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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Lillya, C. Peter , Macknight, William J. , Newman, Richard M. , Su, Wei-Fang A. and Uden, Peter C.(1980) 'Thermal Degradation of Glutamate Polymers', *Journal of Macromolecular Science, Part A*, 14: 8, 1181 – 1196

**To link to this Article: DOI:** 10.1080/00222338008056738

**URL:** <http://dx.doi.org/10.1080/00222338008056738>

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## Thermal Degradation of Glutamate Polymers

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### ABSTRACT

Thermal properties of precipitated samples and films of poly- $\gamma$ -benzyl-L-glutamate (PBG) and poly-L-glutamic acid (PGA) have been studied using TGA, DSC, and pyrolysis. The PBG film was identified as that described by McKinnon and Tobolsky as "form C" ("film A" of Uematsu et al.) using IR, dielectric relaxation, and DSC data. The PGA film is  $\alpha$ -helical (IR) and was further characterized by dielectric relaxation measurements. With the exception of water loss at  $\sim 110^\circ$  from PGA, TGA and DSC measurements reveal only incomplete endotherms corresponding to decomposition. Volatile decomposition products were trapped and identified using combined GC/IR and GC/MS techniques. Identified products were as follows: from PGB-CO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O, toluene, benzaldehyde, benzyl alcohol, and benzoic acid; from PGA-CO<sub>2</sub>, NH<sub>3</sub>, CH<sub>3</sub>OH, acetone, and H<sub>2</sub>O. Only minor differences were noted in GC traces of the total volatile decomposition products in air or in nitrogen streams. No evidence for retained solvent in cast films was obtained.

### INTRODUCTION

Poly( $\alpha$ -amino acids) have long served as effective protein models, especially in studies of the factors which determine conformation of

peptide chains. As a consequence they have been the subject of an enormous body of solution studies [1a-c]. Solid-state studies, which lagged far behind, have gained recent momentum owing to interest in poly( $\alpha$ -amino acids) as potential materials, especially for biomedical applications [2a-b, 3]. Several dynamic mechanical and dielectric studies [4a-n] as well as piezoelectric studies [5a-c] of solid glutamate polymers have appeared. However, relatively few thermal studies of solid ( $\alpha$ -amino acids) have been reported [6a-f]. We report a study of thermal degradation of poly( $\gamma$ -benzyl-L-glutamate) (PBG) and poly( $\alpha$ -L-glutamic acid) (PGA) with emphasis on identification of low molecular weight pyrolysis products.

## EXPERIMENTAL

### General

IR spectra were recorded on Beckman IR-10 and Perkin-Elmer model 727 instruments, and UV spectra were recorded on Beckman UV-ACTA M series and Hitachi-Coleman EPS-3T instruments. Melting points are corrected. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory. All solvents were purified and dried using methods described by Fieser [7] or Riddick [8].

### Poly( $\gamma$ -benzyl-L-glutamate) (PBG)

PBG was prepared by polymerization of a 1% (w/w) solution of  $\gamma$ -benzyl-L-glutamate N-carboxy anhydride in benzene using a sodium methoxide in methanol initiator (anhydride/initiator = 1000/1) according to the method of Blout and Karlson [9]: IR (CHCl<sub>3</sub>) 3300 (N-H), 1740 and 1650 (C=O), 1550 cm<sup>-1</sup> (N-H). Analysis: Calculated for (C<sub>12</sub>H<sub>13</sub>O<sub>3</sub>N)<sub>n</sub>: C, 65.8; H, 6.0. Found: C, 66.27; H, 6.39. Intrinsic viscosities were determined in dichloroacetic acid using an Ubbelohde Viscometer at 25°, and viscosity-average molecular weights were calculated using the Mark-Houwink equation with the calibration of Doty et al. [10]. Typical values fell in the range 2-5 × 10<sup>5</sup> gmole<sup>-1</sup>.

