Thermal Behavior of Aryl-Aliphatic Polyamides

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Synopsis

Low molecular weight poly(p-phenylene sebacamides) and (m-phenylene sebacamides) were prepared by interfacial polycondensation by varying the concentration of p- and m-phenylenediamine in the initial feed. The polymers were characterized by intrinsic viscosity measurement and IR spectra. The relative thermal stability was evaluated by differential thermal analysis and dynamic thermogravimetry in air and nitrogen atmospheres. A systematic dependence of stability on intrinsic viscosity of poly(m-phenylene sebacamide) was observed indicating an endgroup initiation of degradation. No such dependence was observed in poly(p-phenylene sebacamide). A probable mechanism for the thermal degradation has been proposed.

INTRODUCTION

A large number of polyamides from aliphatic-aromatic dicarboxylic acids and aromatic aliphatic diamines have been reported in the literature.[1-6] The properties of these aryl-aliphatic polyamides depend both on the structure and reactivity of the initial substances. The resistance to thermal and thermo-oxidative degradation of aromatic and aliphatic polyamides has received the attention of many research workers.[7-10] However, relatively few investigations have been concerned with the degradation mechanism of aryl-alkyl polyamides. The thermal behavior of some aryl polyamides derived from fumaric and adipic acid[11] and suberic acid[6] has been reported.

The thermal behavior of poly(p- or m-phenylene sebacamide) was, therefore, investigated. The degradation of aliphatic polyamides is believed to proceed by random chain scission of several bonds in the polymer chain.[12] The degradation may also be initiated from the chain ends. Low molecular weight polyamides were, therefore, prepared and the thermal behavior was studied by dynamic thermogravimetry in air and differential thermal analysis.

EXPERIMENTAL

p-phenylene diamine BDH/LR was purified by vacuum sublimation at 120°C. m-phenylene diamine was distilled at 90°C under reduced pressure. Sebacoyl chloride (BDH) and 1,2 dichloro-ethane (High Purity Chemicals/LR) were used as such.

PREPARATION OF POLY(p- OR m-PHENYLENE SEBACAMIDE)

Polymerization of m- and p-phenylene diamine and sebacoyl chloride was carried out by interfacial polycondensation in 1,2 dichloroethane using sodium hydroxide as acid acceptor.[13] A known weight of the diamine was dissolved in

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water containing required amount of sodium hydroxide with constant stirring. The acid chloride in 1,2 dichloroethane was added to this aqueous solution. The stirring was continued for 5 min. The polymer was then collected, washed first with acetone and then with distilled water. The polymer was dried in vacuum oven at 40°C.

To get the low molecular weight polymer, the molar ratio of diamine was kept low (0.0005 to 0.004 M) compared to sebacoyl chloride (0.005 M). The polymers were characterized by intrinsic viscosity determination in concentrated sulphuric acid (98% Analar) using Ubbelhode suspension level viscometer at 35 ± 0.1°C.

Infrared spectra of the polyamides in KBr pellets were recorded by a Hilger-Watt spectrophotometer from 700 to 4000 cm^{-1}. Differential thermal analysis of polyamides was carried out with a Stanton Redcroft Thermal Analyzer from room temperature to 500°C in nitrogen atmosphere using alumina as reference material at a heating rate of 6°C/min. A Stanton HT-D thermobalance was used to study the thermal stability. A 18 ± 2 mg polymer sample was heated in presence of air at a rate of 6°C/min. The thermogravimetric analysis in nitrogen atmosphere was carried out using a Stanton Redcroft TG-750 balance. A 5 ± 1.0 mg sample was heated at the rate of 10°C/min in nitrogen (flow rate 5 cm^3/min).

RESULTS AND DISCUSSION

The intrinsic viscosity of the polymer depended on the molar ratio of the amine to sebacoyl chloride. It was observed that as the m-phenylene diamine concentration was increased from 0.0005 to 0.0035, the intrinsic viscosity also increased (Table I). With p-phenylene diamine on the other hand, an optimum value of $[\eta]$ was obtained and further increase in concentration of amine resulted in a decrease of $[\eta]$. A similar behavior has been reported for the preparation of nylon 610[10] by increasing the concentration of sebacoyl chloride. m-phenylene

