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STUDIES IN POLYMERIZATION OF ω-AMINO ENANTHIC ACID (NYLON-7)

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INTRODUCTION

1.1 Natural and man-made fibres

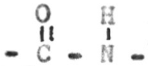
Man has been using cloth since distant past. Formerly the clothes were entirely made up of natural fibres, which were either of vegetable origin such as cotton, flax, linen, hemp, jute, abulka, manila, sisal or of animal origin such as wool, fur and silk. In recent years, because of the increasing population of the world and the land being utilized more for cultivation of food, some limit has to be placed for the production of the natural fibres. In order to make up this scarcity of natural fibres, man-made fibres are needed. These are mainly of two types:[1] (1) regenerated type (i.e. modification of natural fibres) e.g. rayon (cellulose), protein fibres, and (2) synthetic type e.g. polyamides (nylon), polyesters (terylene), polyvinyl derivatives, polyolefines, etc.

The man-made fibres, though inferior in water absorption, breathing etc. to natural fibres, have certain desirable properties like crease resistance, resistance to moisture and also have better tensile strength and elasticity. They can undergo an important textile operation 'setting', while the natural fibres cannot.

The synthetic fibres are generally made by polyaddition reaction of vinyl monomers e.g. polyvinyl alcohol, polyvinyl chloride, polyacrylonitrile, or by polycondensation reactions of difunctional organic compounds e.g. polyamides, polyesters. Among synthetic fibres, nylon is a fibre with a combination of excellent properties. Nylon-66 (for nomenclature see 1.2.1) was first manufactured[2] as it had the required balance of properties and manufacturing cost. Then entered[2] nylon-6, a polyamide from caprolactam.

The present investigation pertains to the study of nylon-7 prepared by polycondensation reaction of ω-amino enanthic acid (ω-AEA).

1.2 Nylons

Nylon is a general term for any long chain synthetic polyamide which has recurring amide linkage ( $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$) and which can be drawn into filaments. Carothers[2-6] was the first to study the reaction of diamine and dibasic acid that gave a polyamide. The terms nylon and polyamide, are often interchangeable.

1.2.1 Nomenclature and common trade names

The nylons are described in short by putting a number next to the word 'nylon'. The number is an abbreviated description of the materials used in the preparation. When there are two numbers, e.g. nylon-66, it means that two reactants (diamine and dibasic acid) are used in forming the polyamide. The first digit represents the number of carbon atoms in diamine chain and the second indicates the number of carbon atoms in the dibasic acid chain. Thus nylon-66 is made by the polycondensation reaction of hexamethylene diamine and adipic acid.

If a single number follows the word nylon, e.g. nylon-6, it means that the polyamide is prepared from a single monomeric substance which is omega-amino acid e.g. ϵ-amino caproic acid. This number is the number of carbon atoms in the recurring polymer unit in the linear chain.

Nylons are known by different trade names in different countries, as summarized in the following table.

Table I

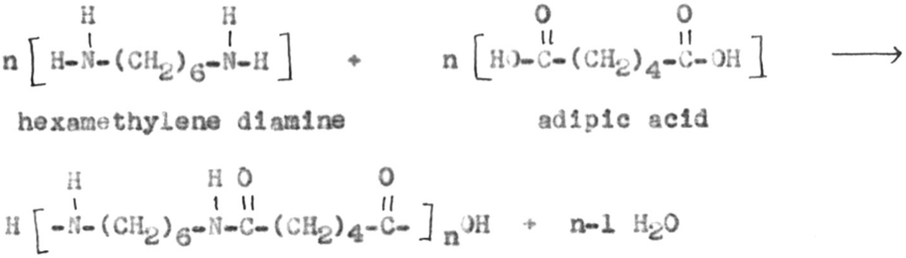
Trade names[1,6,7] of Polyamides (Nylons)

	Nylon	Country
Nylon-66	Akulan	Netherlands
	Amilan	Japan
	Anid-66	USSR
	Nylfrance	France
	Zytel	USA
Nylon-6	Amilan	Japan
	Caprolan	USA, Australia
	Celon	UK
	Chinlan	China
	Dorlon	W.Germany
	Garflon	India
	Garnyl	India
	Grilon	Switzerland, Japan, Brazil
	Jayanka	India
	Jaykaylon	India
	Kapron	USSR, Czechoslovakia
	Modipon	India
	Nirlon	India
	Nylenka	USA
	Perlon	W.Germany, Chile
	Silon	Poland, Czechoslovakia
	Stilon	Poland
Nylon-7	Enanth	USSR
	Enant-7	USSR
Nylon-9	Pelargon-9	USSR
Nylon-11	Rilsan	Italy, France, Brazil, USSR

1.2.2 Polycondensation and ring formation

The polyamides are synthesized mainly by two methods:

(a) Polycondensation of diamine with dibasic acid e.g. hexamethylene diamine when condensed with adipic acid gives to a polymeric amide, which is known as nylon-66



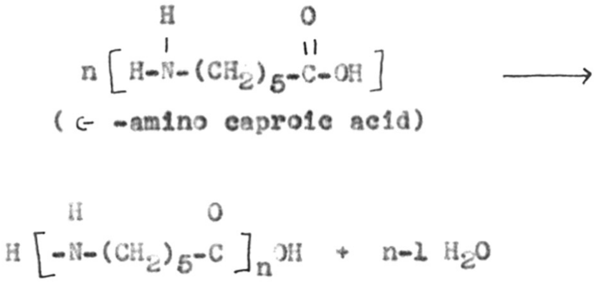
$$n\left[H-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-H\right] + n\left[HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH\right] \longrightarrow$$

hexamethylene diamine adipic acid

$$H\left[-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_nOH + n-1\ H_2O$$

nylon-66

(b) Polycondensation of omega amino acids: e.g. epsilon amino caproic acid when heated at 200-250°C, gives a polyamide by self condensation, e.g. ε-amino caproic acid gives nylon-6.



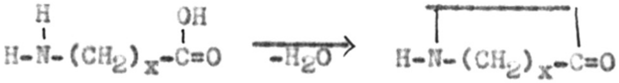
$$n\left[H-\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-OH\right] \longrightarrow$$

(ε-amino caproic acid)

$$H\left[-\overset{H}{N}-(CH_2)_5-\overset{O}{C}\right]_nOH + n-1\ H_2O$$

nylon-6

If the number of carbon atoms in ω-amino acid is 5 or lower than 5, a ring[5,8] or lactam is formed instead of a linear polyamide, due to intramolecular condensation e.g. 4-amino butyric acid and 5-amino valeric acid when heated above their melting points, give respective lactams.

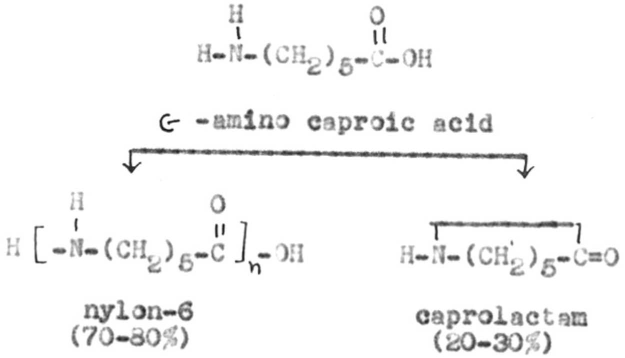


$$\mathrm{H-\overset{H}{N}-(CH_2)_x-\overset{OH}{C}=O} \xrightarrow{-H_2O} \mathrm{H-N-(CH_2)_x-C=O}$$

lactam

where x = 3 or 4.

