polymer review

Some aspects of the thermal stability action of the structure in aliphatic polyamides and polyacrylamides

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A survey of the influence of the polymer structure on the melting/softening point and degradation temperature has been presented. Almost all aliphatic polyamides and polyacrylamides undergo degradation at lower temperatures. Introduction of cycloaliphatic rings and carbon-carbon unsaturated bonds raises the melting point as well as the degradation temperature of the polymers. Substitution of the hydrogen atom on the nitrogen with alkyl groups lowers the melting point as well as the decomposition temperature.

(Keywords: thermal stability; aliphatic polyamides; poly acrylamides; melting/softening point; degradation temperature)

I. INTRODUCTION

For useful high-temperature applications a polyamide must be thermally stable as well as processable. According to Sandler and Karo[1], a polyamide capable of resisting degradation should have the following properties: (a) high melting/softening point, (b) low weight loss as determined by thermogravimetric analysis, and (c) structures that are not susceptible to degradative chain scission or intra- or intermolecular bond formation.

It is evident that it is the melting/softening and decomposition temperatures which are of special concern in relation to the need for high temperature resistant polyamides/polyacrylamides. In this review paper, a survey on the relationship of structure with such properties as melting/softening point and degradation temperature of a polyamide/polyacrylamide has been presented. The discussion includes: (a) polyamides from amino acids and lactams, (b) polyamides from diacids and diamines, (c) polyamides containing cycloaliphatic rings, (d) polyoxiamides, (e) unsaturated polyamides, and (f) polyacrylamides.

II. POLYAMIDES FROM AMINO ACIDS AND LACTAMS

These polyamides are usually prepared by self-condensation of amino acids or by polymerization of lactams. A list of such polyamides and their melting temperatures is given in *Table 1*. The data in *Table 1* refer to nylon-n types: nylon-1 is obtained from isocyanates by homopolymerization; nylon-2 by the base-catalysed reaction of amino acid anhydrides; nylon-3 by the anionic polymerization of either acrylamide or propiolactam; nylon-4,5,6,8,12 by the ring-opening polymerization of lactams; and nylon-7,9,11 by the polycondensation of amino acids. The Table shows that the melting point of the polymer decreases as the chain length increases. This is attributed to the polar amide groups separated by increasingly large number of nonpolar methylene groups, thus decreasing the strength of intermolecular hydrogen bonding.

In spite of considerable attention focussed on the production and utilization of nylons-1, 2, 3, 4, 5, 7, 8, 9, 10, 12 and 13, none of them has yet reached commercial status. This may be due to the fact that some of them, such as nylons-1, 2, 3, 4, 5, etc., depolymerize and re-form monomers in the melt or in solution, while the commercial production of the others has not yet been found to be economically feasible, probably due to high cost of starting materials and intermediates. Besides, most of the β-lactam polymers are soluble in solvents which are unsuitable for solution fabrication.

Softening and decomposition temperatures of some nylons-1, which are prepared from *N*-substituted isocyanates[2], are given in *Table 2*.

The softening or decomposition temperature decreases regularly with the increase in the size of the aliphatic chain

Table 1

Number of carbon atoms in the monomer	Approx. m.p.*, °C.
1	–
2	–
3	320–330
4	265
5	260
6	215–220
7	225–230
8	195
9	197–200
10	173
11	185–187
12	180
13	173

*From various sources

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Table 2

Isocyanate	Polymer temperature (°C)	
	Softening	Decomposition
Ethyl	–	250
n-propyl	180	250
n-butyl	180	209
Isobutyl	173	210–220
n-amyl	145	209
n-hexyl	120	195
n-heptyl	100	180
n-undecyl	45	155
n-octadecyl	40	94
Allyl	180	260–290
9-n-decenyl	75	180–240

Table 3

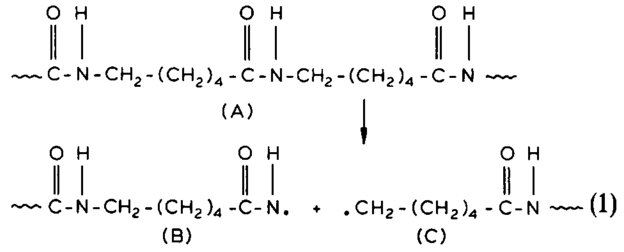
Polymer	m.p. (°C)
4-methyl-	328 (decomp)
4-isopropyl-	330 (decomp)
3,3-dimethyl-	250
4,4-dimethyl-	296 (decomp)
3,3-dimethyl-4-methyl-	360 (decomp)
4,4-dimethyl and 4-methyl-4-propyl-	130–160

attached to the amide nitrogen and then increases with the introduction of π-system. Obviously, the increase in the softening and decomposition temperatures is due to more compact crystal packing and greater delocalization of electrons in the allylic system.

All β-propiolactam polymers decompose into monomers. Melting temperatures of some β-propiolactam polymers[3] are given in *Table 3*.

Nylon-4 has shown <5% weight loss on heating at a rate of 4° min^{-1} from 20° to the decomposition temperature[4]. The degradation of nylon-4 has also been studied systematically under nitrogen[5]. At 240°C, the degradation is first-order with respect to the weight of extractable monomer. The inherent viscosity of the extracted polymer remains unchanged even after the polymer has lost about 25% of its weight in 2 h, indicating preferential decomposition and unzipping of the lower molecular weight chains. However, the thermal stability of nylon-4 seems to be influenced by the nature of the catalyst used in its preparation. Poly-2-pyrrolidinone prepared with pyrrolidone alkali metal or ammonium carbonate activators had thermal stability (time to plastometer viscosity 500p) 545 s, while the one prepared with acetylpyrrolidone catalyst did not have sufficient thermal stability to reach viscosity 500p[6]. Also, nylon-4, prepared by polymerizing 2-pyrrolidone with *N*-acetyl-2-pyrrolidone catalyst, has been found to be laundering resistant and heat resistant[7].

It seems that nylon-6 has been more extensively studied than any of the other members of its class, probably due to its most important commercial status. Galatov *et al.*[8] studied the effect of ageing, during storage, of nylon-6 and concluded that the degradation increases with increasing storage time at 298–303 K/150 kPa in nitrogen atmosphere containing 0.0003% oxygen. Kamerbeck and coworkers[9] have separated the degradation of nylon-6 at processing temperatures into primary and secondary processes. The primary processes are said to consist of homolytic cleavage at nitrogen-carbon bond as follows:



$$\sim\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-CH_2-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-CH_2-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}\sim \quad (A)$$
$$\downarrow$$
$$\underset{(B)}{\sim\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-CH_2-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}\cdot} + \underset{(C)}{\cdot CH_2-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}\sim} \qquad (1)$$

$$(B) \xrightarrow{H} \underset{(D)}{\sim CONH-(CH_2)_5-CONH_2} \qquad (2)$$

$$(C) \longrightarrow CH_2=CH-(CH_2)_3-CONH\sim + H \qquad (3)$$

$$(D) \longrightarrow \sim CONH(CH_2)_5CN + H_2O \qquad (4)$$

$$(B) + (C) \longrightarrow \sim CONH(CH_2)_5-N=C=O + CH_3-(CH_2)_4-CONH\sim \qquad (5)$$

