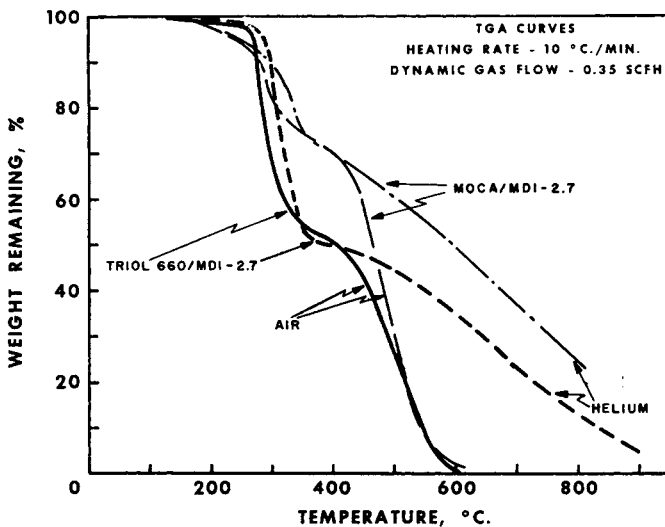


Fig. 2. TGA curves for polymers of triol 660 and MOCA with MDI-2.7.

mer and vaporization of the lower molecular weight polyols and aliphatic fragments formed by further degradation. The char remaining after the first stage was derived primarily from the less volatile, more thermally stable polyisocyanate. The second stage of weight loss involved thermal and oxidative degradation as well as physical attrition of the char.

Qualitatively, the results of Figure 1 agreed well with this interpretation—the dipropylene glycol polymer contained 1.5 times more glycol by weight

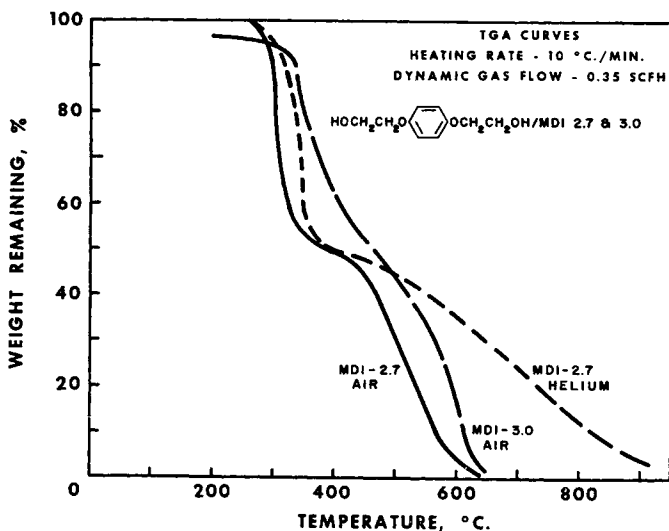


Fig. 3. TGA curves for polymers of bis-(β -hydroxyethyl) ether of hydroquinone with MDI-2.7 and MDI-3.0.

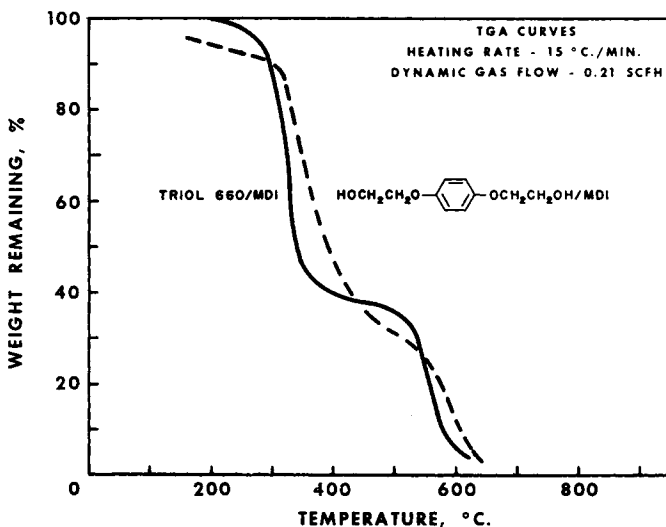


Fig. 4. TGA curves for polymers of bis-(β -hydroxyethyl) ether of hydroquinone and triol 660 with MDI.

than the propylene glycol polymer and showed 1.5 times more weight loss in the first stage. The total first stage weight loss, however, was greater than the weight fraction of glycol and 25-30% must be associated with the polyisocyanate. The latter could be loss of MDI, volatile at these temperatures, or of carbon oxides.