TABLE I
Conditions for Interfacial Polycondensation

Sample No.	Sample code	p-PDA[a]	Amount of m-PDA[b]	SC[c]	$[\eta] \times 10^{-2}$ (cm^3/g)
1	A	0.0005	—	0.005	0.1330
2	B	0.0015	—	0.005	0.1213
3	C	0.0020	—	0.005	0.2650
4	D	0.0025	—	0.005	0.1950
5	E	0.0030	—	0.005	0.3750
6	F	0.0035	—	0.005	0.1125
7	G	0.0040	—	0.005	0.1435
8	A'		0.0005	0.005	0.0180
9	B'		0.0015	0.005	0.0700
10	C'		0.0020	0.005	0.0600
11	D'		0.0025	0.005	0.1875
12	E'		0.0030	0.005	0.1750
13	F'		0.0035	0.005	0.3250
14	G'		0.0040	0.005	0.2750

[a] p-phenylene diamine.
[b] m-phenylene diamine.
[c] Sebacoyl chloride.

diamine is expected to be less reactive than p-phenylene diamine due to the electron withdrawing inductive effect of amino group. The intrinsic viscosities of poly(p-phenylene sebacamides) are higher as compared to poly(m-phenylene sebacamide) even at lower concentration of diamine.

The IR spectra of the polymers were also recorded for characterization (Table II). In all the spectra absorption bands at 3370–3160 cm^{-1} region were present due to the N—H stretching vibration in the amide group. The 3040 cm^{-1} and 2900 and 2840 ± 10 cm^{-1} bands arise due to C—H stretch in aromatic ring and asymmetric and symmetric stretch in CH$_2$ groups. The strong absorption amide I band at 1670 ± 15 cm^{-1} (due to C=O stretch in amides), N—H in plane deformation (amide II) band at 1540 ± 15 cm^{-1}, C—N stretching (amide III) at 1305 cm^{-1} were observed in all the spectra. The C—H out of plane deformation band due to two adjacent hydrogen in p-phenylene sebacamides was observed at 810 cm^{-1}. In m-phenylene sebacamide, the bands due to one lone H atom and three adjacent H atoms were present at 720 and 780 ± 5 cm^{-1}.

The differential thermograms of few polyamides are given in Figures 1 and 2. In poly(p-phenylene sebacamides) only exothermic peaks indicating decomposition reactions are observed. In Table III, the position of various exothermic peaks are given. However, in the isomeric m-phenylene polymers, an endothermic peak was observed which shifts to higher temperature with increase in molecular weight (samples A', B', C', D', E', F', and G', respectively). The endothermic transition in DTA are normally associated with second-order transition or melting or loss of adsorbed water. If this endothermic transition was due to loss of water, one should not expect an increase with increase in [η] (Fig. 2). However, T_m will increase with increasing [η] values. In more-sym-