ε -amino caproic acid presents an intermediate[9] stage in the sense that it forms a linear polyamide (70-80%) as well as lactam (20-30%).



$$\mathrm{H-\overset{H}{N}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-OH}$$

ε -amino caproic acid

$$\mathrm{H\left[-\overset{H}{N}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right]_n-OH} \qquad \mathrm{H-N-(CH_2)_5-C=O}$$

nylon-6
(70-80%)

caprolactam
(20-30%)

ω -amino enanthic acid (which is also known as ω -amino heptanoic acid) and the higher acids in the series, form linear polyamides only[8]. Similar polyamides of the general type $\mathrm{HN-(CH_2)_x-CO-}$, in which x is 5,6,7,8,9,10 and 17 have been prepared[8].

1.2.3 Kinetics of condensation polymerization

The condensation reactions of monofunctional or polyfunctional compounds are similar in nature. Hence the kinetics of condensation polymerization is essentially identical[10] with that of simple condensation.

The rate of reaction of end groups is independent of the size of the polymer molecule to which it is attached. The mobility of the end groups is much greater than that of the entire chain but the reactions take place at very low rates (only about one collision in 10^{13}, leads to chemical reaction).

It is well known that the velocity constant for esterification of dibasic acid with glycol varies only in the region of $n=0$ to 6, where n is the number of carbon atoms between carboxyl end groups. It reaches an asymptotic value with further increase of n and shows no tendency to decrease with increase of molecular size.

The same may be assumed to apply for other types of polycondensation reactions such as those between diamines and dibasic acids or between ω-amino carboxylic acids.

Condensation polymerization is catalysed by acids[10]. In the absence of catalyst, a second molecule of the acid undergoing esterification acts as a catalyst. For the polycondensation reaction between dibasic acid and glycol in the absence of catalyst, the rate of condensation is given by:

$$\frac{-d}{dt}\left[COOH\right] = k\left[COOH\right]^2\ \left[OH\right]$$

since COOH = OH = C, where C is the concentration of -COOH or -OH, the third order[11] reaction may be written as:

$$\frac{-dc}{dt} = kC^3 \quad \text{and } 2\,kt = \frac{1}{C^2} - \text{constant}$$

If p is the extent of reaction, which is defined as the fraction of the functional groups that has reacted at time t, and C_o = initial concentration of functional groups, then

$c = (1-p)\ C_o$ and $2\ C_o^2\ kt = \frac{1}{(1-p)^2} + \text{constant}$

p may be determined from the acid value of reaction mixture obtained by titration. A plot of $\frac{1}{(1-p)^2}$ against

If strong acid is used as a catalyst, the rate of polycondensation can be represented by a second order[11] reaction

$$-\frac{d}{dt}\left[COOH\right] = k'C^2 \ , \quad \text{and}$$

$$C_0k't = \frac{1}{(1-p)} + \text{constant}$$

where k' includes the catalyst concentration which is constant throughout the polycondensation process. A plot of $\frac{1}{(1-p)}$ versus t should be a straight line.

1.3 Nylon-7

Nylon-7 (discovered by Manasse[12] in 1902) is a polyamide obtained o the polycondensation of ω-amino enanthic acid $H_2N(CH_2)_6COOH$. This monomeric ω-amino acid is prepared (like other similar ω-amino acids) by telomerization[13-17].

1.3.1 Telomerization reaction

This reaction involves the addition of one molecule of saturated compound (AB) to several molecules of an unsaturated compound (say $H_2C{=}CH_2$). During the process, the saturated compound splits off into two radicals that lie at the ends of the newly created molecules.

$$A{-}B + n(H_2C{=}CH_2) \longrightarrow A(H_2C{-}CH_2)_nB$$

Here the saturated compound from which the end groups are derived is called the 'telogen' and the unsaturated compound is called 'taxogen'. The product $A(H_2C{-}CH_2)_nB$ is the 'telomer' and the reaction is known as the telomerization reaction. The radical B^* initiates the reaction while the radical A* is abstracted during chain reaction. With this reaction difunctional monomers, with odd and even number of carbon atoms can be obtained by using carbon tetrachloride and tetrachloroethylene respectively. These are then converted into polymers by polycondensation reaction.

Taking carbon tetrachloride (CCl_4) as a telogen, its reaction[13,14] with ethylene ($H_2C=CH_2$) to form a difunctional monomer can be explained through the following steps:

(a) Initiation

The initiator such as benzoyl peroxide or azo-bis-isobutyronitrile[2] decomposes itself to form a free radical (R*). This free radical abstracts one chlorine atom from CCl_4, gets deactivated, giving rise to a new free radical trichloromethyl (CCl_3*) e.g.

$$(C_6H_5COO)_2 \longrightarrow 2\ C_6H_5COO^* \longrightarrow 2\ C_6H_5^* + 2CO_2$$

$$C_6H_5^* + Cl\text{-}C\text{-}\ CCl_3 \longrightarrow C_6H_5Cl + CCl_3^*$$

(b) Propagation

The trichloromethylene radical combines with a molecule of ethylene, giving a new free radical.

$$CCl_3^* + H_2C = CH_2 \longrightarrow Cl_3C\text{-}CH_2\text{-}CH_2^*$$

Some new molecules of ethylene add in turn to this new radical with the formation of a long chain radical $CCl_3(H_2C\text{-}CH_2)^*_n$.

(c) Chain transfer

The chain transfer growth stops when the long chain radical abstracts a chlorine atom from CCl_4 and gets saturated (tetrachloroalkanes) giving rise to a new free radical CCl_3^* :

$$CCl_3(CH_2-CH_2)_n^* + Cl.CCl_3 \longrightarrow CCl_3(CH_2-CH_2)_nCl + CCl_3^*$$

The free radical CCl_3^* formed, again takes part in the reaction with ethylene exactly as in the beginning. This goes on several hundred times till two CCl_3^* radicals combine with one another to form a saturated molecule of hexachloroethane

$$2\ CCl_3^* \longrightarrow (Cl_3C \longrightarrow CCl_3)$$

A mixture of telomers (similar in structure but different in length, C_3, C_5, C_7 etc.) is obtained. These are then separated[14] by repeated fractional distillation. Distillation is carried out under reduced pressure (1-2mm) in order to avoid decomposition of tetrachloroalkanes to trichloroalkenes. The separated telomers can be used to prepare different difunctional compounds which, in their turn, can be polymerized to fibre forming polymers, plastics, perfumes, plasticizers, lubricants etc.

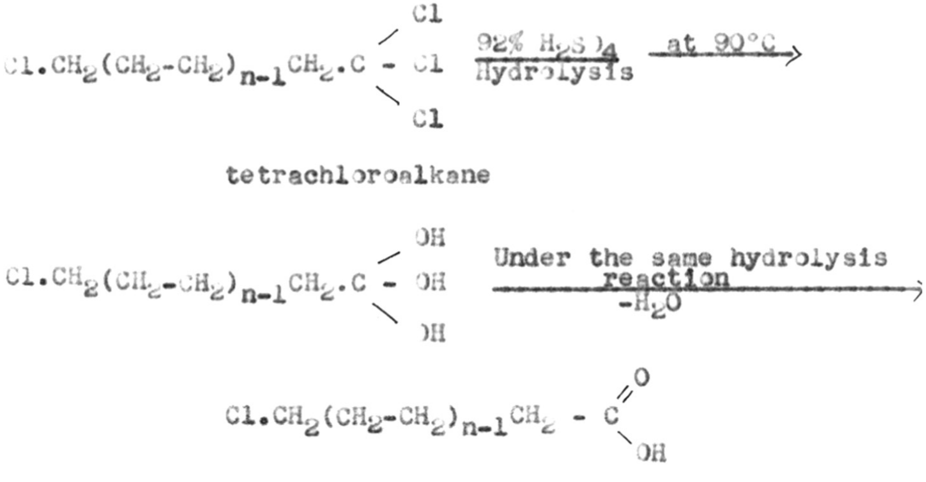
In actual process, ethylene (gas) and carbon tetrachloride together with an initiator are forced together in a stainless steel lined tubular pressure reactor at 10-20°C under 50 atm. pressure when a solution is formed. This solution is continuously passed through spiral reactors at 90-100°C under 100-150 atm. pressure, when telomerization takes place. Varying the conditions of the reaction (pressure and ratio of the reactants) chain length of the telomer can be controlled.