### Poly( $\alpha$ -L-glutamic acid) (PGA)

PBG was converted to PGA by benzyl ester cleavage using HBr in benzene according to the procedure of Blout and Idelson [11]. PBG of  $M_w = 4 \times 10^5$  was suitable for preparation of PGA of  $M_w \sim 1 \times 10^5$ . Crude PGA was purified by solution in 5% aqueous sodium bicarbonate, filtration, and reprecipitation with hydrochloric acid. UV analysis of

a 1% aqueous sodium bicarbonate solution revealed 0.5-1.5% residual benzyl ester groups (assumed  $\epsilon_{261\text{nm}} = 225$ ). Dialysis of a 5% sodium bicarbonate solution of the PGA against water for 24 hr and reprecipitation did not change this value: IR (film cast from  $\text{CHCl}_3$ ) 3300

(N-H), 1730 and 1650 (C=O),  $1550\text{ cm}^{-1}$  (N-H). Analysis: Calculated for  $(\text{C}_5\text{H}_7\text{O}_3\text{N})_n$ : C, 46.5; H, 6.38. Found: C, 47.5; H, 6.38. Viscosity-average molecular weight was determined in 0.1 M NaCl, 0.1 M phosphate buffer, pH = 7.05 according to Hawkins and Holtzer [12].

### Dioxopiperazine Derivative from $\gamma$ -Benzyl-L-glutamate

This compound was prepared according to Buyle [13], mp 173-174° (in Ref. 13: 160°); IR (Nujol) 3200 (N-H), 1720 and 1670 (C=O), 1170 (C-O), 700 and  $750\text{ cm}^{-1}$  (-Ph); NMR (DMSO- $d_6$ )  $\delta$ 1.9 (m, broad, 4,  $-\text{CH}_2$ 's), 2.3 (m, partly obscured by DMSO- $d_5$  signal,  $-\text{CH}_2$ 's), 3.8 (t, broad, 2, -H's), 4.95 (s, 4, benzylic H's), 7.45 (s, 10, Ph), 8.1 (s, broad, 2, N-H).

### Film Preparation

Films for IR spectra and thermal degradation were cast from chloroform (PBG) and 4:1 dioxane/water (PGA) on a mercury surface. Thick films for dielectric relaxation studies were cast by slow evaporation of chloroform solutions in a 9 cm diameter round dish with a plate glass bottom. Several hours immersion in water facilitated the removal of the flexible films from the dish. The films were pressed between glass plates for one week and drying was completed in a vacuum oven (1 torr) for several days. Film thicknesses varied from 12 to 18 mil. Individual films exhibited good thickness homogeneity,  $\sim \pm 2$ -3%.

### Dielectric Measurements

Dielectric relaxation was studied using a General Radio capacitance measuring assembly (Type 1615A) and Eico 377 audio generator. Capacitance, conductance, and loss tangent ( $\tan \delta$ ) were measured at 0.10, 1.0, and 10 KHz. From  $-120^\circ\text{C}$  to room temperature (temperature control  $\pm 0.5^\circ$ ) measurements were made using a 3-terminal Balsbaugh Type LD-3 cell with 53 mm diameter electrodes. From room temperature to  $200^\circ\text{C}$  (temperature control  $\pm 0.1^\circ$ ) a specially-constructed 2-terminal stainless steel cell with 53 mm diameter electrodes was used. Disks (50 mm diameter) of aluminum foil were

attached to the film surface using a thin film of silicone grease to improve contact with the electrodes.

### Thermal Analysis

Measurements were performed using a Perkin-Elmer TGS-1 thermobalance (TG) and a Perkin-Elmer DSC-2 differential scanning calorimeter (DSC). Samples weighing 1-5 mg were heated under nitrogen (1 atm) at rates of 40 and 10°/min (DSC only).