TABLE II
The IR Absorption Bands of Polysebacamides

| Sample A	Sample G	Sample A'	Sample G'
3360 (sh)	3360 (sh)	3280 (s)	3280 (s)
3270 (s)	3260 (s)	—	—
3160 (sh)	—	—	—
3040 (m)	3040 (m)	3050 (m)	3050 (m)
2900 (s)	2900 (s)	2900 (s)	2910 (s)
2840 (s)	2830 (s)	2850 (s)	2850 (s)
1650 (s)	1665 (s)	1680 (s)	1655 (s)
1635 (sh)	1645 (s)	1650 (s)	1635 (sh)
1560 (sh)	1560 (sh)	1560 (sh)	1560 (sh)
1535–48 (s)	1540 (s)	1535 (s)	1530 (s)
—	—	1520 (sh)	1520 (sh)
1510 (s)	1510 (s)	1510 (sh)	1510 (sh)
—	—	1350 (m)	—
1305 (s)	1305 (s)	1305 (s)	1300 (s)
1235 (s)	1230 (s)	1235 (s)	1230 (s)
1175 (s)	1175 (s)	1185 (s)	1165 (s)
1110 (m)	1110 (m)	—	—
955 (s)	955 (s)	925 (m)	950 (m)
875 (s)	—	870 (m)	870 (m)
840 (s)	840 (s)	—	—
810 (m)	810 (m)	—	—
—	—	785 (s)	780 (m)
		750 (m)	—
		720 (m)	720 (m)
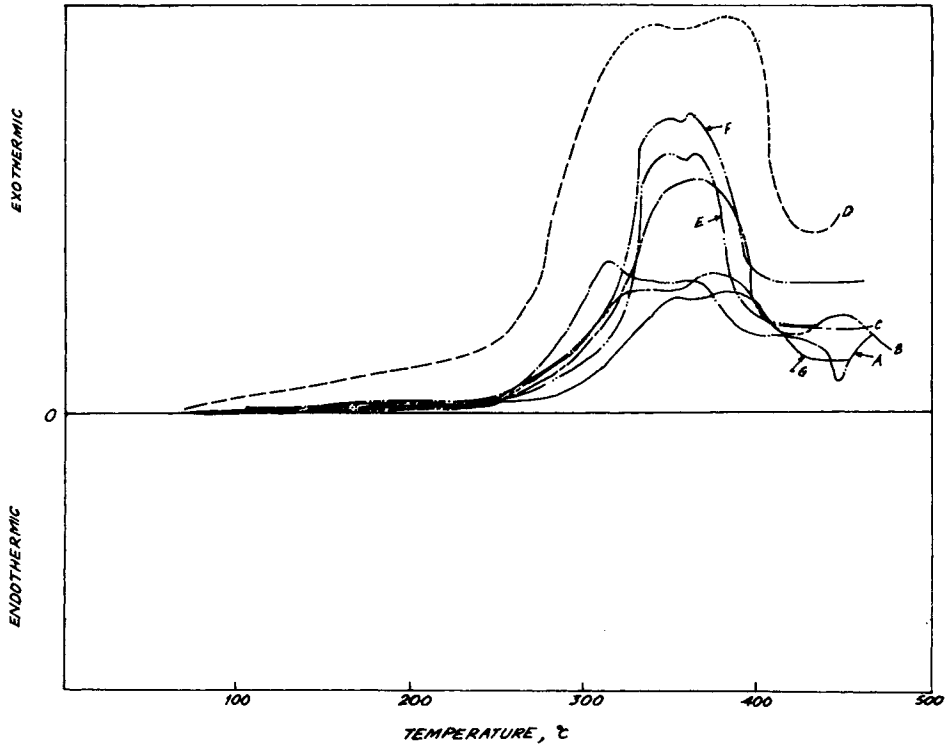
Fig. 1. Differential thermograms of poly(p-phenylene sebacamides).
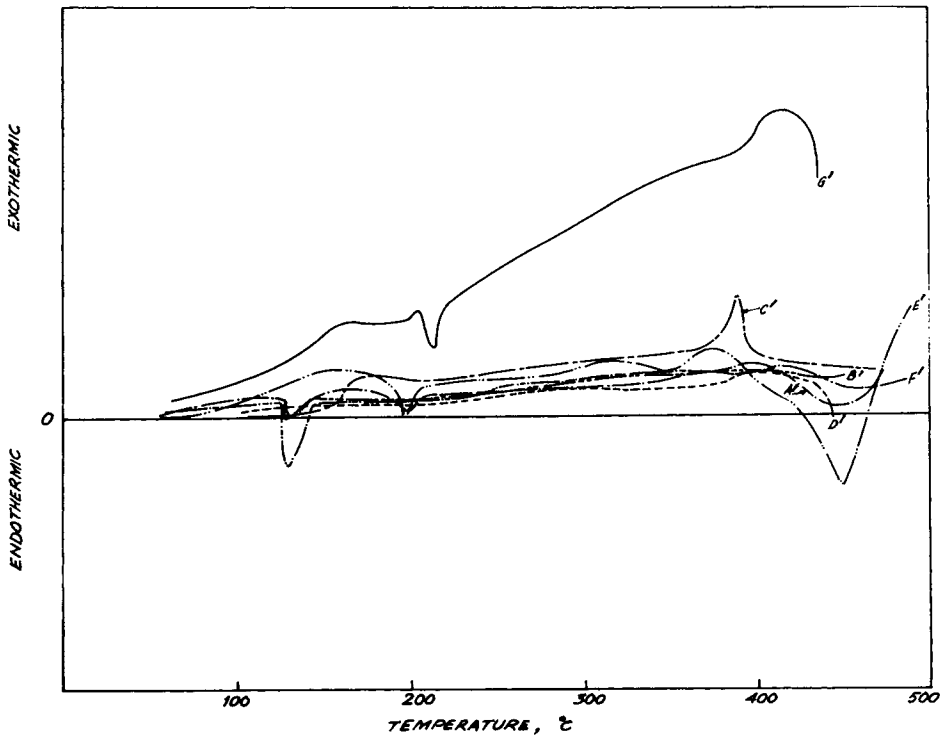