The maximum[14] yield (35%) of a telomer having 7 carbon atoms is obtained with 4-6 moles of ethylene to 1 mole of CCl_4, using azobis-isobutyronitrile as an initiator at 100°C and 105 atm.pressure. Azobis-isobutyronitrile is less dangerous and more efficient than benzoyl peroxide, as the 'cage' effect is not observed with the former.

Because of the lower yield (35%) of this particular telomer having 7 carbon atoms, and difficulties in application of the remaining telomers in the mixture, the process has not been economical so far and hence has not been so progressive. However, pilot plant studies[15,19] are being carried out in Russia and Japan.

(d) Conversion of telomers into difunctional monomers

When tetrachloroalkanes are hydrolyzed[14] with concentrated mineral acid (H_2SO_4, HNO_3) at 90-100°C for 1 hour, all the three atoms of chlorine situated at one end of the molecule are substituted by hydroxyl groups which subsequently are transformed into one carboxyl group.



$$Cl.CH_2(CH_2-CH_2)_{n-1}CH_2.C\begin{matrix}Cl\\-Cl\\Cl\end{matrix}\ \xrightarrow[\text{Hydrolysis}]{92\%\ H_2SO_4}\ \xrightarrow{\text{at }90^\circ C}$$

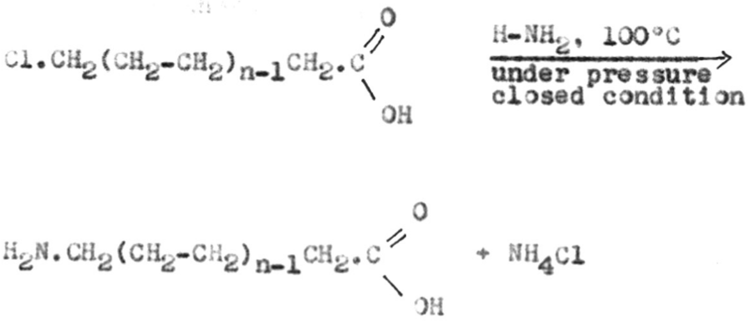
tetrachloroalkane

$$Cl.CH_2(CH_2-CH_2)_{n-1}CH_2.C\begin{matrix}OH\\-OH\\OH\end{matrix}\ \xrightarrow[-H_2O]{\text{Under the same hydrolysis reaction}}$$

$$Cl.CH_2(CH_2-CH_2)_{n-1}CH_2-C\begin{matrix}{}^{\nearrow\!\!\!/}O\\ \searrow OH\end{matrix}$$

ω -chloro acid

When these chloro acids are heated at 100°C in a 25% solution[14] of ammonia, the chlorine atom is substituted by $-NH_2$ group



$$Cl.CH_2(CH_2-CH_2)_{n-1}CH_2.C\overset{O}{\underset{OH}{\lessgtr}} \xrightarrow[\text{under pressure closed condition}]{H-NH_2,\ 100^\circ C} H_2N.CH_2(CH_2-CH_2)_{n-1}CH_2.C\overset{O}{\underset{OH}{\lessgtr}} + NH_4Cl$$

ω -amino acid

This acid is purified[14] to get rid of ammonium chloride, by cation and anion exchange resins.

These ω -amino acids are the monomers for the production of synthetic polyamide fibres, such as nylon-7 (enanth), nylon-6 (caprone) etc.

1.3.2 Polycondensation of ω-amino enanthic acid (ω-AEA) to nylon-7

A concentrated aqueous solution of ω-AEA is heated at 250-260°C in an autoclave lined with stainless steel or enamel, for several hours in nitrogen atmosphere at a pressure of 14-15 atmospheres. The polyamide -nylon 7- is formed by intermolecular polycondensation of ω-AEA.

$$n\ H_2N(CH_2)_6\ COOH \longrightarrow [-HN(CH_2)_6CO-]_n + n\ H_2O$$

ω-AEA nylon-7

The water formed during polycondensation and that from original sulution is driven out by releasing the pressure. The molten polyamide formed is extruded through narrow nozzles into water. It becomes hard solid which is then cut into chips.

In the present work, instead of making a solution, the monomer ω-AEA has been used in the solid form itself. For manufacture solid form is convenient and the polymer from it can directly be melt spun without any difficulty of removing water, reprecipitation, drying and then melt spinning, which is not economical.

1.3.3 Spinning of nylon-7 fibre (melt spinning[20])

The nylon chips are charged to a hopper of the spinning unit and dropped onto a specially designed heated grid where the polymer melts. This molten mass is filtered through special filter packs and then forced through fine holes of a spinneret. The equipment is maintained at temperatures above the melting point of the polymer, and blanketed with an inert gas nitrogen to prevent oxidation. The emerging jets (15-30 microns in thickness) of molten polymer are cooled and solidified by a stream of cold air and are wound over reels rotating at high speed.

Drawing (stretching)

The nylon yarn is passed round the two rollers, the second moving faster than the first one. The yarns are drawn 4-5 times their original length. The drawing orients the polyamide molecules parallel to fibre axis thus increasing crystallinity, tensile strength etc. The yarns are then heated in boiling water to 'set' the yarn in stretched form. The yarns are wound on the bobbin.

1.4 Characterisation of nylon-7

Nylon-7 like other synthetic polymers, contains polymer chains of different sizes. Hence the molecular weight (mol.wt.) assigned to it refers to an average mol.wt. The numerical value assigned to the mol.wt. depends on the way in which the mol.wt. is averaged. In order to characterize a polymer, it is necessary to characterize not only the mol.wt. but also the molecular weight distribution (MWD).

1.4.1 Molecular weight averages

(a) Number average molecular weight : $\overline{M}_n$

It is defined[21] as the total weight of the polymer molecules divided by the total number of molecules. It is measured by weighing the mol.wt. of each species by its mole fraction.

$$\overline{M}_n = \frac{\text{Total weight}}{\text{Total number of molecules}} = \frac{W}{N} = \frac{\sum N_i M_i}{\sum N_i}$$

where W = total weight of mixture, N = total number of molecules, N_i = total number of n-mer, M_i = mol.wt. of n-mer.

Any method involving measurement of colligative properties, such as ebullioscopy, cryoscopy, osmometry and end group analysis measures the number average mol.wt.

(b) Weight average molecular weight: $\overline{M}_w$

The mol.wt. of each species, if weighed by its weight fraction, the weight average mol.wt. is obtained[21].

$$\overline{M}_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i} , \quad \because \quad W_i = N_i M_i$$

where N_i = total number of n-mer, M_i = mol.wt. of n-mer, and W_i = weight of n-mer.

$\overline{M}_w$ is obtained by methods which depend upon the weights of molecules present, such as by light scattering. The high mol.wt. portion affects weight average mol.wt. whereas the number average mol.wt. is greatly influenced by the low mol.wt. fraction in an unfractionated polymer sample.

(c) Z-average molecular weight : $\overline{M}_z$

Z average[21] and similar higher averages (z+1, z+2 etc.) are similarly defined as:

$$\overline{M}_z = \frac{\sum W_i M_i^2}{\sum W_i M_i} = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

M_i = mol.wt. of n-mer, N_i = total number of n-mer and W_i = weight of n-mer.

(d) Viscosity average molecular weight : $\overline{M}_v$

It is derived from viscosity measurements and is expressed[21] by:

$$\overline{M}_v = \left[\sum W_i M_i^a\right]^{1/a} = \left[\frac{\sum N_i M_i^{a+1}}{\sum N_i M_i}\right]^{1/a}$$

where 'a' is a constant, whose value depends upon the polymer-solvent system. When 'a' becomes unity, $\overline{M}_v = \overline{M}_w$. All average values are equal for monodisperse product[22].