The secondary processes consist of hydrolysis of the amide by the water formed to yield ultimately a ketone, carbon dioxide, ammonia and more water.

$$(A) \xrightarrow{H_2O} \sim COOH + H_2NCO \qquad (6)$$

$$2(\sim COOH) \longrightarrow \sim CO\sim + CO_2 + H_2O \qquad (7)$$

$$2(\sim NH_2) \longrightarrow \sim NH\sim + NH_3 \qquad (8)$$

The above mechanism indicates that steric hindrance or absence of hydrogen atoms at the β-position in the amine should result in more thermally stable polyamides. This is supported by the literature information[10] that α,α-dimethyl nylon-3 (II) is more thermally stable than β,β-dimethyl nylon-3 (III).

$$\underset{(II)}{\sim NH-CH_2-C(CH_3)_2-CO\sim} \qquad \underset{(III)}{\sim NH-C(CH_3)_2CH-CO\sim}$$

At 305°C, caprolactam is eliminated; decrease in molecular weight is proportional to the caprolactam evolved, provided it is removed continuously.

A number of investigators has studied thermal degradation of dyed and undyed nylon-6 fibres[11–16]. Thermal degradation at 260°–265°C for 872 days in the absence of oxygen gives 17.4% weight gases containing CO_2, NH_3, H_2O, CO and H_2, and a highly crosslinked solid which is only partially soluble or hydrolysable in formic acid[11]. Strauss and Wall[12] have investigated the thermal stability of nylon-6 of molecular weight 3×10^4, 6×10^4, and 6×10^4 (dried sample) in vacuum. At 350°C, the rates of weight loss (% min^{-1}) are 0.39, 0.63 and 0.33, respectively and the temperatures for 1% weight loss min^{-1} are 378°, 370° and 370°C, respectively, for these polyamides.

The overall activation energies are 27, 34 and 43 kcals, respectively. The increase in the activation energies may be due to the increase in the extent of crosslinking[13]. The very low values of the overall activation energy indicate that a hydrolytic mechanism of breakdown is also operative. This is supported by the increase in the activation energy and the decrease in the rate of weight loss at 370°C for the thoroughly dried sample[12]. The equilibrium monomer concentration for thermal degradation of nylon-6 at 190°C has been found[14] to be 1.5% and that at 220°C lies between 4 and 6%. The polymer rapidly unzips for establishing this polymer–

Table 4

Substituents	Polymer T_m, (°C)
None	220
α-methyl	190
β-methyl	145
γ-methyl	164
δ-methyl	134
ε-methyl	185

monomer equilibrium only if ionic chain cleavage occurs in this temperature region or above.

Niyazi *et al.*[15] observe that polycaprolactam fibres dyed with dichlorotriazine dyes are more stable to thermal degradation than the undyed fibres. This is attributed to the conjugated systems present in the dye and to the substitution of mobile hydrogen atoms of the amino group in the fibre. The weight losses of the undyed and dyed fibres at 400°C in air are 60 and 18%, respectively, compared to 52 and 27%, respectively, on heating in argon. Nagase *et al.*[16] have found CO_2 and ε-caprolactam as the main degradation products of nylon-6 at 320°–350°.

Thermal stability of nylon-6 appears to depend upon the type of method used in its preparation[17]. The polyamide prepared on H_3PO_4 has the same thermal stability as the polyamide obtained on water, but the anionic polyamide decomposes in whole at 350° to ε-caprolactam.

The effects of substituents in the main chain of nylon-6 on the melting temperatures have also been studied[18]. It has been observed that substitution by methyl groups lowers the melting temperature. But the lowering effects of methyl group situated at the α-position are actually less than those of β- or δ-methyl groups (see *Table 4*).

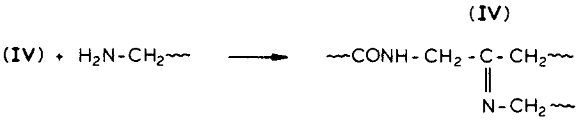
The polycaprolactams obtained by base-catalysed polymerization of caprolactams decompose into polymers of lower molecular weight when heated for prolonged periods at 285°C[19,20].

Several authors[9,17,21–29] have studied oxidative thermal degradation of nylon-6. The depth of oxidation is measured[17] at 200°C by oxygen pressure decrease in the system and the loss in weight by heating in air up to 570°C. It is observed that the polymers obtained on H_3PO_4 in amounts up to 0.01% have better thermo-oxidative stability than on the other acids. The sharp decrease of specific viscosity during the thermooxidative degradation is reduced considerably by adding to H_3PO_4 the α-naphthyl ester of pyrocatecholphosphorous acid. Mukhin and coworkers[21] have shown that the degradation rate of regular polycaprolactam fibre at 350°–500°C in argon and in air is 2–4 fold higher than that of such fibre modified with a phosphorous containing agent. The modified fibre retains almost 50% of its original weight at 500°–550°C, whereas the original polycaprolactam fibres are totally decomposed.

Polycaprolactam fibres, spun from polycaprolactam prepared by continuous polymerization in one particular reactor, exceeds other polycaprolactam fibres in oxidative thermal degradation resistance, probably due to improved supramolecular structure[22]. According to Chaigneau and Le Moan[23], the pyrolysis of nylon-6 in an oxygen-containing atmosphere at 500°C yields gaseous products containing CO_2, CO, H_2, HCN, NH_3, saturated and unsaturated aliphatic hydrocarbons, and aromatic hydrocarbons and condensates (containing nitrogen heterocyclic compounds and polycyclic hydrocarbons). The brown compound formed during thermooxidative degradation of nylon-6 is presumed to be polymers of variable molecular weight[24].

Allen *et al.*[25] have observed rapid oxidation of nylon-6.11,12 over the temperature range 100°–200°C. The following mechanism of formation of ketonic carbonyl groups and their subsequent inter or intra chain condensation reaction has been suggested.

$$\sim\mathrm{CONH{-}(CH_2)_2{-}CH_2}\sim \xrightarrow{O_2} \underset{\text{(IV)}}{\sim\mathrm{CONH{-}CH_2{-}CO{-}CH_2}\sim} \tag{9}$$

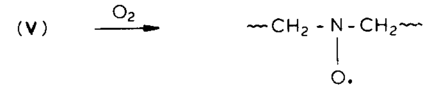


$$\text{(IV)} + \mathrm{H_2N{-}CH_2}\sim \longrightarrow \sim\mathrm{CONH{-}CH_2{-}}\underset{\underset{\mathrm{N{-}CH_2}\sim}{\|}}{\mathrm{C}}\mathrm{{-}CH_2}\sim \tag{10}$$

Several possible explanations have been put forward for the formation of a nitroxide radical from non-terminated and amine-terminated nylon-6. The most plausible explanation is desamination[9], i.e. two amine ends react to form a secondary amine.