Slow pyrolysis and analysis of volatile products were carried out using a Spex Industries Multi-purpose Thermal Analyzer (MP-3) equipped with TC and FID detectors and interfaced with a Varian-Aerograph 2760 gas chromatograph and Norcon 201 rapid scan vapor phase infrared spectrometer. The IR spectrometer is interfaced with a PDP/10E computer for acquisition and processing of spectral data [14]. Samples of 1-10 mg were placed in a platinum boat and heated from 40 to 325° at a rate of 40°/min in a stream of carrier gas (air or nitrogen) and then held at 325° until the detector response curve returned to the base line. The effluent stream may be passed to the detectors and the volatile products then collected in a liquid nitrogen-cooled trap filled with glass beads. TC detection was used primarily in this study. The collected volatile pyrolysis products were then backflushed into the gas chromatograph, and the separate GC fractions were analyzed on stream using IR spectroscopy. Quantitative analyses for ammonia and methyl-, ethyl-, and n-propylamines were carried out by introduction of known amounts of these compounds into the cold trap prior to backflushing in order to calibrate the response of the GC detector and substantiate peak identity.

Flash pyrolysis was carried out using a Chemical Data Systems Inc. CDS-100 Pyroprobe fitted to the injection port of a Perkin-Elmer 990 gas chromatograph which was interfaced with a Hitachi RMU 6L single focusing mass spectrometer using a single-stage jet separator. Samples were added to the platinum ribbon of the Pyro-probe from a microsyringe as 3 drops of a saturated solution (PBG in chloroform, PGA in dioxane/water, and the dioxopiperazine in DMF). The ribbon was then heated to a temperature 10° above the boiling point of the solvent. After repetition of this sequence, the loaded probe was inserted into the GC injection port, immediately heated from ambient temperature to 350°C at a rate of 20°/Msec, and then held at 350° for 20 sec. Mass spectra of individual GC fractions were recorded at ionizing voltages of 80 and 16.5 eV.

The following stainless steel GC columns were employed to separate volatile decomposition products.

1. 6' × 1/8" 4% SE-30 on 80/100 mesh Chromosorb G HP
2. 6' × 1/8" Chromosorb 103
3. 6' × 1/8" 10% Carbowax 20M/2% KOH on 80/100 mesh Chromosorb W AW

Columns 2 and 3 were capable of separating low molecular weight primary amines. Products of slow pyrolysis were separated on Columns 1-3, and flash pyrolysis products were separated on Columns 1 and 3.

## RESULTS AND DISCUSSION

### Dielectric Relaxation Measurements

PBG films cast from chloroform exhibited infrared absorption typical of the  $\alpha$ -helical molecular conformation [1a-c, 15]. PGA films cast from dioxane/water were also shown to possess the  $\alpha$ -helical conformation expected for un-ionized PGA [16]. The films were characterized further by determination of both components of the complex dielectric constant at frequencies from 0.1 to 10 kHz. Relaxations, corresponding to maxima in the dielectric loss ( $\epsilon''$ ) versus temperature plots, are given in Table 1.

The results for PBG are in general accord with others obtained by dielectric, dynamic mechanical, and piezoelectric measurements. All subambient studies have revealed the low temperature,  $\gamma$ , relaxation [4a-b, 4f-h, 5b]. Our value for the activation energy is larger than the 9.5 kcal/mole reported by Wilkes et al. [4h]. The  $\beta$ -relaxation has been reported by many groups [4a-c, 4f-i, 5b-c]. The transition has been detected by other techniques such as dilatometry and determination of creep modulus [17]. Our activation energy agrees well with the 46 kcal/mole value of Hiltner et al. quoted by Wilkes [4h] and the 47 kcal/mole value of Uematsu et al. [4e]. The 65 kcal/mole value determined by Wilkes [4h] is probably too high. Values near 30 kcal/mole have also been reported [4j]. There is general agreement that the  $\beta$ -transition is associated with side chain motion. The high temperature,  $\alpha$ , relaxation has also been found by several