It has been shown that for linear condensation polymers, the mol.wt. distribution is most probable and the different mol.wt. averages are related[21] by:

$$\overline{M}_n : \overline{M}_w : \overline{M}_z :: 1:1+p : \frac{1+4p+p^2}{1+p}$$

where p is the extent of reaction.

When $p \longrightarrow 1$,

$$\overline{M}_n : \overline{M}_w : \overline{M}_z :: 1:2:3$$

1.4.2 Molecular weight determination

Most of the methods of mol.wt. determination are based on measurements of certain properties of polymers in solution. The polymer solutions are nonideal and the measured properties are to be extrapolated to infinite dilution for calculating the mol.wt.

The methods are divided into two classes: (A) physical methods, and (B) chemical methods:

(A-1) Freezing point (cryoscopy) and boiling point (ebullioscopy changes.

The lowering of freezing point of a solvent is proportional to the amount and nature of the substance dissolved in it. For dilute solutions,

$$\Delta t_f = K_f C = K_f \frac{W_A}{W_s} \frac{1000}{M_A}$$

where K_f = molal freezing point depression constant

C = molality of solution

W_A = weight of the solute dissolved in weight W_s of solvent

M_A = mol.wt. of solute

The raising of boiling point of a solvent is proportional to the amount and nature of the dissolved substance. For dilute solutions,

$$\Delta t_b = K_b C = K_b \frac{W_A}{W_s} \cdot \frac{1000}{M_A}$$

where K_b is the molal boiling point elevation constant.

The difficulties in these methods are:

(i) Since these methods depend inversely on the mole fraction of the dissolved solute, the accuracy of the mol.wt. obtained is satisfactory only upto a mol.wt. of about 5000. For higher mol.wts. the concentrations required to obtain measurable changes in temperature and pressure are so high that the above given equations hold no longer.

(ii) the cryoscopic method can be used only at the freezing point of the solvent.

(iii) the ebullioscopic method is used only at the normal boiling point of the solvent. At elevated temperatures, decomposition of solute may take place.

(A-2) Osmotic pressure measurements

The osmotic pressure-mol.wt. relationship is given by:

$$\frac{\pi}{C} = \frac{RT}{\bar{M}_n} + RT\, A_2 C$$

where π = osmotic pressure at concentration C,

R = gas constant

T = absolute temperature

$\overline{M}_n$ = number average mol.wt., and

A_2 = second virial coefficient[2].

The second factor, in the above equation, is the correction term for non ideality of the solution. The major difficulty in osmotic pressure measurement is the permeability of the membrane for low mol.wt. species in the polymer. The membrane should also have a high rate of solvent transfer. Because of these difficulties, it is rather difficult to measure accurately, the mol.wts. less than 25,000.

(A-3) Ultracentrifuge technique

This method involves specialized equipment and elaborate skill. For synthetic polymers it is also difficult to correct for the non ideality of the solutions. The following equation gives the relationship between mol.wt. and the measurable quantities, S_0 - the sedimentation constant, and D_0 - the diffusion constant.

$$M = \frac{RT}{1 - \overline{\vartheta}_A \varrho} \cdot \frac{S_0}{D_0}$$

where $\overline{\vartheta}_A$ = partial specific volume

ϱ = density of the solution

S_0 = sedimentation constant

D_0 = diffusion constant at infinite dilution

M = weight-average or Z-average mol.wt.

Additional information on the mol.wt. distribution can be obtained from ultracentrifuge measurements.

(A-4) Light scattering measurements

Amongst the mol.wt. determination methods available now, the most versatile method is based on the determination of the intensity of the light scattered from polymer solutions. The informations obtained give the weight average mol.wt. thermodynamic interaction parameters and size and shape of the polymer molecule.

The theoretical treatment of Debye, Zimm and others lead to the following equation which connects the intensity of the scattered light to mol.wt.

$$\frac{HC}{\tau} = \frac{1}{\bar{M}_w} + 2 A_2 C$$

where $H = \frac{32 \pi^3}{3 \lambda^4 N_o} \cdot n^2 \left(\frac{dn}{dc} \right)^2$

C = concentration of the solution

τ = turbidity

λ = wavelength of the light used

N_o = Avogadro's number

n = refractive index of the solution

$\frac{dn}{dc}$ = change in refractive index with concentration

$\bar{M}_w$ = weight average mol.wt.

A_2 = second virial coefficient.

The non ideality of the solution is corrected by extrapolating to infinite dilution. The molecular dimensions of the polymer molecule can also be obtained from the angular dependence of the scattered intensity.

(A-5) Viscosity measurements

The macromolecules increase the viscosity of solvent by many fold, in which they are dissolved. The increase in viscosity can be compared to that of the solvent alone. The mol.wt. determination by the viscosity method depends in determining the two constants K and α in the Mark-Houwink[18,23] relationship:

$$[\eta] = K \bar{M}^{\alpha}$$

where $[\eta]$ is the intrinsic viscosity defined as:

$$\lim_{C \to 0} \frac{\eta_{sp}}{C} \qquad \text{or}$$

$$\lim_{C \to 0} \frac{\ln \eta_r}{C}$$

where η_r is the relative viscosity and $\eta_{sp} = \eta_r{}^{-1}$

For nonelectrolyte high polymers, the value of α lies between[2] 0.5 to 1.0. The viscosity measurements are simple and easier to perform with the requisite accuracy. However, the mol.wt. determined by viscosity method is not absolute and the procedure has to be standardised against an absolute method such as light scattering, osmotic pressure, end group analysis etc.

When many measurements (of mol.wts. of a series of polymer samples, prepared under different conditions) have to be made, a single point method is used. This method is the most practical method, especially in industries.

(A-6) Electron microscopy and low angle X-ray scattering methods have also been used for mol.wt. determination of polymers under favourable conditions.

(B-1) End group analysis

In condensation polymers, the end groups are left detectable. and can be measured by titrating the polymer in solution against a suitable acidic or basic titrant. Since this method actually counts[24] the number of molecules present, it gives $\overline{M}_n$

$$\overline{M}_n = \frac{10^6 . y}{n}$$

where y = 1 or 2 according to whether the groups are at one
or both ends

and n = end group concentration in microequivalents per gram.

Since the method measures the effect of small group on a large chain, the accuracy decreases as the mol.wt. increases. This method is applicable for mol.wt. upto 20,000 to 25,000. Recently, the dye interaction method[25] has been suggested to measure the end groups of vinyl polymers also even upto a mol.wt. of a million, in the polymer. A particular dye reacts with a particular end group and the intensity (depth) of the dye is compared with some standard colorometrically. The number of end groups is calculated therefrom.

1.4.3 Fractionation of nylon-7

Nylon-7, like other polymers, being heterogeneous with respect to mol.wt. can be characterized in terms of mol.wt. distribution. The nature of such distribution has an important effect on the properties of the polymer. Such distribution curve can be drawn from the experimental data, which in its turn, is obtained by the separation of the whole polymer into fractions each of which is more homogenous in mol.wt. than the original polymer.

These fractionation processes are of two types[24]:
(a) preparative in which actual fractions are isolated, and
(b) analytical in which, without separating the individual fractions, the distribution curves are obtained. Both the types are based on solubility behaviour in the sense that the solubility of homogeneous polymer fraction, in a suitable solvent, decreases with increase in mol.wt.

Choice of fractionation technique

(A) Preparative fractionation

(A-1) Fractional precipitation

Fractional precipitation method is mostly used for preparative fractionation. The fractional precipitation of a polymer from its solution in solvent-nonsolvent mixture may be achieved by three different methods: (a) by progressive addition of non solvent (precipitant), (b) by solvent evaporation, and (c) by cooling. The first one involves the stepwise addition of a non solvent to a polymer solution. The highest mol.wt. fraction, being the least soluble, precipitates first. This is removed by settling and decanting the supernatant liquid. The addition of non solvent to the decanted solution is repeated to get the second highest mol.wt. fraction and so on.