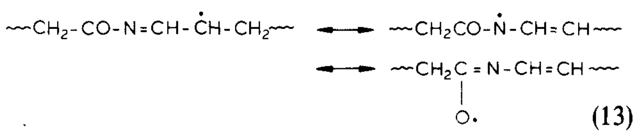
$$\begin{array}{c} \sim\mathrm{NHCO{-}(CH_2){-}NH_2} + \mathrm{H_2N{-}(CH_2)_5{-}CONH}\sim \\ \downarrow \\ \underset{\text{(V)}}{\sim\mathrm{NHCO{-}(CH_2)_5{-}NH{-}(CH_2)_5{-}CONH}\sim} + \mathrm{NH_3} \end{array} \tag{11}$$

The secondary amine is then oxidized to form nitroxide at 260°–290°C[26].



$$\text{(V)} \xrightarrow{O_2} \sim\mathrm{CH_2{-}}\underset{\underset{\mathrm{O\cdot}}{|}}{\mathrm{N}}\mathrm{{-}CH_2}\sim \tag{12}$$

A conjugated system with an unpaired electron is also believed to be formed.



$$\begin{array}{l} \sim\mathrm{CH_2{-}CO{-}N{=}CH{-}\dot{C}H{-}CH_2}\sim \longleftrightarrow \sim\mathrm{CH_2CO{-}\dot{N}{-}CH{=}CH}\sim \\ \qquad \longleftrightarrow \sim\mathrm{CH_2}\underset{\underset{\mathrm{O\cdot}}{|}}{\mathrm{C}}\mathrm{{=}N{-}CH{=}CH}\sim \end{array} \tag{13}$$

Therefore, a mechanism which proposes initial attack of oxygen on the nylon with resultant decomposition of hydroperoxides to conjugated double bond systems is consistent with the observations[28,29].

The melting point of a polymer seems to be dependent on its morphology. Thus, the melting point of α-nylon-12 is ≈173°C, which is lower by 6°–7°C than that of the γ-form[30]. Also, the melting point of α-nylon-6 is ≈220°C, which is higher by 7°C than that of the γ-form[31,32]. Chiang and Sibilia[33] have measured the peroxide radical concentrations from nylon-6 fibres mechanically stretched in air at room temperature. It has been observed that: (a) for fibres with the same initial draw temperature, the total number of chain scissions at the breaking point increases with the initial draw ratio, and (b) for fibres with the same initial draw ratio, the total number of chain scissions at the breaking point increases with the initial draw temperature. The chain scissions occur primarily at the carbon–carbon bonds adjacent to the amide group[34].

Lloyd *et al.*[35] have studied the fracture behaviour in nylon-6 fibres. Bond rupture is governed by the theory of absolute reaction rate with a stress-aided activation energy. The tauter chains rupture first. Temperature has two effects on macroscopic strength: (a) temperature assists the atomic stress in breaking the bonds by decreasing their 'strength', which in turn results in increasing the rate of bond scission and (b) temperature also loosens the molecular structure and in this way modifies the distribution of stress in the tie chains.

Nylon-7, which is prepared by heating methyl 7-aminoheptanoate at 270°C for 5 h, is stable in the molten state at 250°C for over 24 h[36]. Products of molecular weight 15 200–30 000 give useful fibre, and moulding resins of properties similar to nylon-6,6. Nylon-8 is fairly thermally stable. The melt contains small amounts of monomer and oligomer even at long standing times. The usefulness of this polymer is limited by low melt temperature and high costs of the intermediate compared to nylon-6. The low water vapour transmission rate has given nylon-11 the big advantage over other polymers, but its high cost has limited its applications. The pyrolysis of nylon-11 in an oxygen-containing atmosphere at 500°C gives products similar to those obtained in the pyrolysis of nylon-6 under similar conditions[23]. Thermal stability time of nylon-12 at a moisture content of 0.01% is >1 h and at 0.22–0.27% is 0 min under similar conditions of temperature[37].

III. POLYAMIDES FROM DIACIDS AND DIAMINES

Melting points of some nylons prepared from diacids and diamines are given in *Table 5*. Within the series there is an odd–even relationship in which linear polyamides with an even number of carbon atoms between amide groups possess higher melting temperatures than those of comparable molecular weight having an odd number of carbon atoms. This reflects the greater packing ability of the polyamides having even number of carbon atoms in the polymer chain backbone. The production of low molecular weight intractable cyclic amides from dibasic acids and diamines has been reported in the literature[38–44]. But the formation of high molecular weight polymeric products by the reaction of diacids with diamines was first recognized by Carothers[45–50]. Many of these polyamides have been spun into fibres which are named 'nylon' by the Du Pont Company.

Table 5

Nylon type	m.p.*, °C
Nylon–2,10	254
Nylon–4,6	278
Nylon–4,7	233
Nylon–4,8	250
Nylon–4,9	223
Nylon–4,10	239
Nylon–5,5	198
Nylon–5,6	223
Nylon–5,7	183
Nylon–5,8	202
Nylon–5,9	178
Nylon–5,10	195
Nylon–6,6	265
Nylon–6,10	209
Nylon–8,6	235
Nylon–8,10	197
Nylon–9,6	204–205
Nylon–9,10	174–176
Nylon–10,1	200
Nylon–10,2	229
Nylon–10,6	230
Nylon–10,10	194
Nylon–11,10	168–169
Nylon–12,6	208–210
Nylon–12,10	171–173

* From various sources

There are conflicting reports on the melting point of nylon-4,6. Gaymans *et al.*[51] prepared high molecular weight nylon-4,6 from the salt of 1,4-diaminobutane and adipic acid. The resulting polymer has varying melting temperatures 283°–319°C, depending on the thermal history of the sample. The melting point of 278°C reported for nylon-4,6 by Carothers[48] has been confirmed by Coffman *et al.*[52]. However, Beaman and Cramer[53] have found a melting point of 308°C for the bulk polymer and 283°C for a melt-spun fibre, while Ke and Sisko[54] have quoted a value of 293°C for the same polymer.

While nylon-2,4, prepared from ethylenediamine and *N,N'*-ethylenedisuccinimide, decomposes under nitrogen at >305°C without melting[55], the polysuccinimide, made by reacting *N,N'*-hexamethylenedisuccinimide with hexamethylenediamine, undergoes the following changes at 200°–400°C in air and *in vacuo*[56]:

(a) an increase in molecular weight due to interaction of the end groups;

(b) decomposition to form low-molecular-weight polyamides and monomers;

(c) crosslinking due to internal interactions; and

(d) rupture of the amide rings with evolution of gases, e.g. NH_3, H_2O, CO, CO_2, C_2H_6, C_3H_6, C_4H_{10} and $EtNH_2$.