TABLE 1. Dielectric Relaxations of PBG and PGA

Sample	Relaxation region	Relaxation temperature ( $^{\circ}$ C)			Activation energy (kcal/mole)
		0.1 kHz	1.0 kHz	10 kHz	
PBG	$\alpha$	112.5	113.4	-	-
	$\beta$	31.4	39.4	49.8	46
	$\gamma$	-63.8	-54.2	-40.6	19
PGA	$\alpha$	-	25.5	24.3	-
	$\beta$	-43.7	-24.4	-2.2	14

investigators [4b-c, 4f, 4i-1, 18], though Wilkes [4h] did not find a maximum in this region. The relaxation behavior of our film identifies it as "film A," cast by Uematsu et al. [4i, 4l] from chloroform and 1,2-dichloroethane. This is also the film described as "form C" by McKinnon and Tobolsky [17]. DSC data (below) further confirms this identification.

PGA was studied previously by Wilkes et al. [4h] who detected no maxima in the dielectric loss ( $\epsilon''$ ) versus temperature curve. Their dynamic mechanical studies at three frequencies showed relaxations as maxima in the  $\tan \delta_m$  versus temperature curve at 28 and  $\sim 60^\circ$  (110 Hz). Our dielectric data are in rough agreement with the dynamic mechanical data.

### TGA and DSC Measurements and Decomposition Temperatures

Powder samples, shown to be  $\alpha$ -helical by infrared spectroscopy, were studied thermogravimetrically in a nitrogen atmosphere at a heating rate of  $40^\circ/\text{min}$ . PBG samples exhibited initial weight loss near  $250^\circ\text{C}$  while PGA samples began to lose water at  $110^\circ$ . Uematsu et al. [4i] reported no weight loss for PBG up to  $160^\circ$ . However, Obata and Ogawa, using a slower heating rate ( $3^\circ/\text{min}$ ), reported initial weight loss for PBG at  $\sim 160^\circ$  [6b]. A higher initial weight loss temperature is expected for a higher heating rate [19]; the  $90^\circ$  difference is larger than expected from this factor alone, however. Boni et al. [6d], using a heating rate of  $10^\circ/\text{min}$ , observed initial and maximum weight losses as  $\sim 225$  and  $305^\circ$ , respectively. Our values,  $\sim 240$  and  $360^\circ$ , are higher by reasonable amounts.

DSC curves for powder and film samples of PBG and PGA under nitrogen exhibited only incomplete endotherms corresponding to decomposition. Significant deviation from the base line began in the  $240$ - $280^\circ$  region and increased with the heating rate. Uematsu et al. [4i] have studied PBG films cast from chloroform by DTA using a heating rate of  $10^\circ\text{C}/\text{min}$ . They report single endotherms beginning at  $\sim 170^\circ$ . These data make it clear that PBG and PGA undergo no phase changes in the  $50$  to  $150^\circ$  domain within the time scale of these experiments. Furthermore, their thermal and dielectric behavior confirms that our PBG films are of "form C" [17]. Forms A and B [17, 4i-1] possess further elements of structure such as stacks of benzene rings or superhelices and exhibit significantly different thermal and dielectric properties.

Thermal decomposition temperatures are presented in Table 2. For DSC experiments, decomposition temperature is defined as the intercept of the base line and the slope of the endotherm. For TGA it is defined as the temperature at which weight loss was first detected. Temperatures at which volatile decomposition products were first detected when samples were heated in a gas stream in the Multipurpose

TABLE 2. Thermal Decomposition Temperatures

Sample	Heating rate (°C/min)	Decomposition temperature (°C) <sup>a</sup>			
		DSC(N <sub>2</sub> )	TGA(N <sub>2</sub> )	MP-3(He)	MP-3(air)
PBG powder	40	297	246	255	220
	10	264			
PBG film	40			254	214
	10	256			
PGA powder	40	257	110 <sup>b</sup>	249	238
	10	246			
PGA film	40			263	
	10	278			

<sup>a</sup>DSC: average of three runs for PBG powder, one run for other samples. TGA: average of two runs per sample. MP-3: average of four runs per sample.