In case of fractional precipitation, by solvent evaporation, the precipitant must have a vapour pressure sufficiently below that of the solvent so that the solvent is preferentially removed when vacuum is applied to the vessel.

Precipitation by cooling is based on a decrease in the temperature of the system causing a decrease in the solvent power. This presents some difficulties (i) many polymers are not completely precipitated by cooling alone, (ii) the use of high temperatures creates stability problems.

(A-2) Fractional solution

In this technique the polymer is shaken with a solvent of limited power. The more soluble low mol.wt. fraction goes into the supernatant layer, at equilibrium. The layer can be decanted off and the low mol.wt. polymer is recovered from it as the first fraction. The next higher and still higher fractions are similarly obtained using solvents of progressively increasing solvent power.

This technique is advantageous as (a) fractionation can be carried out with a very small quantity of polymer, e.g. 1 gram or even less, (b) the higher mol.wt. fractions contain less amount of low mol.wt. tail because the lowest mol.wt. fraction is obtained first and then higher and higher mol.wt. fractions are obtained, last, (c) the method is automatic (once the flow of solvent and rotation of fraction collectors are adjusted, it goes automatically till all the fractions are collected). But the difficulties observed are (i) it is difficult to establish true equilibrium between solid polymer and the extracting liquid phase, (ii) judgement of fraction size is difficult, (iii) large quantities of solvents are required. Recent developments in solution fractionation technique have been used as an efficient technique for analytical fractionation.

(B) Analytical method

Turbidimetric titration

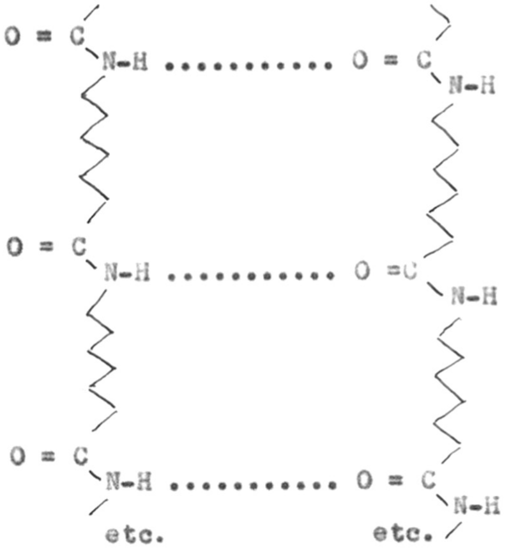
This is a very rapid analytical method for obtaining a qualitative picture of polymer distribution.

When a dilute solution of polymer is titrated with precipitant (non-solvent), with constant shaking, a point is reached at which the highest mol.wt. fraction, which is the least soluble, begins to precipitate out producing some turbidity. This turbidity increases progressively as more non solvent is added. A stage comes when all the polymer is precipitated and the turbidity becomes constant. By measuring the turbidity, the precipitated polymer at any stage can be weighed optically. An integral distribution curve can be derived from these data.

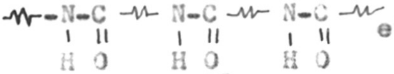
1.5 Properties and uses of nylon-7

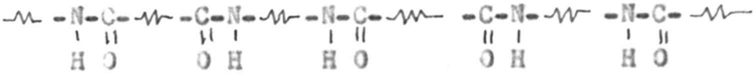
1.5.1 Structure

The amide groups in nylon-7, as in case of other nylons[13,26] are spaced regularly along the chain. The hydrogen atom of $-\underset{H}{N}-$ group has a strong tendency to interact with the oxygen of - group in neighbouring chain thus forming a hydrogen bond[26].



Structure of nylon-7

Hydrogen bond (dotted lines) playes an important role in the crystallization of nylon. In the nylons from ω-amino acids, the sequence of the chain atoms in one direction[27] (e.g.  $\sim \underset{\substack{\|\\O}}{C}-\underset{\substack{|\\H}}{N} \sim \underset{\substack{\|\\O}}{C}-\underset{\substack{|\\H}}{N} \sim \underset{\substack{\|\\O}}{C}-\underset{\substack{|\\H}}{N} \sim$ etc.) is the reverse of that in the opposite direction (i.e.  $\sim -\underset{\substack{|\\H}}{N}-\underset{\substack{\|\\O}}{C} \sim \underset{\substack{|\\H}}{N}-\underset{\substack{\|\\O}}{C} \sim \underset{\substack{|\\H}}{N}-\underset{\substack{\|\\O}}{C} \sim$ etc.). On the other hand, the diamine-diacid derived[28] nylons have this sequence independent of the direction.



$$\sim -\underset{\substack{|\\H}}{N}-\underset{\substack{\|\\O}}{C}- \sim -\underset{\substack{\|\\O}}{C}-\underset{\substack{|\\H}}{N}- \sim -\underset{\substack{|\\H}}{N}-\underset{\substack{\|\\O}}{C}- \sim \; -\underset{\substack{\|\\O}}{C}-\underset{\substack{|\\H}}{N}- \sim -\underset{\substack{|\\H}}{N}-\underset{\substack{\|\\O}}{C}- \sim$$

In other words, nylons from ω-amino acids are unsymmetrical[27] while those from diamines and dibasic acids are symmetrical[27]. In the former type of nylons, if the molecule is reversed for end to end, the detailed array (crystal structure) is also inverted.

The carbon chain between two polar groups is longer for nylon-7 than for nylon-6 by one methylene -CH_2- group. This increases the elasticity of the molecule of nylon-7. It also improves the physico-mechanical properties (tensile strength, Young's modulus, flexibility etc.) of the nylon-7 fibre.

1.5.2 Physical properties

Nylon-7 is a semi-crystalline, white polyamide. It is thermostable[12,29] in an inert atmosphere upto 300°C (melting point 225°C). Heating at 250°C for 24 hours has no decomposition effect. Enanth (nylon-7) has better thermal and light stability[30] and better elasticity than nylon-66 or nylon-6. Some physical properties are summarised and compared to that of other nylons in Table[12] II.

1.5.3 Chemical properties

It is resistant to basic as well as acidic reagents and is insoluble in most of the organic solvents. It is highly resistant to the oxidizing agents.

1.5.4 Uses

It is used[31] in the form of film, for food packaging, in making[13] socks, stockings, underwears, fishing nets, electrolysis materials, filtering cloth, cables etc.

The polyamide, nylon-7 is used as a tyre cord[14,19] material as well as in the manufacture of bearings and other parts in textile machinery subject to friction of non-ferrous metals. Nylon-7 has immense potentialities for future application

Table[12] II

Physical properties of polyamides from ω-amino acids

Polyamide	$-NH(CH_2)_nCO-$	M.P °C	Moisture regain % at 20°C and 65% relative humidity	Density (of high crystalline polymer)	Sticking temperature °C
1. Nylon-6	n=5	214	4.7	1.14	208
2. Nylon-7	n=6	225	2.6	1.10	220
3. Nylon-8	n=7	185	1.8	1.08	181
4. Nylon-9	n=8	194	1.45	1.06	190
5. Nylon-10	n=9	177	1.25	1.04	172
6. Nylon-11	n=10	182	1.20	1.04	173

1.6 Scope of the present work

Upto the present date, a great many polyamide resins have been synthesised and studied. But quite a few are being produced commercially. These are nylon-66, nylon-6, nylon-610 and nylon-11.

Nylon-7 is more advantageous[16] than nylon-6 in the sense that nylon-7, after polymerization, contains negligible amount of monomer. Hence it is suitable for spinning and drawing without any washing or extraction.

With a view to study the optimum conditions of polycondensation of ω-AEA to nylon-7, a systematic study has been carried out in the present work. Polycondensation reactions of ω-AEA have been studied with and without catalysts at 200-300°C for 15 minutes to 7 hours, in an inert atmosphere, and the polymer (nylon-7) has been characterized according to the following scheme.