Nylon-6,6 yields[9] similar products of degradation as nylon-6 at the processing temperature and at 305°C. Besides, nylon-6,6 is much less thermally stable than nylon-6,10 or nylon-6 and starts to gel, i.e. crosslink, after being heated for about 14 h under steam at 300°C. As the polyamides from higher acids, such as nylon-6,10 and nylon-6,12, do not crosslink on heating for prolonged periods, the crosslinking of nylon-6,6 has been related to the adipic acid moiety[57,58]. Nylon-6,6 is also rendered brittle by heating at 250°C for 2 h or at 70°C for 2 years[9]. The degradation is suspected to be initiated, by a free-radical chain reaction, at the carbon atom alpha to the nitrogen[59]. However, H_2O, H_2, CO_2, CO, NH_3 and hydrocarbons are the main products of degradation of nylon-6,6 in absence of oxygen[16,60–62]. The activation energy of thermal degradation is reported to be 43 ± 3 kcal[16].

The most labile bond in this polymer for homolytic cleavage at elevated temperature is believed to be the amine carbon–nitrogen bond. Scission of this bond may result in the formation of a primary amide group and an olefin. Water may be produced by dehydration of the primary amide and the excess water may hydrolyse the amide groups in the polymer chain forming carboxylic acids which, in turn, may decarboxylate at 300°–500°C to yield carbon dioxide[63]. Thermal degradation of aliphatic polyamides from 1,6-hexamethylenediamine and various aliphatic dicarboxylic acids at 340°–380°C/(10^{-2}–10^{-3} Torr) has been studied by Fedotova *et al.*[64]. According to them, thermal stability of nylon-6,8 (I), nylon-6,10 (II), and nylon-6,6 (III) increases in the order: III, II, I. The temperature (T_d) at which the degradation starts, the relative weight losses (W_r) at 340°C, and the weight loss activation energies (E_a) are given in *Table 6*.

Thermo-oxidative degradation of the same polymers has been studied by the same authors in oxygen at 360°–380°C (200 Torr). Polymer (III) is the polymer which is most

Table 6

Polymer	T_d (°C)	W_r (%)	E_a(kcal mole^{-1})
I	340	1	53.0
II	300	2.3	57.5
III	280	7.8	35.2

susceptible to thermal oxidative degradation, while the stability of (II) is about the same as that of (I). The temperature at which the oxidative degradation starts and the weight loss activation energies of I, II and III are: >350°, >320° and 280°C; and 47.2, 41.6 and 40.0 kcal, respectively. The stability of the polymers is attributed to the formation of facile hydrogen bonds, leading via intermolecular reaction to more stable crosslinked structures, and to the accessibility to the attack of oxygen.

Several authors have studied thermo-oxidative degradation of nylon-6,6 and nylon-6,10 under various conditions[23,65–71]. The products of thermo-oxidative degradation of nylon-6,6 and nylon-6,10 at 500°C have been found[23] to be similar to those obtained by the pyrolysis of nylon-6 under similar conditions, although East *et al.*[65] observed carboxylic acids, amines, diamines and amino acids as additional products. Thermal oxidation of fractionated poly(hexamethyleneadipamide) and poly(hexamethylenecaproamide) has also been investigated[66]. It has been observed that lower molecular fractions are more susceptible to thermal oxidation than the higher ones. There is a change in the molecular weight of the fractionated polyamides before and after the thermo-oxidative treatment, indicating that the degradation occurs in the middle and at the ends of the polymer chain. A polyamide containing >2–4 weight% low molecular weight fractions is more susceptible to thermal oxidation.

The oxidative degradation of nylon-6,6 has been investigated also in aqueous solutions at elevated temperature[67]. The degradation products identified are carboxylic acids and amines. Formation of hydroperoxide has also been detected. There is a significant effect of pH on the rate and extent of degradation. The rate of degradation increases with pH until a maximum is reached at pH 8.3, after which the rate again decreases. At any given pH, the intrinsic viscosity decreases with the increase in the concentration of the carboxylic acid. The concentration of amine decreases with the extent of oxidation in unbuffered solutions and in solutions buffered at pH 5.3 and 6.2 for the undrawn, and at pH 7.2 for the drawn, polymer.

Jellinek and Dunkle[68] observed the evolution of HCN from nylon-6,6 during thermo-oxidative degradation at temperatures from ≈300–695°C. Below ≈300°C the evolution of HCN is controlled by chemical decomposition and above 300°C the evolution is controlled by diffusion. Oxidation of HCN becomes noticeable above 530°C and ignition occurs at 590°C. The activation energy for the oxidation of HCN before ignition (590°C) is reached is 47 kcal. It has been observed that only a small fraction of the nitrogen in the polymer is transformed to HCN by oxidation, while the majority of nitrogen groups forms other nitrogeneous products[69–71].

Degradation of nylon-6,6 and nylon-6 in the presence of chemicals has been investigated under different conditions[72–75]. Jellinek and Chaudhuri have studied the degradation of nylon-6,6 in the presence of nitrogen dioxide, ozone, oxygen and near-u.v. radiation. The degradation kinetics can be expressed by 'weak'-link random degradation. The function relationship between nitrogen dioxide pressure and chain scission rate constants has been found to be linear. Degradation of nylon-6 and nylon-6,6 has been studied in presence of chemicals in aqueous medium also[73–75]. Number-average molecular weights of 2100 and 2500 have been observed in 5% aqueous hydrochloric acid at 72°C[73], while in 0.2% aqueous sodium hydroxide at 98°C the lamellar folds of nylon-6,6 are effectively removed during degradation[74]. Hughes and Bell[75] have reported selective degradation of amorphous regions in nylon-6,6 refluxing in 95% hydrazine. Unannealed samples lose about 40% weight in about 100 h, while the annealed samples lose about 30% weight during this period.

Table 7

Code	Substituent	T_m (°C)
6,6	–	265
6, α Me6	methyl	166
6, α Et6	ethyl	95
6, α Bu6	n-butyl	105
6, α , α' DMe6	dimethyl	115
6, α , α , α ', α' TeMe6	tetramethyl	115

Table 8

Code	Substituent	T_m (°C)
6, β Me6	methyl	200
6, β Et6	ethyl	152
6, β Bu6	t-butyl	110
2,5 DMe6,6	dimethyl	175

Table 9

Acid	Diamine	Softening point (°C)
6	6	265
6	N-methyl 6	145
6	*N, N'*-dimethyl 6	–75

Lateral substituents on the α-carbon atom of the dibasic acid moiety of nylon-6,6 decrease the melting temperature with the increase in the size of the hydrocarbon group[76,77]. This is shown in *Table 7*.

Also substituting[77] about 50% of the hydrogens attached to nitrogen with isobutyl groups reduces the melting temperature of nylon-6,10 from about 228°C to 155°C. The effects of beta substituents on melting temperatures of nylon-6,6 are given in *Table 8*.

It is evident from the Tables that methyl and ethyl groups lower the melting temperatures less when the substituent is on the β-carbon atom. This indicates that the further removed the substituent is from the amide group the less is its effect on the melting temperature. The more pronounced effect of an α-methyl group in lowering the melting temperature in nylon-6,6 more than in nylon-6 is attributed to the structural difference between the repeated units of these two polymers[18]. The effects of substituents on the nitrogen atom of the amide group upon the softening points of nylon-6,6 and nylon-6,10 are given in *Table 9* and *Table 10*, respectively[77–80]. Replacing about 36% of the hydrogens attached to nitrogen of the

Table 10 Nylon-6, 10

N-isobutyl substitution, (%)	Softening point (°C)
0	225
25	180
40	170
50	155
60	145
75	105

Table 11

X	R	*n*	m.p. (°C)
$-(CH_2)_6-$	Me	16	52
$-(CH_2)_8-$	Et	16	55

amide group by methoxy methylation of nylon-6,6 results in a decrease of about 115°C in melting point[81,82]. However, polyamides, prepared by reacting *N*,*N'*-dialkyldiamines, (RNHXNHR), with dibasic acids, $HO_2C(CH_2)_nCO_2H$, possess very low melting points[83]. This is shown in *Table 11*.