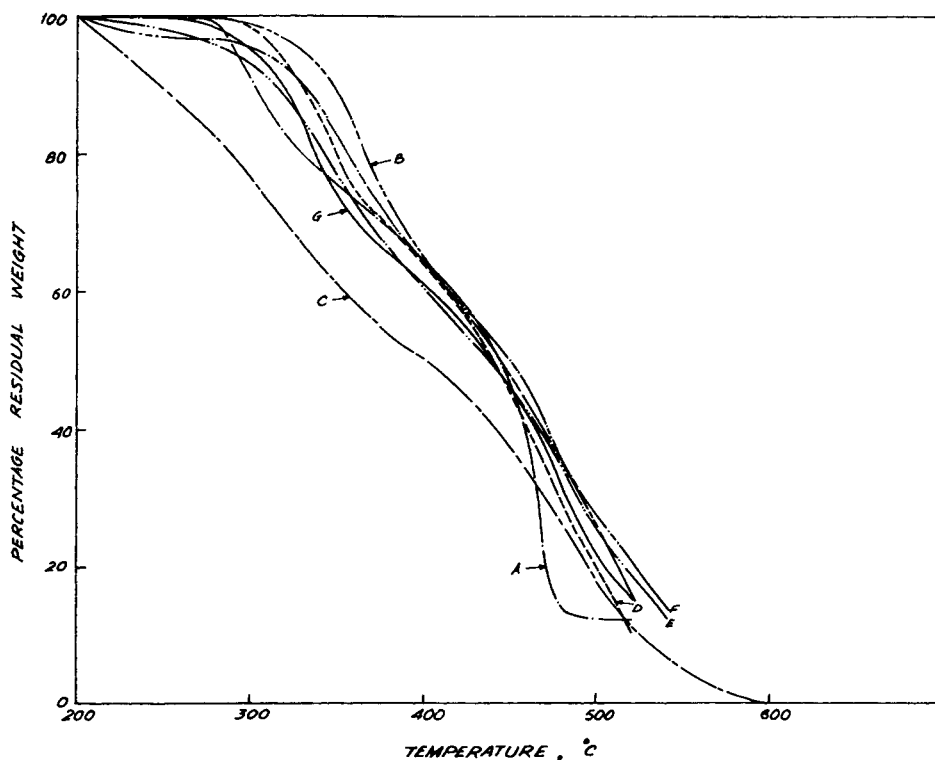Fig. 2. Differential thermograms of poly(m-phenylene sebacamides).

Fig. 3. Primary thermograms of poly(p-phenylene sebacamides) in air.

metrical poly(p-phenylene sebacamides), the $[\eta]$ values are higher than the poly(m-phenylene sebacamides) and so the endothermic transition are not observed because they might be coinciding with exothermic decomposition reaction. The T_m is also expected to be higher in poly(p-phenylene sebacamides) than poly(m-phenylene sebacamides) of similar molecular weights.

The primary thermograms of the polymer samples were obtained (Figs 3 and

TABLE III

The Exothermic (+) and Endothermic (−) Peaks of Poly(Phenylene Sebacamides) as Observed by Differential Thermal Analysis