(1) Effect of time and temperature on polycondensation reactions

(2) Effect of acidic and basic catalysts

(3) Determination of mol.wt. by end group analysis and viscometry

(4) Fractionation by fractional precipitation by addition of non solvent

(5) Molecular weight distribution

(6) Infra red spectrum of nylon-7

CHAPTER-II

EXPERIMENTAL

The polycondensation reactions of ω-AEA were carried out under extremely dry and inert atmosphere of nitrogen gas as the polymer formed in the molten stage was sensitive to oxygen in the air and got charred otherwise. CO_2 can as well be used[32,3 instead of nitrogen. The nitrogen gas was purified, oxygen freed by successively passing through three columns(each of eight inches) of Fieser's solution[34] and washed free of sulfurous gases in a bubbler containing aqueous saturated basic lead acetate solution. It was then washed with distilled water in the next bubbler and dried over calcium chloride, sulfuric acid, phosphorous pentoxide, potassium hydroxide pellets and silica gel in all-glass purification train. This pure and dry nitrogen was now admitted to the polymerization tube through polyethylene tubing.

2.1 Reagents and solvents

(a) Fieser's solution[34]

It was prepared by dissolving 15 gms. of sodium hydrosulphite per hundred millilitres of an aqueous solution of 20 gms. of potassium hydroxide, followed by 2 gms. of anthraquinone sulfonic acid (sodium salt). The solution was blood red when fresh but turned dull brown when exhausted, with the formation of white scum.

(b) Sulfuric acid

Reagent grade sulfuric acid (sp.gr.1.84) was used to dissolve the crude polymer for reprecipitation, in order to remove the unpolymerized monomer and low mol.wt. tails (oligomers).

(c) m-cresol

A technical grade m-cresol contains only m-cresol with some traces[35] of p-cresol. m-cresol (obtained from V/o Sojuzchimexport, Moscow, USSR) was freed from its p-isomer and was purified as follows.

100 gms. of m-cresol was mixed with equal volume of sulfuric acid and stirred with a glass rod until no more streaking was noticeable. The mixture was then heated for 3 hours at 103-105°C. After careful dilution with 200-300 mls. of water, the diluted mixture was heated to the boiling point and then steam distilled until all the unsulphonated cresol was removed. It was cooled and extracted with ether. Evaporated the solution until the boiling point reached the decomposition temperature of the sulphonate (133-135°C) and then introduced steam. m-cresol was then distilled under reduced pressure.

(d) Benzyl alcohol (BDH, reagent grade, India)

Benzyl alcohol contains some amount of benzaldehyde[35]. It was purified by shaking with aqueous potassium hydroxide and extracted with ether. After washing, the extract was treated with saturated sodium bisulphite solution, filtered, washed and dried over potassium carbonate. The ether was removed by evaporation. Benzyl alcohol was distilled under reduced pressure and the middle fraction was collected and dried.

(e) Ethylene glycol (BDH, reagent grade, India)

It was dried[35] over anhydrous sodium sulphate and fractionated twice. The middle cut was used.

(f) Formic acid (Reagent grade, May & Baker Ltd. England)

It was distilled under reduced pressure at room temperature in order to prevent its decomposition[35] into water and carbon monoxide at its normal boiling point i.e. 100°C.

(g) Monomer : ω-amino enanthic acid

The monomer was obtained from the Institute of Elemento Organic Compounds, Moscow, USSR, and was found to be quite suitable for direct polycondensation since the melting point was quite agreeable with that given in the literature (195°C) and it was therefore assumed to be pure.

2.2 Polycondensation reactions

2.2.1 Apparatus

The polymerization tube (Fig.1) was made of pyrex glass, 6" in length and 1½" in diameter. One end of it was closed and the other was fitted with B29 (F) joint. An adapter with B29 (M) joint at one end and B14 (F) at the other end, having a side tube provided with a stopcock, was fitted to the polymerization tube. Nitrogen inlet with B14 (M) joint was

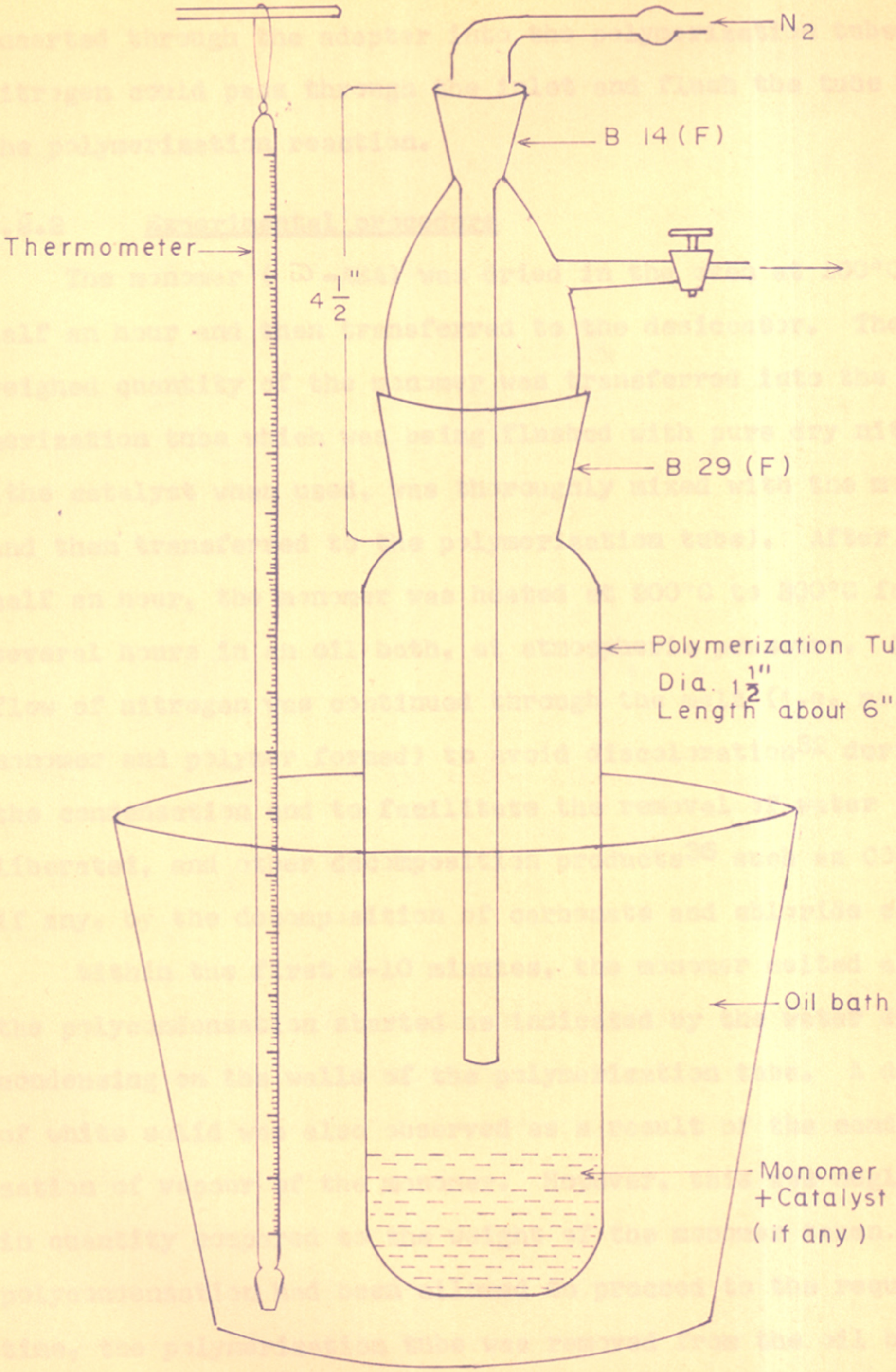


Fig. I POLYMERIZATION APPARATUS

inserted through the adapter into the polymerization tube so that nitrogen could pass through the inlet and flush the tube during the polymerization reaction.