Insertion of hetero atoms, such as oxygen or sulphur, in place of one of the carbon atoms in the main chain of either the dibasic acid or the diamine results in lowering the melting point of the polyamide. This is attributed to irregularity in packing and greater freedom of movement about the oxygen or sulphur atom. Ogata *et al.*[84] have studied the effects of cyano and thiocyano substituents in the acid moiety upon melting temperatures. Thus, the polyamide obtained by condensing hexamethylenediamine with diethyl α,α'-dicyano adipate melts at 60°–67°C, while the one obtained by condensing hexamethylenediamine with diethyl α,α'-dithiocyano adipate decomposes at 150°–160°C.

IV. POLYAMIDES CONTAINING CYCLOALIPHATIC RINGS

When a segment of the aliphatic polyamide main chain is replaced by a ring segment, the melting temperature and hence, the thermal stability increases due to the decrease in the flexibility of the polymer chain. Such improvements in thermal stability have been observed[85–100] with the introduction of cycloaliphatic rings in the polymer main chain. Speck[85] obtained fibre-forming polyamides having high degree of thermal stability by reacting dodecanedioic acid with bis(*p*-aminocyclohexyl)methane, 2,2-bix(*p*-aminocyclohexyl)propane, bis(4-amino-3-methylcyclohexyl)methane, and bis(4-amino-2-methylcyclohexyl)methane, respectively. While increased content of 4-aminocyclohexanecarboxylic acid in 4-aminocyclohexanelactam-ε-caprolactam copolymer has been found[86] to cause an increase in the thermal and thermo-oxidative stabilities, the study on depolymerization of polyamides on the basis of the lactam of 4-aminocyclohexanecarboxylic acid has revealed[87] that the rate of depolymerization decreases through the series: polycaprolactam, 4-aminocyclohexanecarboxylic acid lactam-caprolactam polymer, and 4-aminocyclohexanecarboxylic acid lactam polymer (**I**). The low depolymerization of (**I**) is attributed to a low mobility of molecular chains of the polymer.

The depolymerization rate also decreases significantly with increasing molecular weight. The effect of isomorphous replacement of ε-aminocaproic acid in nylon-6 by 4-aminomethylcyclohexanecarboxylic acid has been studied[88]. The d.t.a. and t.g.a. data of the 4-aminomethylcyclohexanecarboxylic acid (**II**)-caprolactam copolyamide show that incorporation of (**II**) raises the melting point, T_g, T_c, and stability of nylon-6. However, the polyamide containing the cyclohexyl ring only in the diacid unit seems to possess very low T_g[89]. Thus, the polyamide from 3-cyclohexyladipic acid and $H_2N(CH_2)_6NH_2$ has $T_g = 82°C$ and a softening point of 121°C. Polyamides, such as those prepared by reacting 1,4-cyclohexanediacetic acid with 1,4-cyclohexanebis(β-ethylamine) and containing cyclohexyl rings in both the diacid and diamine units, possess melting points (210°–200°C) similar to those of nylon-6 and nylon-6,6, but with higher moduli and greater tensile strengths[90]. However, the polyamide containing two cyclohexyl rings fused together and prepared from 3,3'-diaminodicyclohexane and adipic acid, possesses a very high T_g (155°C)[90].

According to Ridgway[94a], the T_g of polyamides containing a 1,4-cyclohexane ring does not differ much from that of the corresponding polymers containing the *p*-benzene ring. The same author[94b] has prepared polyamides by reacting linear, aliphatic dicarboxylic acids of six to twelve carbon atoms with 1,4-cyclohexanebis(methylamine) (CBMA) and 1,4-cyclohexanebis(ethylamine) (CBEA), respectively. The melting temperatures of the *trans* cyclohexylene polyamides and those of phenylene(*p*-xylylenediamine) analogues are given in *Table 12*. The higher melting temperatures of the *trans*-cyclohexylene polyamides over those of the phenylene analogues has been attributed to the increased rigidity and greater symmetry in the *t*-CBMA polymers.

The melting temperatures of the *trans*-CBMA polyamides are compared with those of *trans*-CBEA polyamides in *Table 13*. The melting temperatures of *t*-CBEA polyamides average 16°C higher than those of the corresponding *t*-CBMA polymers, indicating an odd–even effect. With shorter chain diacids, this difference between *t*-CBEA and *t*-CBMA is more pronounced.

The melting points of the *cis*-CBMA polyamides and those of *cis*-CBEA polyamides are given in *Table 14*. The

Table 12

Polymer	T_m (°C)	Polymer	T_m (°C)
t-CBMA-6	345	PXD-6	333
t-CBMA-7	293	PXD-7	284
t-CBMA-8	311	PXD-8	305
t-CBMA-9	275	PXD-9	263
t-CBMA-10	300	PXD-10	281
t-CBMA-12	278	PXD-12	272

Table 13

Polymer	T_m (°C)	Polymer	T_m (°C)
t-CBMA-6	345	*t*-CBEA-6	348
t-CBMA-7	288	*t*-CBEA-7	291
t-CBMA-8	308	*t*-CBEA-8	300
t-CBMA-9	268	*t*-CBEA-9	259
t-CBMA-10	293	*t*-CBEA-10	273
t-CBMA-12	280	*t*-CBEA-12	255

Table 14

Polymer	T_m (°C)	Polymer	T_m (°C)
c-CBMA-6	248	*c*-CBEA-6	172
c-CBMA-7	182	*c*-CBEA-7	110
c-CBMA-8	220	*c*-CBEA-8	158
c-CBMA-9	195	*c*-CBEA-9	96
c-CBMA-10	208	*c*-CBEA-10	132
c-CBMA-12	199	*c*-CBEA-12	110

Table 15

Dibasic acid	Diamine	T_m (°C)
Glutaric	III	280–290
Adipic	III	345
Pimelic	III	290–293
Suberic	III	308–311
Azelaic	III	270–275
Sebacic	III	295–300
Dodecanedioic	III	275–278

c-CBEA polyamides unexpectedly melt considerably lower than the *c*-CBMA polymers. This is attributed to the low crystallinity of the *c*-CBEA polyamides, which reflects the poorer ability of the *c*-CBEA system to accommodate itself in polymer chains. In contrast, the *c*-CBMA polyamides are reported to be crystalline.