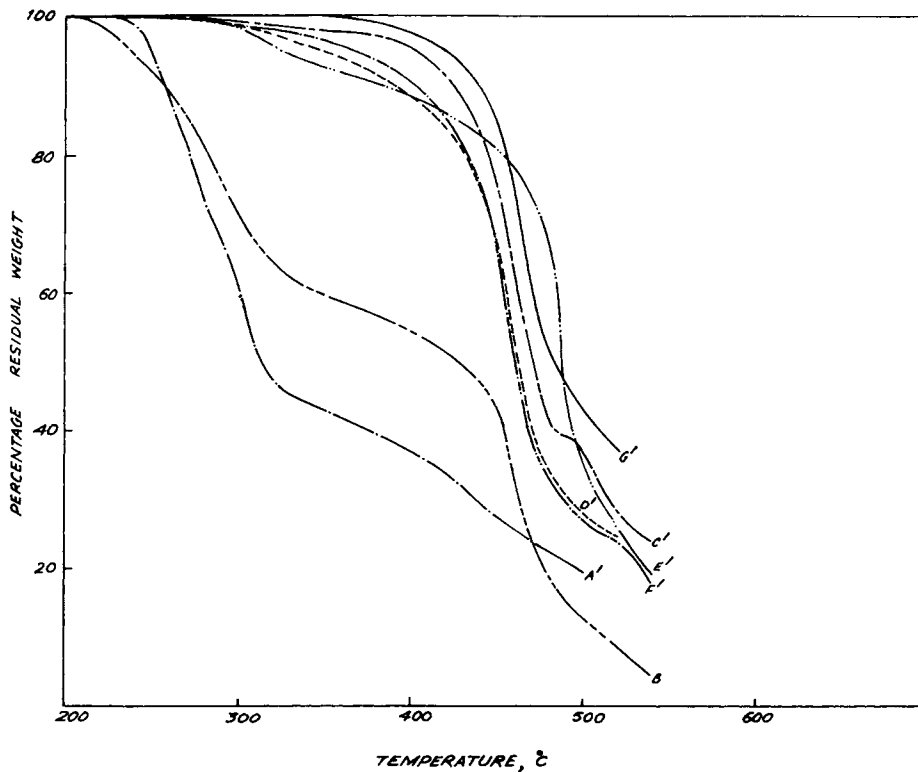| Sample No.	Sample	Endothermic	Exothermic
1	A	—	316,446(−)
2	B	—	360–393(+),420(−)
3	C	—	364(+)
4	D	—	340(+),386(+),430(−)
5	E	—	348(+),364(+)
6	F	—	346(+),362
7	G	—	
8	A′	128(−)	416(+)
9	B′	132(−)	388(+)
10	C′	130(−)	388(+)
11	D′	—	392(+)
12	E′	197(−)	350(+)
13	F′	198(−)	400(+)
14	G′	124(−)	410(+)

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Fig. 4. Primary thermograms of poly(m-phenylene sebacamides) in air.

4) by plotting the percent residual weight vs temperatures and from these the temperatures of 10%, 20%, 30%, 40%, and 50% decomposition in air were calculated (Table IV).

TABLE IV
Thermal Properties of Poly(Phenylene Sebacamides) in Air

Sample	Temperature at various % decomposition					IPDT
	10	20	30	40	50	
A	300	330	380	420	445	416
B	350	366	388	415	446	434
C	248	290	320	356	400	385
D	330	350	380	414	442	425
E	314	344	370	402	438	420
F	332	358	382	414	450	427
G	320	338	364	404	440	415
A'	258	273	286	302	315	361
B'	258	284	304	350	430	388
C'	425	445	455	462	472	468
D'	394	434	448	458	464	456
E'	388	454	478	485	488	466
F'	404	434	446	455	462	456
G'	440	456	465	472	482	476

TABLE V
Thermal Properties of Poly(Phenylene Sebacamides) in Nitrogen Atmosphere

| Sample | Temperature at various % decomposition | | | | | IPDT[a] |
	10	20	30	40	50	
A	100	310	360	410	450	435
B	310	400	430	482	508	470
C	178	244	296	344	392	403
D	360	410	436	468	508	468
E	320	380	432	500	572	454
F	300	356	384	412	432	429
G	360	408	436	444	460	442
A′	230	250	264	301	380	379
B′	180	300	364	392	412	433
C′	400		448	480	496	469
D′	290	385	470	490	500	460
E′	256	366	432	456	468	424
F′	340	390	412	424	346	411
G′	412	460	468	490	492	472

[a] Integral procedural decomposition temperature.

To get a more semiquantitative data regarding the relative thermal stabilities, the integral procedural decomposition temperatures[14] (IPDT) were calculated from the primary thermograms in the temperature range of 200°–500°C. The thermal behavior of poly(p-phenylene secabamide) and poly(m-phenylene sebacamide) is found to be different. There is a progressive increase in thermal stability as $[\eta]$ is increased in case of polyamides derived from m-phenylene diamine (A′–G′) (in Table IV). The IPDT values of poly(m-phenylene sebacamides) increase with increasing $[\eta]$, even the lowest molecular weight sample was stable upto 240°C. In the polymers derived from p-phenylenediamine, on the other hand, no regular relationship between $[\eta]$ and the percent of weight loss is observed. IPDT values of polymer samples A, B, D, E, F, and G are comparable (±10°C) although $[\eta]$ of sample E was comparatively higher. Sample C was the least stable although $[\eta]$ was higher than A and B samples.