Figure 2 includes the TGA curve for a foam prepared from the polymeric isocyanate and a 660 hydroxyl number triol formed by addition of approxi-

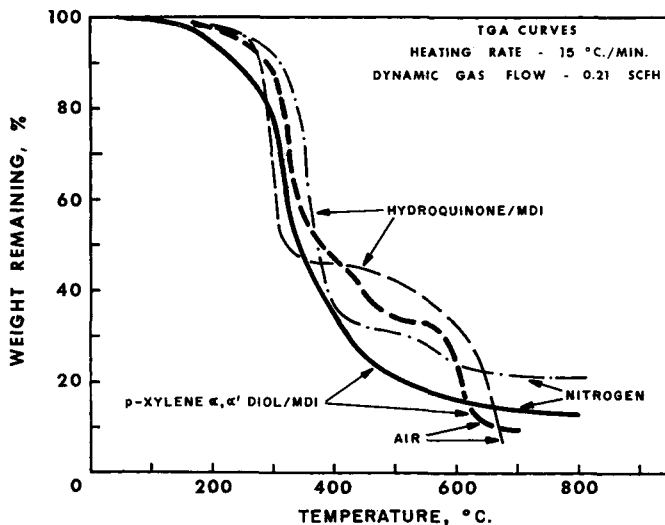


Fig. 5. TGA curves for polymers of hydroquinone and *p*-xylene- α,α' -diol with MDI.

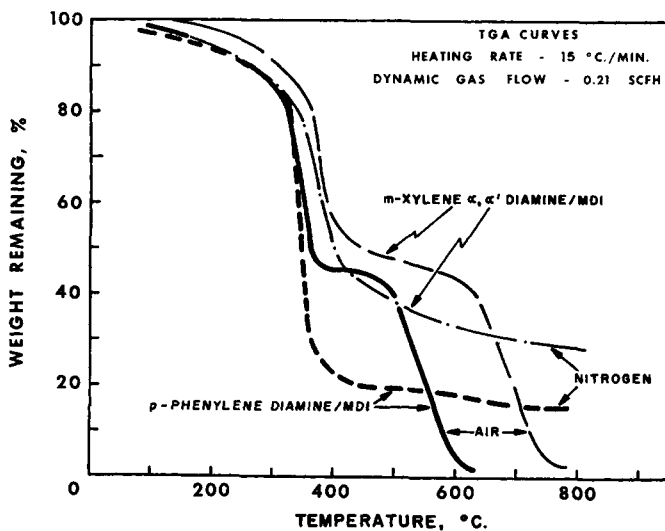


Fig. 6. TGA curves for polymers of *p*-phenylenediamine and *m*-xylene- α,α' -diamine with MDI.

mately 1 mole of propylene oxide to each of the three hydroxyl groups of glycerine. The curve obtained in air could be superimposed on the Figure 1 curve for the dipropylene glycol-based polymer.

The TGA curves of the propylene glycol and triol 660/MDI-2.7 foams in helium, also shown in Figures 1 and 2, were similar in the first stage to the air curves. The second stage in each case was replaced by a slower, almost linear loss of weight extending to temperatures above 900°C.

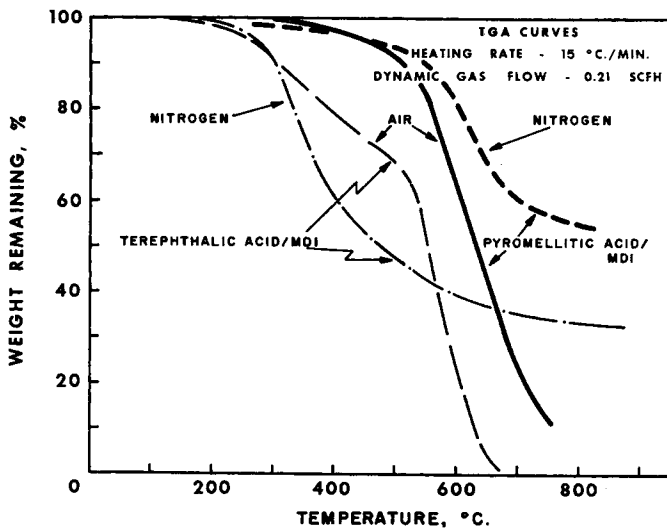


Fig. 7. TGA curves for polymers of terephthalic acid and pyromellitic acid with MDI.

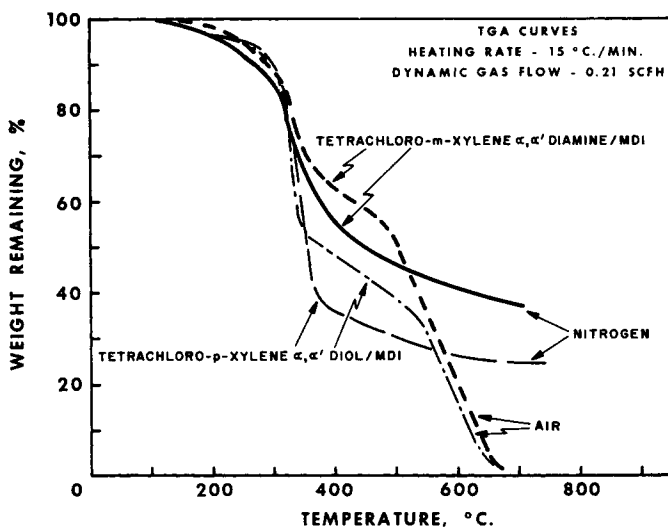


Fig. 8. TGA curves for polymers of tetrachloro-*p*-xylene- α,α' -diol and tetrachloro-*m*-xylene- α,α' -diamine with MDI.