The effects of *cis*/*trans* structures in the cyclohexane moiety of the polyamide have also been investigated[92,93,95,101–114]. Bell *et al.*[93] have observed that *trans*-1,4-cyclohexane rings are as effective as aromatic rings in raising the melting points of the polyamides. *Table 15* shows the variation in the melting temperatures of the polyamides prepared from *trans*-1,4-cyclohexanebis(methylamine) (III) and various dibasic aliphatic acids.

According to Prince *et al.*[95], the melting points of the 1,4-bisaminomethylcyclohexane *cis*/*trans*-copolyamides decrease with increasing *cis*-diamine content and increasing diacid chain length, but the T_g and thermal stability have been found to be independent of diamine isomer content. Zhubanov and coworkers[101] also have observed that the polyamides from the *trans*-diamine have higher melting points than those from the *cis*-diamine. But a copolyamide[102] from bis(*p*-aminocyclohexyl)methane of 54% *trans*–*trans* configuration, $H_2N(CH_2)_9NH_2$, and $HO_2C(CH_2)_8CO_2H$ possesses $T_g = 104$°C. The polyamide prepared[103] from 1,10-dodecanedicarboxylic acid and 1,2-bis(*p*-aminocyclohexyl)ethane containing >75% *trans*–*trans* stereoisomer has a high softening point (270°C).

The increase in the length of the side-chain hydrocarbon attached to the cyclohexane ring decreases the melting temperature of the polymer. For example, polyamides from *trans*-1,4-cyclohexanebis(ethylamine) and dicarboxylic acids have good dimensional stability and lower melting point than the corresponding polyamides derived from cyclohexanebis(methylamine)[104]. Muromova *et al.*[105] have reported polyamides and fibres based on ω-amino acids containing cyclohexane rings in the main chain. Thus, polyamides from *trans*-4-aminocyclohexylacetic acid, *trans*-β-(4-aminocyclohexyl) propionic acid, and *trans*-4-(aminomethyl(cyclohexylacetic acid did not melt up to 416°, 490° and 425°C, respectively, and decomposed at higher temperatures.

Kalmykova and coworkers[106] have investigated the preparation and properties of polyamides based on diamines with cyclohexyl rings. The diamine used is *trans*-1,4-diaminocyclohexane (I) and the acids used are: adipic acid (II), azelaic acid (III), sebacic acid (IV), and dodecanedioic acid (V). The melting points of some of these polyamides and the 4,4′-diaminobicyclohexyl (VI)–(III) polyamide are given in *Table 16.*

Some typical polyamides in this *cis*/*trans* series and their melting points are given below: *Cis*- and *trans*-isomers of *N*-ethyl-1,4-cyclohexanediamine-adipic acid polymer[107], 276°C; 80–100 mole% *trans*-1,3-bis(aminomethyl)cyclohexane–adipic acid polymer[108], 250°C; bis(4-aminocyclohexyl)methane (70% *trans*–*trans* content)–1,14-tetradecanedicarboxylic acid polymer[109], 290°–300°C; *trans*-1,2-dicarboxycyclopropane (VII)–hexamethylenediamine[110] polymer, 299°C; (VII)–bis(*p*-aminocyclohexyl)methane[110] polymer, >360°C; *trans*-1,2-diaminocyclobutane-adipic acid polymer[111], ≈285°C; *trans*-γ-(4-aminocyclohexyl)butyric acid–caprolactam polymer[112], 254°–255°C; *trans*-2-(4-aminocyclohexy)1,1–dimethylethylamine (VIII)—the *cis*-isomer of (I)-adipic acid polymer[113], 200°C.

Inoue and Hoshino[92] have studied thermal properties of polyamides containing 72/28 *cis*/*trans* isomer ratio of 1,3-cyclohexanebis(methylamine) (1,3-CBMA). In this study, the glass-transition temperature of polyamides 1,3-CBMA-*n* ($n = 6, 8, 10, 12$) from 1,3-CBMA and *n*-carbon dicarboxylic acids have been examined. The polyamides and their T_g's are given in *Table 17.* The authors have pointed out that the T_g of a *cis*-isomer is greater than that of a *trans*-isomer. For example, the T_g of 97% *cis* and 93% *trans*-1,3-CBMA-6 polymers are 97° and 84°C, respectively. The higher T_g for the *cis*-isomers has been explained by the restricted chain mobility due to steric hindrance of the *cis*-1,3-cyclohexane ring. *Table 17* also shows that the T_g's of 1,3-CBMA-n polymers measured by d.s.c. decrease gradually as the monomer-unit length increases. This is attributed mostly to the reduction of the number of rings in the polymer main chain.

Tokareva *et al.*[114] have investigated the preparation and thermal properties of copolyamides of *cis*-γ-(3-amino-cyclohexyl)butyric acid (I) with ζ-aminoenanthic acid (II), and *trans*-β-(4-aminocyclohexyl)propionic acid (III). The copolyamides and their melting points are given in *Table 18.* It is evident from the Table that as the amount of (I) in a copolyamide increases, the melting point first

Table 16

Amine	Acid	m.p. (°C)
I	III	415–420
I	IV	420–430
I	V	390–400
VI	III	420–425

Table 17

Polymer	T_g (°C)
1,3-CBMA-6	98
1,3-CBMA-8	78
1,3-CBMA-10	64
1,3-CBMA-12	61

Table 18

Comonomer	Mole % (I)	m.p. (°C)
II	7.9	220
II	20.5	200
II	30.0	190
II	34.2	180
II	43.8	110
II	53.9	125
II	71.0	250
II	82.5	275
II	100.0	300
III	9.6	infusible
III	23.6	infusible
III	48.5	340
III	73.5	308
III	88.1	270
III	94.6	284
III	100.0	300

decreases, reaches a minimum, and then increases. This may be explained in terms of enthalpy and entropy changes at the melting temperature. The melting temperature, $T_m = \Delta H/\Delta S$, is directly proportional to enthalpy change and inversely proportional to entropy change. In the copolyamide, the regularity with which the monomer units are spaced along the chain backbone is gradually reduced as the amount of the monomer (I) increases. This results in reduction of the number of hydrogen bonds which, in turn, causes reduction in ΔH. Again, as the amount of the monomer (I) increases, a gradual reduction in the regularity in the arrangement of monomer units occurs until a threshold value of the amount of the monomer (I) is reached after which the regularity of the arrangement of the monomer units again increases. At the threshold value of the amount of the monomer (I), therefore, the value of ΔS is maximum and, as ΔH is low, the T_m is minimum. As the amount of (I) increases past the threshold value, ΔS gradually decreases and, as simultaneously ΔH increases gradually, T_m starts increasing.