The thermal degradation of polyamides in nitrogen atmosphere were also carried (Figs. 5 and 6) and the various decomposition temperatures and IPDT values are reported in Table V. Initial decomposition temperatures are lowered down in nitrogen atmosphere, but at a later stage the samples are found to be more stable. The IPDT values of poly(p-phenylene sebacamides) are generally found to be higher in nitrogen atmosphere than in air. However, no such trend is observed in poly(m-phenylene sebacamides). One should be cautious in comparing the two sets of results simply because the heating rates in the two atmosphere were different.

The endgroup per unit weight of polymer will be more in low molecular weight samples. This implies that in poly(m-phenylene sebacamides) endgroup initiated degradation takes place. The endgroup participation may be due to (a) further polymerization with liberation of water which may cause hydrolytic
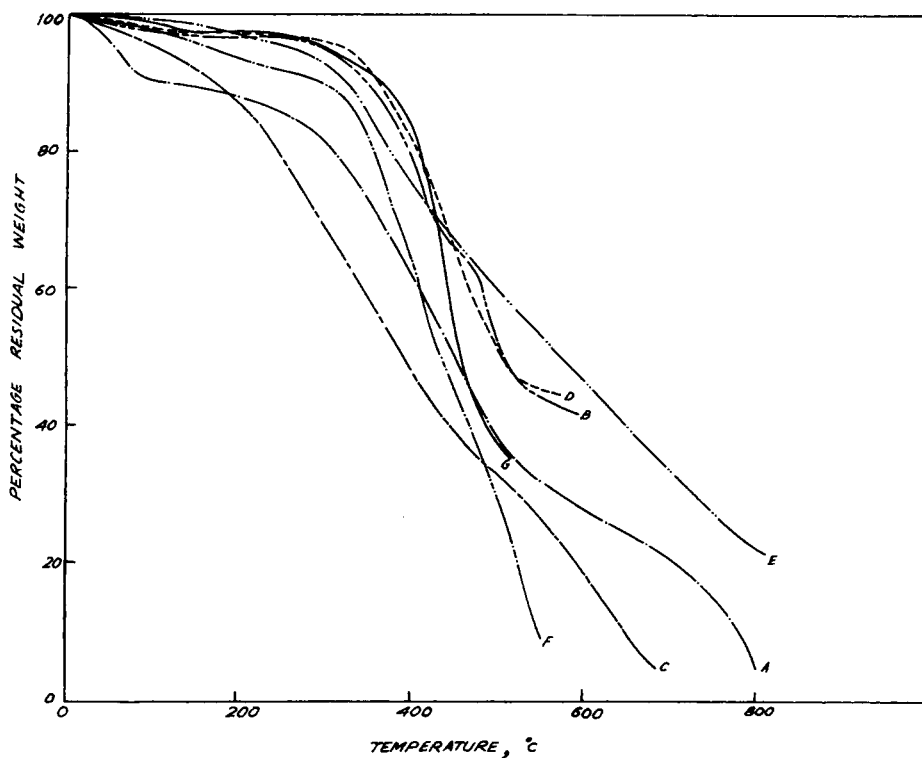
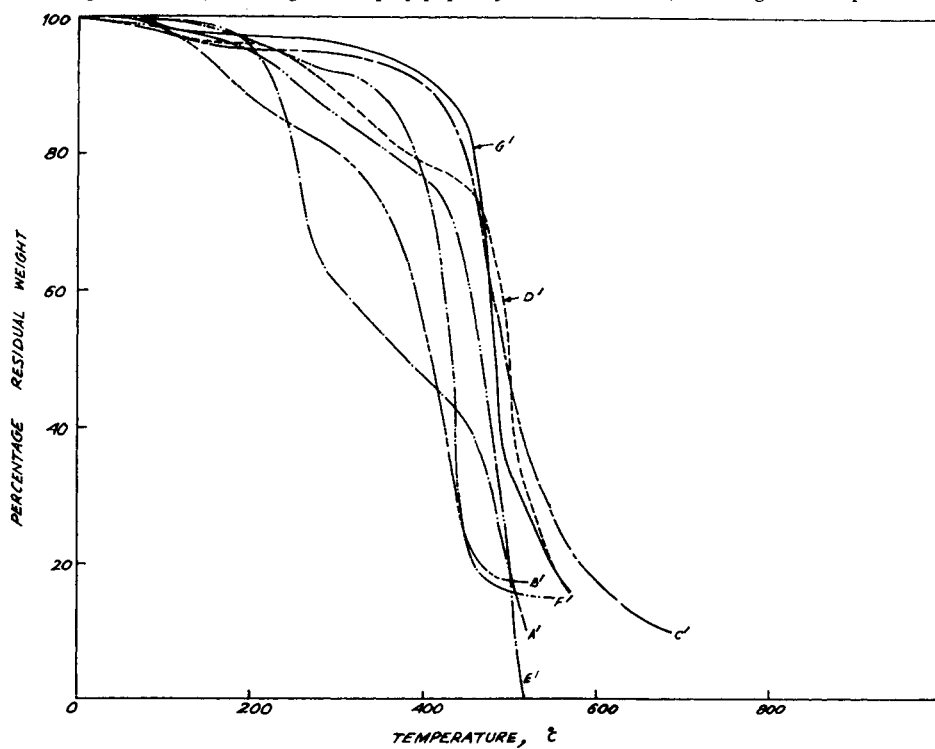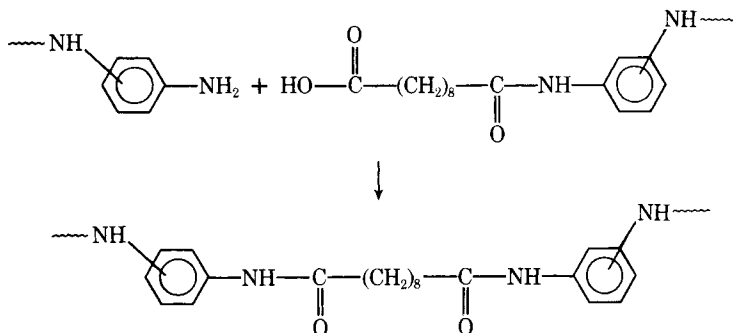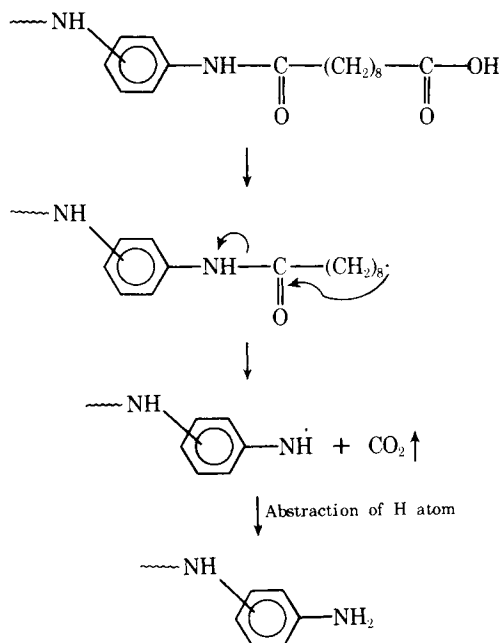Fig. 5. Primary thermograms of poly(p-phenylene sebacamides) in nitrogen atmosphere.