2.2.2 Experimental procedure

The monomer (ω-AEA) was dried in the oven at 100°C for half an hour and then transferred to the desiccator. The weighed quantity of the monomer was transferred into the polymerization tube which was being flushed with pure dry nitrogen (the catalyst when used, was thoroughly mixed with the monomer and then transferred to the polymerization tube). After about half an hour, the monomer was heated at 200°C to 300°C for several hours in an oil bath, at atmospheric pressure. The flow of nitrogen was continued through the melt (i.e. melted monomer and polymer formed) to avoid discoloration[32] during the condensation and to facilitate the removal of water liberated, and other decomposition products[36] such as CO_2, HCl, if any, by the decomposition of carbonate and chloride catalysts.

Within the first 8-10 minutes, the monomer melted and the polycondensation started as indicated by the water drops condensing on the walls of the polymerization tube. A deposit of white solid was also observed as a result of the condensation of vapour of the monomer. However, this was negligible in quantity compared to the weight of the monomer taken. After polycondensation had been allowed to proceed to the required time, the polymerization tube was removed from the oil bath and the product was cooled under nitrogen. The crude polymer was light gray, hornlike and hard. Sometimes the surface of the polymer turned black which might be either due to charring (oxidation of the -CH_2 group to carbon) or due to partial depolymerization[32]. The depolymerization can be due to thermal cracking, catalytic decomposition etc. The charred portion was, however, found to be negligible.

2.2.3 Purification of the crude polymer

The polymer contained small amounts of oligomers (i.e. low mol.wt. products). To discard them, the crude polymer was dissolved in sulfuric acid which took about a week for dissolution. The solution was then poured into a large amount (about 50 times of its own volume) of water. The precipitated polymer was allowed to settle (or to float in some cases), which required another week. The polymer was then recovered on G-4 sintered disc, washed with distilled water till acid free. It was then washed with methanol and dried under reduced pressure in a vacuum oven set at 80°C till constant weight of the polymer was obtained.

2.3 Determination of the molecular weight of the polymer

2.3.1 End group measurements of the polymer

Both the end groups (viz. carboxyl -COOH and amino -NH_2) were titrated in benzyl alcohol[37]. Direct titration was preferred over conductometric or potentiometric titrations for general use on account of its rapidity and high accuracy.

(a) Carboxyl end groups measurements

About 0.1 - 0.2 gm. of the vacuum dried polymer was dissolved in 10 mls. of benzyl alcohol in a conical flask by refluxing for 15 minutes. 0.1 ml. of 1% phenol-phthalein[24] indicator was added. The hot solution was titrated to the pink end point, against 0.02 N solution of potassium hydroxide in ethylene glycol from a microburette. The blank titration on the reagents was carried out but was found to be unnecessary, as the smallest possible drop of the titrant was enough to change the color. Ethylene glycolic potassium hydroxide solution was standardized daily against 0.02 N oxalic acid.

(b) Amino end groups measurements

About 0.1 - 0.2 gm. of the vacuum dried polymer was dissolved, as above, in 10 mls. of benzyl alcohol by refluxing for 15 minutes. 0.1 ml. of thymol blue[24,38] indicator was added and the solution was titrated to the pink end point with 0.02 N hydrochloric acid. The blank titration was found to be unnecessary. Hydrochloric acid was conveniently standardized against 0.1 N sodium hydroxide which was standardized against 0.02 N oxalic acid.

(c) Calculation of the end groups

The end group concentration is measured[24] in terms of the gramme-number of end groups per unit weight of polymer. This is the same as the number of gramme-equivalents of end group per unit weight, the unit weight being chosen to be 10^6 g. The end group concentration is expressed in μ equiv./g. The end groups were calculated as follows:

No. of $-COOH$ groups = Milligrams of KOH required per gm. of the polymer

No. of $-NH_2$ groups = Milligrams of HCl required per gm. of the polymer

1000 mls. of 1 N KOH = 1 equivalent of KOH

$$(X \times N) \text{ mls. of } 1\ N\ KOH = \frac{XN}{1000} \text{ equivalents of } KOH$$

where X = titration reading

N = normality of KOH, or

$$(X \times N) \text{ mls. of } 1\ N\ KOH = \frac{XN}{1000} \times 10^6 \text{ microequivalents}$$

$$= Y$$

Z mg. of polymer = Y micro equivalents

$$1000 \text{ mg. of polymer} = \frac{1000 \times Y}{Z} = \text{No. of } -COOH \text{ groups}$$

$-NH_2$ groups were similarly calculated.

(d) Calculation of molecular weight

The relationship[24] used between number average mol.wt. ($\overline{M}_n$) and measured end groups was:

$$\overline{M}_n = \frac{10^6 . y}{n}$$

where n = total number of end groups, and

y = 1 or 2 according to whether the measured end groups are at one or both ends of the polymer molecule

2.3.2 Viscometry

Viscosity measurements were carried out in m-cresol with Ostwald U-tube viscometer suspended in a thermostatic bath at 25 ± 0.01°C. The flow times of solvent and stock solution were noted till at least two values agreed within 0.2 second.

Intrinsic viscosities were calculated by single point viscosity method, using the relationship[39]:

$$[\eta] = \frac{\sqrt{2}}{C} \sqrt{\eta_{sp} - \ln \eta_{rel}}$$

where $[\eta]$ = intrinsic viscosity, a reduced valued of η_{sp}/C at infinite dilution

C = concentration of the solution in gm./100 mls.

η_{sp} = specific viscosity

η_{rel} = relative viscosity

The mol.wts. were calculated from the intrinsic viscosities thus obtained, using Mark-Houwink's equation[2,42,43].

$$[\eta] = K\overline{M}_v^{\alpha}$$

where K and α are constants, and $\overline{M}_v$ = viscosity average mol.wt. The constants K and α were calculated from the plot of log $[\eta]$ vs. log $\overline{M}_n$ from end group analysis. The original figures of the mol.wts. have been rounded up and presented in this work.

2.4 Fractionation of the polymer

The fractionation was carried out by fractional precipitation method. Different solvent-nonsolvent systems were tried for fractionation (Ref. p. 41).

Out of these, formic acid (solvent)-formic acid + water (non solvent) system was used in preference to other systems (Ref. p. 64).

2.4.1 Apparatus

The fractionation flask (Fig.II) was made from a three necked 2 litre flask by altering its bottom to a wide cone and sealing a stopcock of 2 mm. bore to its apex, for withdrawing the lower phase. The flask was provided with a mercury seal stirrer, thermometer and an opening for introducing nonsolvent. The flask was totally immersed in a thermostatic bath controlled at 30 ± 0.1°C.