V. POLYOXAMIDES

Polyoxamides usually possess higher melting points than the analogous polyamides from longer-chain aliphatic diacids. Also, incorporation of oxamide sequences in random or block structures with common polyamides has been found to improve their physical properties and mechanical performance[115-118]. Polyoxamides are reported to possess some interesting characteristics. These are: (a) unusually high modulus[118-124], (b) high melting temperature[118-125], and (c) high thermal and light stability[121]. The higher thermal stability of the polyoxamides may be attributed to the (a) existence of extended planar zigzag conformation with stronger hydrogen bonds than those of simple polyamides[126] and (b) stiffness of the oxamide part of the zigzag structure due to the quasiconjugated prototropic systems constituting the coplanar structure. Quantitative studies of thermal stability of polyoxamides are few. However, thermal stability of polyoxamides has been mentioned in different literature reports[121,126-131]. The only report which is pertaining to the thermal degradation of polyoxamides is that of Krasnov[132]. According to Krasnov, the polyoxamides, prepared by interfacial liquid-gas polycondensation, possess lower thermal stability than those prepared by melt polycondensation. The lower thermal stability of the former is attributed to the presence of acidic impurities which enhance the degradation reactions in addition to the usual homolytic scission of the C–N bond. The CO_2/CO ratio has been shown to decrease with the increase in temperature.

Shalaby *et al.*[131] have studied thermal degradation of aliphatic polyoxamides, nylon-12,2, -10,2, -8,2, and -6,2 at 100°–500°C in nitrogen. All the polymers lost from 97–99% weight at 500°C. The maximum degradation in the temperature range of 400°–500°C is attributed to the differences in their molecular structures. Catastropic decomposition occurs at 400°–475°C in all polyoxamides. Nylon-12,2, prepared in the presence of phenylphosphonic acid or *p*-toluenesulphonic acid, undergoes faster degradation than those prepared without any catalyst. This is consistent with the findings of Krasnov[132]. This may also explain the difficulties encountered in early attempts[118-124] to obtain high molecular weight polyoxamides via catalysed bulk polycondensation. Shalaby *et al.*[131] have suggested that CO is a major degradation product in aliphatic polyoxamides at 400°–500°C. This is consistent with the data illustrated in *Figure 1*, which show a decrease in the polyoxamide stability with the increase in weight fraction of the CO precursor, i.e. –CO–CO– group. The authors have concluded that the unusual physical and mechanical properties of aliphatic polyoxamides can be attributed to their highly symmetrical backbone which is shown to exist as an extended planar zigzag, with extremely stiff and highly polar oxamide moieties. The low thermal stability of the polyoxamides in the temperature range of 400°–500°C may be caused by the thermally labile amide groups in the high energy oxamide system. The –HN–CO–CO–NH– residue is likely to undergo homolytic thermal scission at –C(O)–C(O)– and –C(O)–N– bonds. However, these polyoxamides have been found comparable in thermal

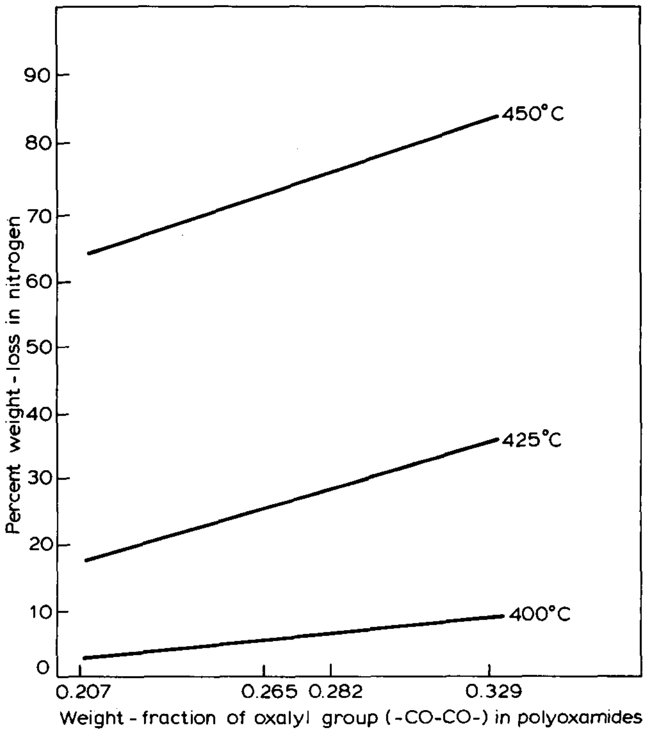


Figure 1 Plot showing a decrease in the polyoxamide stability with increases in the weight fraction of the CO precursor

Table 19

Oxamide	Acid chloride	m.p. (°C)
N,N′-bis(2-aminoethyl)	Sebacyl chloride	323 (302, dec)
N,N′-bis(3-aminopropyl) (1)	" "	276
N,N′-bis(4-aminobutyl) (2)	" "	291
N,N′-bis(6-aminohexyl) (3)	" "	257
N,N′-bis(7-aminoheptyl) (4)	" "	248
N,N′-bis(8-aminooctyl) (5)	" "	244
N,N′-bis(9-aminononyl) (7)	" "	234
N,N′-bis(10-aminodecyl) (8)	" "	231
N,N′-bis(11-aminoundecyl) (9)	" "	221
N,N′-bis(12-aminododecyl) (10)	" "	217
N,N′-bis(*trans*-4-methylene-aminocyclohexane-methylene) (11)	" "	335
N,N′-bis(cis-4-methylene-aminocyclohexane-methylene) (12)	" "	274

Table 20

Oxamide	Acid chloride	m.p. (°C)
N,N′-bis(2-aminoethyl)	Azelaoyl	343
(1)	"	290
(2)	"	300
N,N′-bis(5-aminopentyl) (13)	"	268
(3)	"	254

Table 21

Oxamide	Acid chloride	m.p. (°C)
N,N′-bis(2-aminoethyl)	Suberoyl	348
(1)	"	295
(2)	"	310
(13)	"	273
(3)	"	260

Table 22

Oxamide	Acid chloride	m.p. (°C)
(2)	Pimeloyl	301
(13)	"	273
(3)	"	259

stability to conventional polyamides, such as nylon-6,6, -6 and -12.

The synthesis of polyamides from short-chain diacids, such as oxalic acid, has been found to be difficult because of the thermal instability and volatility of the intermediates and side reactions with the polymerization media[133].

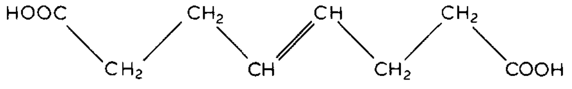
Chang and Vogl[134] have synthesized copolyoxamides from diamine-oxamides and aliphatic diacid chlorides. The melting points of the polyamides are given in *Tables 19*, *20*, *21*, *22* and *23*, respectively for sebacyl chloride, azelaoyl chloride, suberoyl chloride, pimeloyl chloride and adipoyl chloride. A regular odd–even alternation effect on melting temperatures is observed. The melting temperatures of the copolyoxamides decrease with the increase in the chain length of the diamine portion. The t.g.a. studies have revealed that all polymers have an initial degradation temperature between 300° and 350°C. The lower degradation temperature is characteristic for the regular polyoxamides which have highly polar groups. For example, all polymers from N,N′-bis(2-aminoethyl)oxamide have an initial decomposition temperature of 300°–310°C, while the regular copolyoxamides obtained from N,N′-bis(6-aminohexyl)oxamide have initial degradation temperatures of 360–370°C. The melting point decreases in the order:

adipoyl > pimeloyl > suberoyl > azelaoyl > sebacyl

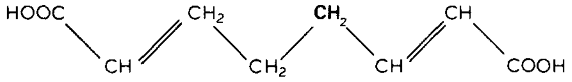
VI. UNSATURATED POLYAMIDES

Aliphatic unsaturated polyamides have been synthesized from long chain unsaturated acids or fumaric and methyl-substituted fumaric acids[135–141]. Polyamides prepared from fumaric acid are infusible, while the ones obtained from 2-methylfumaric and 2,3-dimethylfumaric acids[140] show melting or softening points.