<sup>b</sup>Loss of water began at 110°.

Thermal Analyzer (MP-3, see Experimental) are also included. Differences between film and powder samples are small, and the DSC results exhibit the expected dependence on heating rate [19]. Heating in air gives volatile products at lower temperatures than heating in helium. Traces of oxidation products may be responsible. However, no major differences between pyrolysis products in these two atmospheres were noted (see below). Owing to their mode of definition, the decomposition temperatures in Table 2 are far above the maximum practical service temperatures for PBG and PGA materials [20].

### Identification of Major Pyrolysis Products

PBG and PGA were pyrolyzed using the Multipurpose Thermal Analyzer (MP-3) in a stream of air or helium by heating from 40 to 325°C at 40°/min (see Experimental). The collected products were separated using a gas chromatograph interfaced to an on-line infrared spectrometer. Major pyrolysis products are listed in Tables 3 and 4 and gas chromatograms are shown in Figs. 1-3. The standard SE-30 column was unsuitable for the separation of low molecular weight amines and aldehydes. However, chromatography on Carbowax 20M/KOH or Chromosorb 103 (Fig. 3) allowed identification of water and



TABLE 3. Major Pyrolysis Products from PBG<sup>a</sup>

Compound	GC peak (Fig. 1)	Comparison with authentic sample <sup>b</sup>		IR comparison with literature
		GC	IR	
Carbon dioxide	R	-	-	c
Ammonia		+	-	
Water		+	+	c
Toluene	U	+	+	
Benzaldehyde	Y	+	+	d
Benzyl alcohol	Z	+	+	d
Benzoic acid	BA	+	+	d

<sup>a</sup>Heated from 60 to 325° C at 40°/min under helium or air.

<sup>b</sup>+: Satisfactory comparison made. -: No comparison made.

<sup>c</sup>The Sadtler Infrared Prism Standard Spectra, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

<sup>d</sup>D. Welti, Infrared Vapor Spectra, Heyden, London, 1970.

TABLE 4. Major Pyrolysis Products from PGA<sup>a</sup>

Compound	GC peak (Fig. 2)	Comparison with authentic sample <sup>b</sup>		IR comparison with literature
		GC	IR	
Carbon dioxide	U	-	-	c
Ammonia		+		
Methanol	V	+	+	d
Acetone	W	+	+	d
Water	X	-	+	c

<sup>a</sup>Heated from 60 to 325° at 40°/min under helium or air.

<sup>b</sup>+: Satisfactory comparison made. -: No comparison made.

<sup>c</sup>The Sadtler Infrared Prism Standard Spectra, Sadtler Research Laboratories, Inc., Philadelphia, Pennsylvania.

<sup>d</sup>D. Welti, Infrared Vapor Spectra, Heyden, London, 1970.

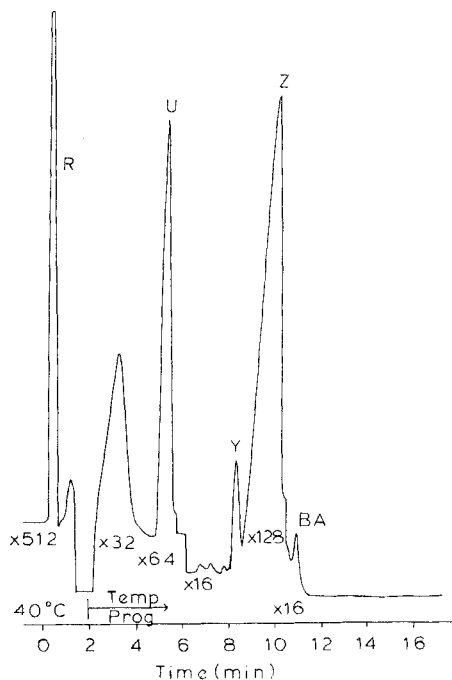


FIG. 1. Gas chromatogram of PBG pyrolyzate (air atmosphere). Column, 6 ft  $\times$  1/8 in. o.d. 4% SE 30 silicone gum at 80/100 mesh Chromosorb G.HP. Temperature programmed from 40 to 300°C at 20°C/min. Detector attenuations as shown. Peaks as noted in Table 3.