Similar curves obtained from the DuPont instrument and shown in Figures 5-8 indicated a greater first-stage weight loss, then a more gradual loss at the higher temperatures. Apparently, the first-stage processes with and without oxygen are similar and involve bond rupture as noted previously. The second stage, however, was more rapid in air and is largely oxidative.

Figure 2 also includes TGA curves of MOCA/MDI-2.7 polymers in air and in helium. Remaining solvent accounted for the weight loss below 250°C. The curves for the MOCA-based polyurea were similar in both

air and helium to those given by the polyurethanes and differed mainly in a higher percentage of char formation after the first stage of weight loss. The greater amount of char was associated with the more thermally stable, less volatile chlorinated diphenylmethane structure of MOCA.

Support for the correlation between nonvolatile, thermally stable monomers and char formation was given by the TGA curves of Figure 3 for polymers prepared from the bis-(β -hydroxyethyl) ether of hydroquinone and both MDI-2.7 and a higher molecular weight MDI-3.0. Curves in air and helium for the MDI-2.7 polymers were similar to those previously described and indicated complete decomposition and volatilization of the hydroquinone ether during the first stage. The more branched MDI-3.0 based polymer decomposed initially at a higher temperature and formed more char throughout the temperature range examined.

The importance of the molecular weight and branching of the polyisocyanate is also shown in Figure 4, the TGA curves in air of polymers from difunctional MDI and triol 660 or bis-(β -hydroxyethyl) ether of hydroquinone. Although these curves were obtained using the DuPont instrument, the greater first-stage weight loss was apparent in comparison to the Figure 2 and 3 curves of polymers based on the same coreactants with MDI-2.7.

The superior char-forming ability of the branched MDI-2.7 polyisocyanate in comparison to 2,4-tolylene diisocyanate, 1,6-hexane diisocyanate, and 3,3'-dimethoxy-4,4'-biphenylene diisocyanate was shown in previously reported² TGA curves for polymers prepared from these diisocyanates and a polyoxypropylene triol.

In order to evaluate more fully the influence of bond type on thermal stability and flammability, TGA curves on Figures 5-8 were obtained for a series of polymers having similar structures and prepared from difunctional MDI. Coreactants were chosen to form polyurethanes, polyureas, a polyamide, and a polyimide, and because of the thermal instability of the aliphatic polyethers, were aromatic and of either the phenylene or xylylene structure. For comparison, polymers were prepared from chlorinated coreactants. All measurements of this series were made using the DuPont instrument and nitrogen rather than helium as the inert atmosphere.

The patterns of weight loss of polyurethanes prepared from hydroquinone and *p*-xylene- α,α' -diol (Fig. 5) and of polyureas prepared from *p*-phenylene diamine and *m*-xylene- α,α' -diamine (Fig. 6) were similar to those previously discussed. Two distinct stages appeared in air, and a single stage followed by slow attrition in nitrogen. A comparison of nitrogen and helium atmospheres showed no differences in the effects of the two inert gases.

Of the four polymers, the first stages of weight loss of the polyureas appeared at slightly higher temperatures than those of the polyurethanes, and the 45-50% first-stage weight loss of the polyurethanes was greater than the 35-40% shown by the polyureas. Concurrently, the first-stage weight loss temperatures of polymers prepared from active hydrogen compounds of the xylene structure were higher than those of polymers

TABLE II
Summary of TGA Data for Branched Isocyanate-Based Polymers

Polymer	Atmos.	First stage		Second stage		Wt. remaining, % at °C.
		Temp., °C.	Wt. loss, %	Temp., °C.	Wt. loss, %	
Propylene glycol	Air ^a	250-300	24	415-565	61	0/570
	He ^a	256-295	32			10/1000
Dipropylene glycol Triol 660	Air ^a	255-325	40	438-520	46	0/530
	Air ^b	292-343	54	525-590	35	0/675
	Air ^b	270-324	41	440-570	42	0/590
	He ^a	288-345	46			4/1000
Ph(OC ₂ H ₅ OH) ₂	Air ^b	315-408	53	540-640	28	0/650
	Air ^a	290-325	45	464-600	45	0/640
	He ^a	312-355	47			0/950
	Air ^a	312-400	33	555-635	33	0/640
MOCA	Air ^a	272-308	14	432-551	44	0/630
	He ^a	314-354	16			8/1000

^a In Robert L. Stone instr., 10°C./min.

^b In DuPont instr., 15°C./min.