Lanzetta *et al.*[142] have obtained polyamides containing unsaturated main chain from *trans*-4-octen-1,8-dioic (4-OD) acid (I) and *trans*-2-*trans*-6-octadien-1,8-dioic (2,6-ODD) acid (II) and linear aliphatic dimaines or piperazine.



(I)



(II)

The melting points of the polyamides are given in *Table 24*. The odd–even alternation effect is exhibited in a homologous series. The polyamides from 4-OD show high molecular weights and crystallinities and T_m above 500 K, whereas the ones obtained from 2,6-ODD are amorphous or very weakly crystalline and infusible and decompose without melting in nitrogen at temperatures

Table 23

Oxamide	Acid chloride	m.p. (°C)
N,N′-bis(2-aminoethyl)	Adipoyl	359
(1)	"	303
(2)	"	325
(13)	"	281
(3)	"	268

Table 24

Diamine	Acid	Polymer T_m (°C)
1,3-diaminopropane	4-OD	271
1,4-diaminobutane	"	294
1,5-diaminopentane	"	256
1,6-diaminohexane	"	259
1,7-diaminoheptane	"	249
1,8-diaminooctane	"	256
1,9-diaminononane	"	248
1,10-diaminodecane	"	243
Piperazine	"	252
1,4-diamino-*trans*-2-butene	"	301
1,6-diaminohexane	2,6-ODD	infusible
1,7-diaminoheptane	"	"
1,10-diaminodecane	"	"
Piperazine	"	"

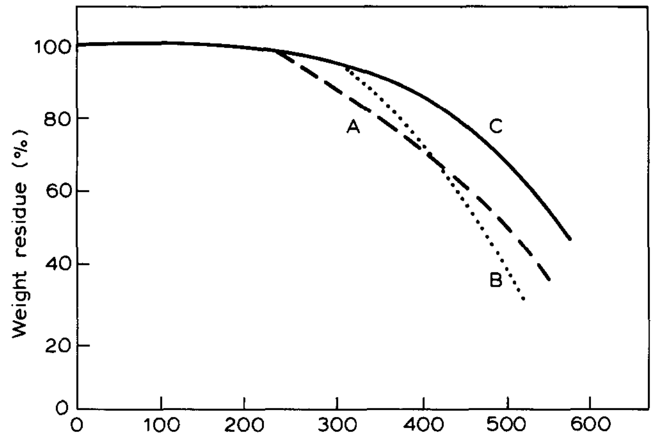
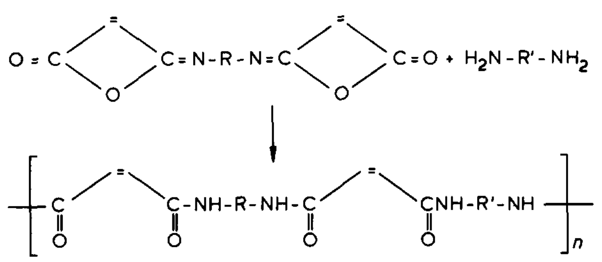


Figure 2 T.g.a. curves of polyamides under nitrogen. Curve (A): HMB polymer; curve (B): MDHB polymer; curve (C): ODOB polymer. ($\Delta T = 5°C\ min^{-1}$)

higher than 550 K. The T_m of the 4-OD polyamides are 20°–40°C higher than those found in the literature for the corresponding polyamides from suberic acid[143]. The T_m's of nylon-6,8, 4-OD-HMD, nylon-7,8 and 4-OD-HPMD are 241°C, 259°C, 220°C and 249°C, respectively. These differences are attributed to the stiffness arising from the presence of the double bonds in the polymer main chain. An analogous effect is found introducing a second double bond in the amine moiety: 4-OD-TEMD, T_m 294°C; 4-OD-BDM, T_m 301°C.

Imai and coworkers[144] have synthesized polymaleamides (I) by ring-opening polyaddition of *N,N'*-disubstituted bisisomaleimides with diamines

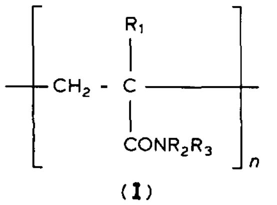


(I)

The polymers (I) are high-molecular-weight, do not show any clear melting temperature in d.t.a. and begin to decompose at a temperature ranging between 200° and 300°C under nitrogen (t.g.a.). These polyamides are somewhat less thermally stable than aliphatic polyfumeramides[135]. The t.g.a. curves of the polyamides under nitrogen are given in *Figure 2*.

VII. POLYACRYLAMIDES

The softening temperatures of some polyacrylamides of the type (I) are given[145–150] in *Table 25*.



$$\left[-CH_2-\underset{CONR_2R_3}{\overset{R_1}{C}}- \right]_n$$

(I)

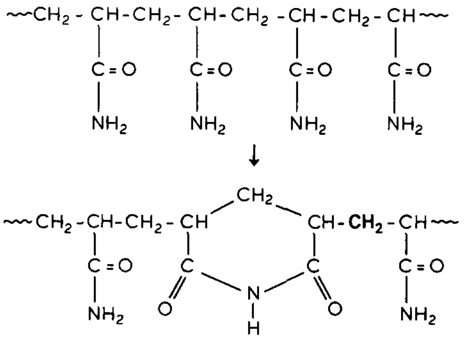
Table 25

R_1	R_2	R_3	Approx. softening temperature (°C)
H	H	H	210
H	H	CH_3	20
H	H	iso-C_3H_7	100–125
H	H	*t*-C_4H_9	200–210
H	H	cyclo-C_6H_{11}	210–220
H	CH_3	CH_3	100
CH_3	H	CH_3	205
CH_3	H	*t*-C_4H_9	220–250
CH_3	H	Cyclic-C_6H_{11}	235–248

All the polyacrylamides decompose at their softening temperatures. Some of the properties observed in the polyacrylamides are stated below:

1. Softening temperatures of polymethacrylamides are usually higher than those of the corresponding acrylamides.
2. Softening temperatures of *N*-monoalkylsubstituted polyacrylamides are lower than those of unsubstituted ones; disubstitution lowers the softening temperature further.
3. Long alkyl groups lower the softening range to room temperature or below, while branched alkyl groups on nitrogen raise the softening range above that of similar *N*-alkyl derivatives.
4. Crystalline polymers soften at much higher temperatures than the amorphous ones.

The polyacrylamides also suffer intra- and intermolecular imidization even at the conditions of temperature of polymerization as follows:



(14)

The thoroughly cross-linked intermolecular imidization renders the polymer quite insoluble in water.

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