Fig. 6. Primary thermograms of poly(m-phenylene sebacamides) in nitrogen atmosphere.

degradation of the back bone

~~~NH—⬡—NH$_2$ + HO—C(=O)—(CH$_2$)$_8$—C(=O)—NH—⬡—NH~~~

↓

~~~NH—⬡—NH—C(=O)—(CH$_2$)$_8$—C(=O)—NH—⬡—NH~~~

(b) the decarboxylation of carboxyl end groups followed by cyclization may be another way of end group participation

~~~NH—⬡—NH—C(=O)—(CH$_2$)$_8$—C(=O)—OH

↓

~~~NH—⬡—NH—C(=O)—(CH$_2$)$_8$·

↓

~~~NH—⬡—NH· + CO$_2$↑

↓ Abstraction of H atom

~~~NH—⬡—NH$_2$

Similar mechanism for fully aromatic polyamides have been proposed.[15]

In poly(p-phenylene sebacamides) where no such end group participation is obvious even at low molecular weight one may propose a random scission of C—C, C—N, C—H bonds leading to low molecular weight volatile products. The C—N bond fission may be favoured in this case because the resulting NH—⬡—NH· radical can be stabilized by delocalization over the ring and p-NH group which may not be possible in poly(m-phenylene sebacamides).

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