TABLE III
Summary of TGA Data for Linear Isocyanate-Based Polymers^a

Polymer	Atmos.	First stage		Second stage		Wt. remaining, % at °C.
		Temp., °C.	Wt. loss, %	Temp., °C.	Wt. loss, %	
Hydroquinone	Air	275-310	49	520-680	40	0/700
	N ₂	320-390	62			20/800
<i>p</i> -Xylenediol	Air	310-340	45	570-640	26	0/650
	N ₂	275-340	36			14/800
<i>p</i> -Phenylenediamine	Air	310-340	50	475-625	40	0/650
	N ₂	310-400	70			15/800
<i>m</i> -Xylenediamine	Air	360-390	35	630-750	43	0/750
	N ₂	340-390	39			28/800
Terephthalic acid	Air	250-500	32	500-650	65	0/700
	N ₂	250-500	50			33/800
Pyromellitic acid	Air			520-750	77	0/750
	N ₂			550-675	33	55/800
Cl ₄ <i>p</i> -xylenediol	Air	300-350	42	525-650	38	0/670
	N ₂	320-360	53			25/800
Cl ₄ <i>m</i> -xylenediamine	Air	320-350	17	490-670	52	0/675
	N ₂	310-350	20			37/800

^a DuPont instr., 15°C./min.

prepared from compounds of the phenylene structure. Among the individual polymers, the *m*-xylene- α,α' -diamine-based polyurea showed least weight loss at highest temperature. Differences among the remaining three polymers were minor.

The thermal stability of the polyimide prepared from pyromellitic acid and MDI is shown in the TGA curves of Figure 7. The curves agreed well with those published previously by Scoog and co-workers.⁶ The TGA curves of the terephthalic acid-MDI polyamide, also given in Figure 7, indicated greater thermal stability than those of any of the series of polymers except the polyimide. Weight loss occurred in a pattern different from those shown previously, although two stages were still apparent. The first, a slow but steady loss from about 250 to 500°C. accounted for approximately 30% of the sample. The more rapid second stage accounted for the remaining sample and occurred at 500–650°C.

The TGA curves of Figure 8 for the tetrachloro-*p*-xylene- α,α' -diol and tetrachloro-*m*-xylene- α,α' -diamine-based polymers showed decomposition at the same temperatures observed for the unchlorinated polymers. Char formation, however, was greater.

Characteristics of the TGA curves of polymers prepared from branched polyisocyanates and polyols are summarized in Table II and similar data for the linear polymers are given in Table III. Considered together, the results were similar for all polymers except the polyamide and polyimide. In air, serious weight loss began at 225–300°C., and two distinct stages of loss appeared, most often at 250–350°C. and 450–650°C. The normally steeper slope of the first-stage TGA curves as compared to the second-stage curves indicated that the initial decomposition was more rapid than the following conversion of char to volatile products. Comparison of the TGA curves in air and an inert atmosphere showed that the initial decomposition process involved oxidation only to a minor extent. The distinct second stage of weight loss seen in air vanished in the inert atmospheres and was attributed to char oxidation.

DTA Measurements and Heat of Combustion

DTA curves corresponding to many of the TGA curves of the previous section are shown in Figures 9–12. Each polymer selected was examined in a dynamic air atmosphere. In addition, comparative measurements in flowing helium were made for the four branched polymers of Figures 9 and 10. Temperatures of important thermal changes are summarized in Table IV.

With few exceptions, DTA measurements in air showed distinct exothermic changes at the temperatures of major weight loss found by TGA. Curves of the majority of unchlorinated polyurethanes, polyureas, and of the polyamide contained exothermic peaks at the two major decomposition temperatures.

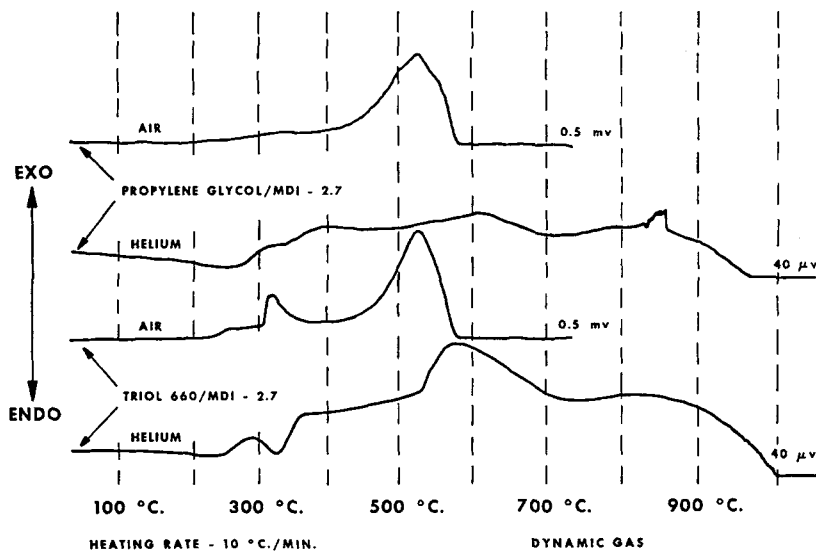


Fig. 9. DTA curves for rigid foams prepared from propylene glycol and triol 660 with MDT-2.7.