ammonia among the pyrolysis products. Peak Y (Fig. 2), noted on pyrolysis of PGA, has the IR characteristics of a carboxylic acid; absorption at 3600, 1800, 1400, 1200, and 1000  $\text{cm}^{-1}$ . Acetic acid has a shorter retention time than water on this column, thus peak Y is presumably a higher carboxylic acid. Major pyrolysis products did not vary with carrier gas. A minor exception is the unidentified material (IR 2350, 1680, 960, 930  $\text{cm}^{-1}$ ) which appears as a small peak between carbon dioxide (R) and toluene (U) (Fig. 1) when PBG is pyrolyzed in air. No difference between film and powder samples was detected. Koleske and Lundberg [4b] have ascribed the difference in dynamic mechanical behavior between newly-cast and aged PBG films to plastization by retained solvent in the former. We detected no retained casting solvents, chloroform or dioxane, in film samples aged 1 week to several months after casting.

Owing to the paucity of nitrogen compounds identified among the volatile pyrolysis products, the nitrogen balance in pyrolysis was

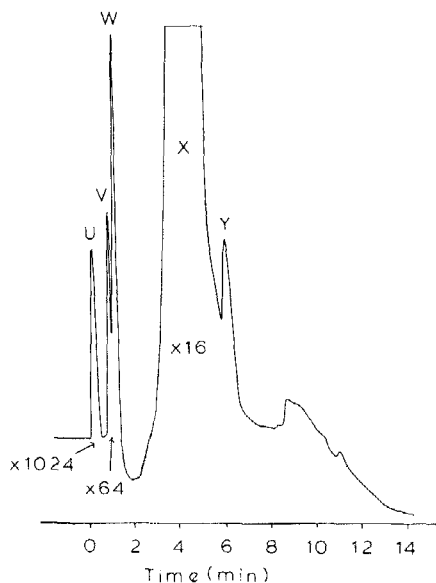


FIG. 2. Gas chromatogram of PGA pyrolyzate (air atmosphere). Column and temperature programming as in Fig. 1. Detector attenuations as shown. Peaks as noted in Table 4.

investigated. TGA runs were made under conditions which simulated the preparative pyrolyses to determine the percent nonvolatile residues, while the residues from preparative pyrolyses of 10 mg polymer samples were analyzed for nitrogen. Ammonia in the pyrolysates was determined quantitatively (see Experimental). At the same time the absence of methyl-, ethyl-, and propylamines in the pyrolyzate was demonstrated by gas chromatographic comparisons with authentic samples. Specifically, a 10-mg sample of either polymer produces less than 3.3, 5.3, and 4.4  $\mu\text{g}$ , respectively, of the above 3 primary amines. The nitrogen balance summarized in Table 5 shows that a large fraction of nitrogen is present in unidentified volatile pyrolysis products. These may be less volatile polar species needing novel GC approaches for characterization.