That of the pyromellitic acid-MDI polyimide also showed a sharp exothermic peak at the primary weight loss temperature but in addition contained an endothermic peak at a higher temperature.

TABLE IV
Summary of DTA Data

Polymer		Atmos.	Temp. of initial change, °C.		Temp. of exothermic change, °C.	
			°C.	°C.	°C.	°C.
Propylene glycol	MDI-2.7	Air	225	250	530	
		He	263		330	615
Triol 660	MDI-2.7	Air	235	270	325	520
		He	250	290	375	600
Ph(OC ₂ H ₅ OH) ₂	MDI-2.7	Air	235	260	315	370
		He	245	300	375	600
MOCA	MDI-2.7	Air	235	290		540
		He	252		370	620
Hydroquinone	MDI	Air	230		345	530
<i>p</i> -Xylenediol	MDI	Air	235		315	550
<i>p</i> -Phenylenediamine	MDI	Air	230		360	530
<i>m</i> -Xylenediamine	MDI	Air	265		350	560
Terephthalic acid	MDI	Air	230		355	535
Pyromellitic acid	MDI	Air	520			570
Cl ₄ <i>p</i> -Xylenediol	MDI	Air	265		300	520
Cl ₄ <i>m</i> -Xylenediamine	MDI	Air	225		340	520

^a Endothermic peak at 665°C.

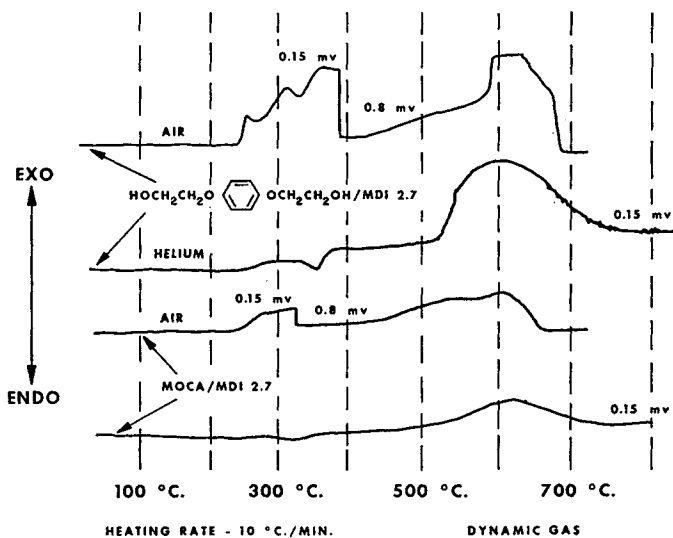


Fig. 10. DTA curves for polymers of bis-(β -hydroxyethyl) ether of hydroquinone and MOCA with HDI-2.7.

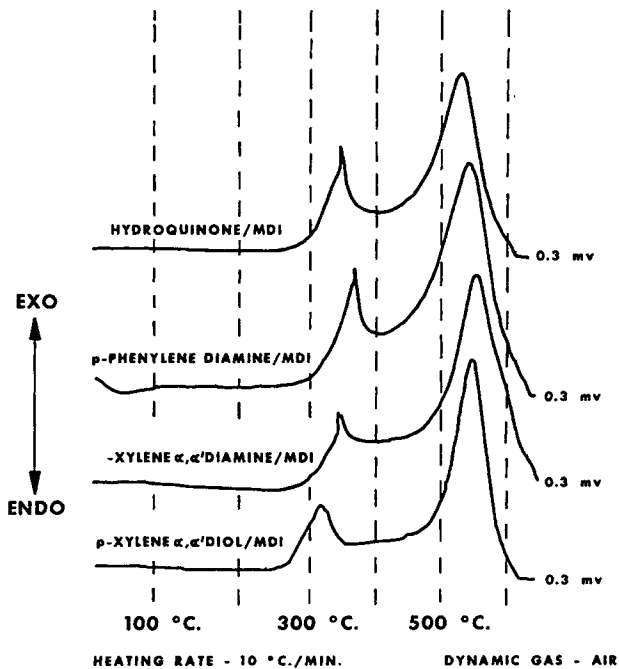


Fig. 11. DTA curves for polymers of hydroquinone, *p*-xylene- α,α' -diol, *p*-phenylene diamine, and *m*-xylene- α,α' -diamine with MDI.

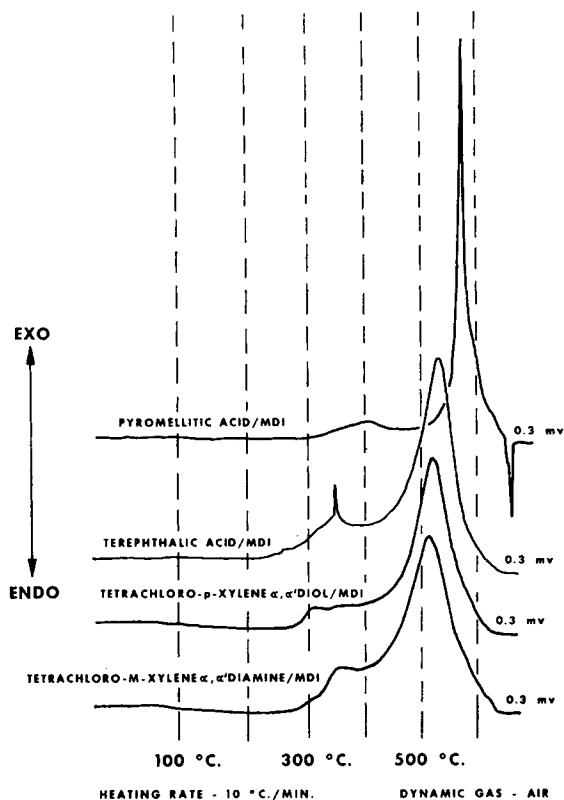


Fig. 12. DTA curves for polymers of terephthalic acid, pyromellitic acid, tetrachloro-*p*-xylene- σ,α' -diol, and tetrachloro-*m*-xylene α,α' -diamine with MDI.

Comparison of the curves of Figures 9 and 10 showed that the exothermic peaks, allowing for the differences in instrument sensitivity, were more than tenfold larger in air than in helium. Heat was produced, therefore, mainly by oxidation of the sample and its degradation products. The DTA curves also indicated that the major portion of the heat produced appeared in the second peak and could be attributed to oxidation of the char. The DTA technique, however, determines only the temperature change of the solid sample and does not record, in most measurements in a dynamic atmosphere, heat produced by oxidation of gaseous decomposition products. In actual combustion, this process creates the flame and is responsible for much of the heat of combustion.

That much of the heat of combustion was not detected by DTA measurements is shown in Table V. Integration of the area under the DTA curves of Figures 11 and 12 allowed the total heat evolved to be calculated. Although the samples were completely converted to gaseous products by the treatment, the heat produced in the solid sample was only about one-third the thermodynamic heat of combustion as measured by oxygen bomb

TABLE V
Heats of Combustion of Model Polymers

Coreactant	Heat of combustion, cal./g.			
	Calc. (MDI)	O ₂ bomb, ASTM D-2015-62T (MDI)	(MDI-2.7)	DTA (MDI)
Propylene glycol	6629		6757	
Dipropylene glycol	7002		6551	
Triol 660	6972		6590	
Ph(OC ₂ H ₅ OH) ₂	6687	6398	6583	
MOCA	6532	6383	6524	
Hydroquinone	6731	7428		2066
<i>p</i> -Xylene- α,α' -diol	7054	6909		1917
<i>p</i> -Phenylenediamine	7167	6974		2050
<i>m</i> -Xylene- α,α' -diamine	7461	7102		2268
Terephthalic acid	7564	6234		2217
Pyromellitic acid	6582	6474		1909
Cl ₄ <i>p</i> -Xylene- α,α' -diol	4718	6009		1543
Cl ₄ <i>m</i> -Xylene- α,α' -diamine	5008	5738		1915

calorimetry and confirmed by calculations from standard bond energies. The differences were caused mainly by failure of the DTA method to measure the heat produced by oxidation of gaseous degradation products and by incomplete oxidation. Since neither the DTA nor thermodynamic heats of combustion varied greatly among the samples tested while flammability did change, the heat generated and the temperature during an actual fire appear to be governed by the extent and rate of fuel oxidation.

Flammability

The flammability of a cast or compression-molded strip of each model polymer was determined by the simple test described earlier. The results (Table VI) and molecular structure divide the polymers into four classes. Polyurethanes containing the largely aliphatic propylene glycol, dipropylene glycol, triol 660, and bis(β -hydroxyethyl) ether of hydroquinone behaved similarly when burned. Those based on difunctional MDI melted readily and, when polymers were prepared from the two low molecular weight glycols, burning ceased after removal of the igniting flame. The triol 660-MDI and hydroquinone ether-MDI polymers, however, continued to burn until the sample strips were consumed. Similar polyurethanes prepared from MDI-2.7 formed a solid char when burned and, in the case of the polymer prepared from triol 660, substitution of the more branched polyisocyanate was accompanied by an improvement in flammability rating from burning to self-extinguishing.

In addition to molecular branching, the flammability of polymers of this group varied inversely with the equivalent weight of the aliphatic constituent, and directly with the concentration of more thermally stable diphenylmethane structure in the polymer. The number of aliphatic ether