Flash pyrolysis in the injection port of a gas chromatograph interfaced with a mass spectrometer was conducted as a supplement to the above experiments. PBG produced all the compounds generated by slow pyrolysis. Products were identified by their mass spectral fragmentation patterns. An additional product appeared in the gas chromatogram. Its odd integer molecular weight, 183, identified it as a nitrogen-containing compound, and its major fragment ions (Table 6) are consistent with the N-benzylaniline structure: 106,

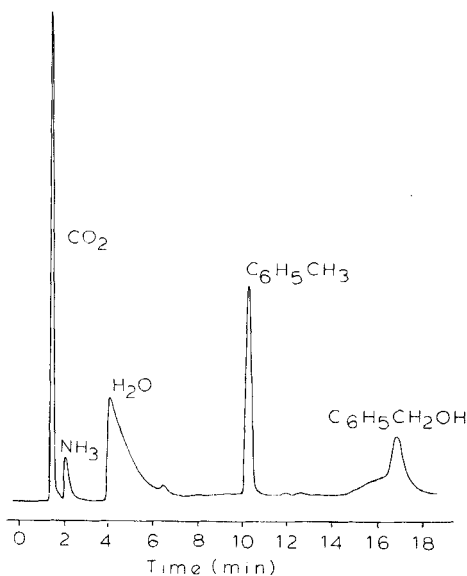


FIG. 3. Gas chromatogram of PBG pyrolyzate (helium atmosphere). Column 6 ft  $\times$  1/8 in. o.d. stainless steel, Chromosorb 103. Temperature programmed as in Fig. 1.

TABLE 5. Nitrogen Balance for Pyrolysis of 10 mg Polymer Samples

	Total N (mg)	Nonvolatile residue (%) <sup>a</sup>	N in residue (mg) <sup>b</sup>	N detected as NH <sub>3</sub> (mg)	Undetected N in volatile products (mg)
PBG	0.639	30.15	0.401	0.083	0.155
PGA	1.085	38.87	0.528	0.023	0.534

<sup>a</sup>Determined by TGA.

<sup>b</sup>Determined by nitrogen analysis of residue from MP-3 pyrolysis.

TABLE 6. Fragmentation of N-Benzylaniline in the Mass Spectrometer

Source	Molecular and fragment ions, m/e (relative intensity)								
Pyrolysis product	184(9)	183(50)	179(10)	106(20)	105(20)	104(5)	91(100)	77(60)	65(14)
Authentic sample <sup>a</sup>	184(10)	183(40)		106(20)	105(5)	104(25)	91(100)	77(60)	65(25)
Aldermaston <sup>b</sup>	184(13)	183(75)		106(20)			91(100)	77(20)	65(14)

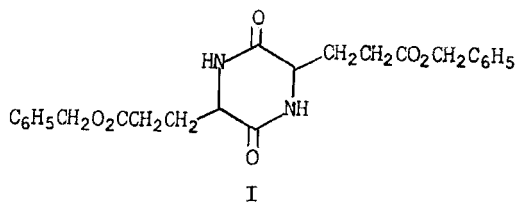
<sup>a</sup>Spectrum recorded using the GC/MS system.

<sup>b</sup>Peak Index of Mass Spectra, 2nd ed., Mass Spectrometry Data Centre, AWRE, Aldermaston, Reading, 1974. Also reported among the 8 most intense peaks were 182(28) and 28(17).

$\text{CH}_2=\text{NHC}_6\text{H}_5$ ; 91,  $\text{C}_7\text{H}_7^+$ ; and 77,  $\text{C}_6\text{H}_5^+$ . Table 6 contains a comparison of the important high mass ions observed for this pyrolysis product with those from an authentic sample of *N*-benzylaniline recorded with our GC/MS system and with data from the Aldermaston collection. The observed intensity differences are not unexpected, especially since with GC introduction the sample pressure in the ion source changes somewhat as the spectrum is scanned. The  $m/e$  179 ion, however, must arise from an impurity, unresolved by gas chromatography, since it appears neither in the spectrum of authentic *N*-benzylaniline nor in the Aldermaston spectrum.