TABLE VI
Model Polymer Flammability Measurements

Polymer		Flammability ($2\frac{1}{2} \times \frac{1}{2} \times \frac{1}{8}$ in. strip)			
		In. burned	Min. to exting.	Obsv.	Rating ^a
Propylene glycol	MDI	0.5	0.5	Melt	SE
	MDI-2.7	0.25	1.0	Char	SE
Dipropylene glycol	MDI	0.5	0.5	Melt	SE
	MDI-2.7	0.25	0.7	Char	SE
Triol 660	MDI	2.5	0.8	Melt	Burned
	MDI-2.7	0.25	1.0	Char	SE
Ph(OC ₂ H ₅ OH) ₂	MDI	2.5	1.0	Melt	Burned
	MDI	2.5	1.2	Char	Burned
MOCA	MDI	2.5	0.5	Char	Burned
	MDI-2.7	2.5	0.5	Char	Burned
Hydroquinone	MDI	2.5	1.8	Char	Burned
<i>p</i> -Xylenediol	MDI	2.5	1.8	Melt	Burned
<i>p</i> -Phenylenediamine	MDI	2.5	2.3	Char	Burned
<i>m</i> -Xylenediamine	MDI	0.75	0.85	Char	SE
Terephthalic acid	MDI	0.16	2.0	Char	SE
Pyromellitic acid	MDI	0.5	0.7	Char	SE
Cl ₄ <i>p</i> -Xylenediol	MDI	0.16	0.5	Char	NB
Cl ₄ <i>m</i> -Xylenediamine	MDI	0	0.5	Char	NB

^a See text.

TABLE VII
Flammability Variation with Polyol Structure and Equivalent Weight

Alcohol	Equivalent weight	Ether groups per OH	Flammability of MDI-based polymer
Propylene glycol	38	0	SE
Dipropylene glycol	67	0.5	SE
Triol 660	85	1.0	Burned
Ph(OC ₂ H ₅ OH) ₂	99	1.0	Burned

groups in the polymer may have had secondary influence. Both factors are shown in Table VII for the MDI-based polymers.

From the viewpoint of molecular structure, flammability was decreased by increased branching of the more thermally stable component, here the polyisocyanate. Branching of the aliphatic alcohol, in these experiments, had no detectable effect. The presence of the phenylene structure in the hydroquinone ether did not improve flame resistance. Experience in formulating rigid urethane foams has shown, however, that propylene oxide adducts of some heterocyclic compounds, for example sucrose, are helpful in preparing flame-resistant materials.

The linear aromatic polymers fell naturally into three groups. Those prepared from MDI and MOCA, hydroquinone, *p*-phenylenediamine, and *p*-xylylene- α,α' -diol all burned. The first three polymers were typical of most aromatic structures and formed a solid char. The *p*-xylylene- α,α' -

diol-based polyurethane, however, formed a viscous melt and dripped from the test strip when burned.

Contrasting with these polymers were those based on *m*-xylene- α,α' -diamine, terephthalic acid, and pyromellitic acid, all of which formed solid chars when ignited but which were self-extinguishing when the igniting flame was removed. In a separate third class were the two polymers based on chlorinated xylene derivatives. No flame could be seen on strips of either polymer when the igniting source was removed and no melting of the sample occurred.

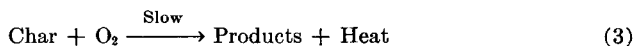
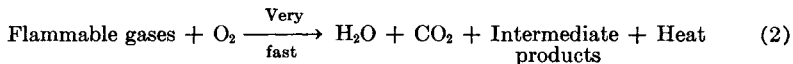
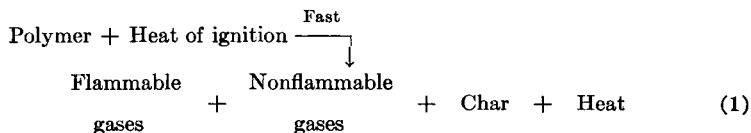
The differences among the three polymer groups were related to the ease of polymer decomposition and to the flammability of the products initially produced. The polyurethanes and aromatic polyureas prepared from MOCA, hydroquinone, *p*-phenylenediamine, and *p*-xylene- α,α' -diol decomposed at relatively low temperatures, primarily to derivatives of the original reactants. Derivatives of the nonisocyanate components were readily formed at flame temperatures and were sufficiently volatile and flammable to propagate combustion.

The three self-extinguishing polymers were thermally more stable, and required higher temperatures to produce high enough concentrations of volatile products to ensure flame propagation. The flame resistance of the two chlorinated polymers was the result of the formation of nonflammable chlorinated aromatic products during ignition of the sample. Since the initial products of thermal decomposition did not burn, the source of heat for flame propagation did not exist.

Polyisocyanates of the diphenylmethane type did not significantly decompose to flammable products. Not only was the molecular structure thermally stable and relatively nonvolatile, but free polyisocyanates formed in early stages of decomposition would be expected to react rapidly at these high temperatures to form polycarbodiimides and other high molecular weight products.

DISCUSSION

The combustion of organic polymers can be thought of in terms of a generalized three-step mechanism.



According to this mechanism, the propagation of combustion depends on decomposition of the polymer, when ignited, to give volatile products

which burn rapidly with evolution of heat to continue the process. Reducing the flammability of a polymer, then, requires lowering the concentration of volatile flammable products formed during and after ignition. This requirement can theoretically be satisfied in several ways: (1) synthesis of polymers containing low concentrations of precursors of flammable gases; (2) use of molecular structures which, because of stable bond types and crystallization, decompose with difficulty; (3) incorporation of molecular segments which are not volatile and which tend to form solid chars after decomposition of the polymer; (4) flameproofing of the likely volatile segments; (5) addition of materials which catalyze char formation; (6) dilution of the polymer with nonflammable materials.

The first four possibilities were demonstrated in the reported work. In the series of polyurethanes prepared from aliphatic polyols, the most likely sources of flammable gases were the aliphatic starting materials. Reducing their concentration by substitution of propylene glycol for higher molecular weight reactants produced a less flammable polymer.

The same series of polymers showed a reduction in flammability with increased branching of the polymeric isocyanate. In this case, its branched polybenzyl structure was the most thermally stable portion of the polymer molecule and an increase in molecular weight both increased char formation and lowered the concentration of initial volatile products.

The low flammability of polymers based on thermally stable bond types was shown by the polyimide which produced only low concentrations of volatile products under 400°C. and was difficult to ignite. Most flame resistant of the experimental polymers were those in which the most probable volatile fragment of decomposition, the xylene nucleus of the non-isocyanate reactant, was made nonflammable by chlorination.

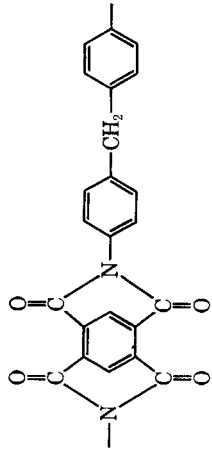
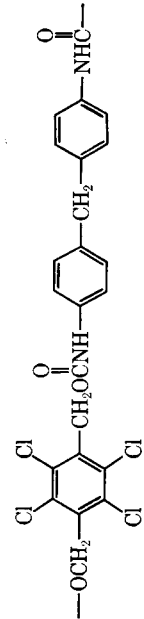
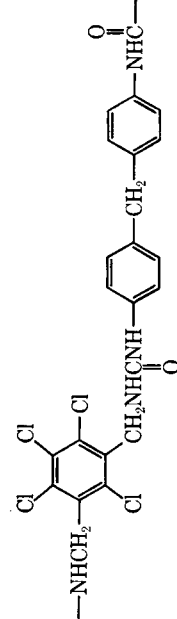
The relationship between flammability and the rapid formation of volatile products in the first stage is shown more completely in Table VIII. Despite the close similarity in structure and composition, particularly of the aromatic polymers, flammability varied widely. The ease of polymer decomposition to volatile products is given in terms of the temperatures at which 20% and 40% of the original sample weight was volatilized in the TGA measurements.

The data specify the temperature and extent of the initial decomposition processes and show good correlation with flammability test results. The dipropylene glycol polyurethane decomposed at a relatively low temperature, but was classed self-extinguishing because sample melting caused physical separation of the ignited and unburned portions.

The nonchlorinated aromatic polymers are listed in order of increasing temperatures for 20% or 40% TGA weight loss, an order which agrees with decreasing flammability. The three polymers which burned were ranked by decreasing TGA weight loss in the order hydroquinone-MDI, *p*-xylene- α,α' -diol-MDI, and *p*-phenylenediamine-MDI. The three self-extinguishing polymers were similarly ranked *m*-xylene- α,α' -diamine-MDI, terephthalic acid-MDI, and pyromellitic acid-MDI. Since the low flammability

TABLE VIII
Comparison of the Flammability and Thermal Decomposition Temperatures of MDI-Based Polymers

Coreactant	Structure of repeating unit	Temp., °C., of TGA weight loss in air of		Flammability
		20%	40%	
Dipropylene glycol		280	320	SE (melts)
Hydroquinone		280	300	Burned
<i>p</i> -Xylenediol		310	340	Burned
<i>p</i> -Phenylenediamine		320	350	Burned
<i>m</i> -Xylenediamine		360	390	SE
Terephthalic acid		380	580	SE

Pyromellitic acid		560	605	SE
Cl ₄ p-Xylenediol		320	335	Nonburning
Cl ₄ m-Xylenediamine		330	430	Nonburning

of the chlorinated polymers depends on a different factor, they must be treated as a separate group.

The data do not appear to relate flammability to a particular mechanism of thermal decomposition. Among the polyurethanes, for example, those prepared from simple glycols and the polyether triol 660 would be expected to decompose by a combination of dissociation to alcohol and isocyanate, formation of an olefin and primary amine, and formation of a secondary amine.² The hydroquinone polyurethane, on the other hand, decomposed almost entirely by direct dissociation and the *p*-xylene- α,α' -diol polyurethane by both dissociation and secondary amine formation. Polymer flammability depended only indirectly on the decomposition mechanism and directly on (1) primary bond strength, therefore temperature of decomposition; (2) concentration of volatile decomposition products; (3) flammability of the volatile products. Fire-resistant polymers based on polyisocyanates can be prepared by using structural elements which are thermally stable and nonvolatile or which form noncombustible volatile products during thermal decomposition.

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