Flash pyrolysis of the PGA sample was complicated by inability to remove all of the dioxane/water solvent prior to pyrolysis. Both of these solvents were prominent in the gas chromatogram of pyrolysis products, and only small amounts of other products were detected. When GC Column 3 (see Experimental) was used, two products were present at levels adequate for mass spectral investigation: these were carbon dioxide and a new compound which exhibited the following mass spectrum:  $m/e$  (relative intensity) 101 (weak), 87 (weak), 73 (31), 58 (12), 44 (100), 41 (12), 30 (33), 18 (50). This spectrum corresponds to an aliphatic amine  $\text{C}_6\text{H}_{15}\text{N}$ . *n*-Hexyl- and di-*n*-propyl- and triethylamines as well as amines with  $-\text{NHC}_2\text{H}_5$ ,  $-\text{N}(\text{CH}_3)_3$  groups can be ruled out because they produce most abundant ions with  $m/e \neq 44$  [21]. The mass spectra of 2-hexyl- and *n*-amylmethylamines give reasonable fits to the observed spectrum, the former being closer. Neither, however, produces an abundant ion at  $m/e = 73$  [21]; positive identification must await comparison with authentic samples.

Dioxopiperazines are produced during pyrolysis of peptides [22], but would probably not be detected by the GC procedures employed. They have also been implicated as intermediates in the pyrolysis of  $\alpha$ -amino acids [22, 23]. Pyrolysis of dioxopiperazine (I) under helium in the multipurpose thermal analyzer produced a pyrolysate which according to GC analysis was qualitatively identical to that produced by PBG.



Direct introduction of PBG into the ion source of the mass spectrometer by means of a heated solid probe produced ions attributable to I and its fragmentation products as well as ions with  $m/e$  above the

dipeptide region up to  $m/e$  550. These observations permit, but do not require, intermediacy of I in PBG pyrolysis.

PBG pyrolysis products are dominated by those produced from the labile benzyl ester moiety. They are almost certainly produced by cleavage of the relatively labile C-O bonds to give benzyl and benzyloxy radicals. Hydrogen abstraction reactions would then produce toluene and benzyl alcohol, while disproportionation of benzyloxy radical [24] would give benzyl alcohol and benzaldehyde. Oxidation of the latter would give benzoic acid. Speculation about the origin of *N*-benzylaniline is not justified at this point.

The major PGA pyrolysis products should, when a significant number of minor products become known, help provide information about how the peptide chain is broken during pyrolysis. Very little other information is available about poly( $\alpha$ -amino acid) pyrolysis. Kato et al. [6e] have studied ninhydrin-positive products from heating some amino acid polymers. Cleavage of peptide linkages occurred and side chain modifications led to production of new amino acids. PGA (MW = 7000) when heated in air at 200° gave glycine, alanine, glutamic acid, and Glu-Glu [6e]. Poly(glycine) and poly(L-methionine) were also studied. The same group has also reported racemization of amino acid residues when poly-(L-Ala) and PGA were heated at temperatures from 180 to 300°. PGA degraded to give a low molecular weight fraction which was more highly racemized than the remaining high molecular weight polymer [6f].

A growing body of information about pyrolysis products from proteins and protein-containing mixtures exists [6e-f, 22, 25]. Since free amino acids are produced when poly( $\alpha$ -amino acids) [6e] and proteins [25] are pyrolyzed, data on amino acid pyrolysis [23, 26] are also relevant. Data for glutamic acid itself have not been published, however. Judged by the results of these studies, the major products of PGA pyrolysis are typical. Yet many classes of volatile compounds previously identified as amino acid or protein pyrolysis products such as low molecular weight amines, nitrogen heterocycles, nitriles, and aldehydes remained undetected in our study. Data on several poly( $\alpha$ -amino acids) and information about minor pyrolysis products are needed before decomposition mechanisms can be discussed meaningfully.

#### ACKNOWLEDGMENTS

Indispensable assistance in use of the pyrolysis and mass spectral equipment was provided by Dr. David Henderson and Mr. Eugene Guzik. We gratefully acknowledge an NIH Biomedical Research Support Grant, allocated by the University of Massachusetts, in partial support of this work.

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