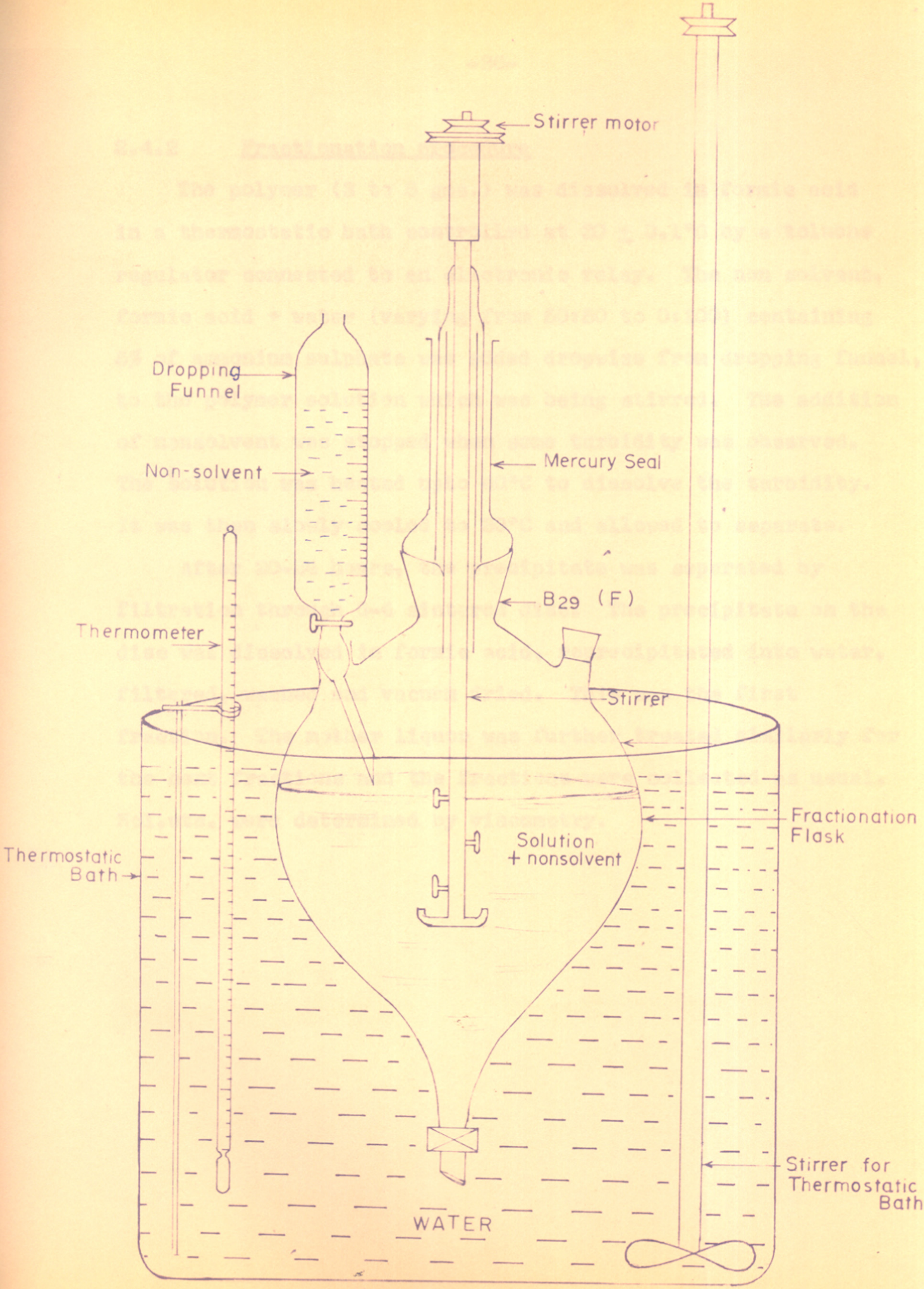


Fig.II FRACTIONATION ASSEMBLY

2.4.2 Fractionation procedure

The polymer (3 to 6 gms.) was dissolved in formic acid in a thermostatic bath controlled at 30 ± 0.1°C by a toluene regulator connected to an electronic relay. The non solvent, formic acid + water (varying from 50:50 to 0:100) containing 5% of ammonium sulphate was added dropwise from dropping funnel, to the polymer solution which was being stirred. The addition of nonsolvent was stopped when some turbidity was observed. The solution was heated upto 40°C to dissolve the turbidity. It was then slowly cooled to 30°C and allowed to separate.

After 20-24 hours, the precipitate was separated by filtration through G-4 sintered disc. The precipitate on the disc was dissolved in formic acid, reprecipitated into water, filtered, washed and vacuum dried. This was the first fraction. The mother liquor was further treated similarly for the next fractions and the fractions were collected as usual. Mol.wts. were determined by viscometry.

CHAPTER-III

RESULTS

The monomer ω-amino enanthic acid, when heated for several hours above its melting point (195°C) gave an undistillable solid polymer (nylon-7) by polycondensation reaction. The polymer was light gray in colour, tough and hornlike in appearance and was insoluble in most of the solvents.

This polycondensation reaction can be explained by the equation.

$$n\ H_2N(CH_2)_6COOH \longrightarrow [-HN(CH_2)_6CO-]_n + nH_2O$$

which is autocatalytic[12,40,41] in nature. Nitrogen helped to remove water formed during polycondensation. The reaction was studied with and without catalysts at 200-300°C for various time durations (15 minutes - 7 hours). The monomer amount was kept constant for all reactions in order to study the relative effect of temperature, time and catalysts. The results i.e. the percent conversion of monomer to polymer and the mol.wts. of the polymers obtained are given in respective tables. Besides the results of fractionation of nylon-7 have been given. The number average mol.wts. by end group measurements are also calculated and compared with those by intrinsic viscosity method. Lastly, the constants K and α in Mark-Houwink equation[2,23,42,43] for calculation of viscosity average mol.wt ($\overline{M}_v$) from intrinsic viscosity $[\eta]$ have been calculated.

3.1 Effect of temperature on polycondensation of ω-AEA (without catalyst)

The polycondensation was studied at temperatures ranging from 200-300°C for one hour. The results are presented in Table No.III.

Examination of Table No.III indicates that the temperature 200°C (which is very near to the melting point of the monomer i.e. 195°C) was sufficient for polycondensation but the yield and mol.wt. of the polymer were very low. At temperatures between 210-220°C, yield attained a steady value which remained constant upto 300°C (Fig.III-c). In the range between 200-300°C, mol.wt. was found to increase linearly with temperature (Fig.III=A) (Ref.p. 58).

3.2 Effect of time on polycondensation of ω-AEA (without catalyst)

The reaction was studied for different time intervals at 260°C. The results are shown in Table No.IV.

Table No.IV shows that the yield remained nearly constant (91-93%) for the time interval of 15 minutes to 7 hours. It means that even the period of 15 minutes was enough to polymerize the monomer (ω -AEA), though the mol.wt. of the polymer was low. With the increase in time, the mol.wt. of the polymer increased (Ref. p. 60). The percent conversion vs. time and mol.wt. vs. time have been shown in Figs. III-D and III-B respectively.

3.3 Effect of catalysts on the polycondensation of ω-AEA

Different acidic as well as alkaline catalysts were used to catalyze the polycondensation of ω-AEA.

3.3.1 Effect of acidic catalyst on polycondensation of ω-AEA

The following organic and inorganic acids were used as catalysts: acetic acid, oxalic acid, succinic acid, phthalic acid, benzoic acid, phosphoric acid and boric acid. The yields of the polymers and their respective mol.wts. with different acids have been tabulated in Table No.V.

Under the usual experimental conditions, addition of acetic acid, oxalic acid and succinic acid did not have any catalytic effect upon the polycondensation of ω-AEA. The yields of the polymers obtained were of the same order but the mol.wts. were considerably low. Benzoic acid and phthalic acid presented an intermediate state in the sense that they gave slightly higher mol.wt. polymers than those with aliphatic acids but the mol.wts. were lower than those with inorganic acids such as phosphoric acid and boric acid. Boric acid gave the highest mol.wt. polymer (Ref. p. 61).

3.3.2 Effect of alkaline catalyst on polycondensation of ω-AEA.

The following alkalies and salts were used as catalysts. Sodium hydroxide, sodium carbonate, potassium carbonate, calcium chloride, ammonium chloride and potassium hydroxide with phthalic anhydride. The results are given in Table No.VI.

Table No.VI shows that the yield was almost constant in all the cases. Using alkaline catalysts there was no increase in the mol.wt. of the polymers. On the contrary, the mol.wts. of the polymers with alkaline catalysts were lower than that without catalysts (Ref. p. 62).

3.3.3 Effect of distilled water on polycondensation of ω-AEA

The yield and mol.wt. of the polymer obtained in presence of 1% (by wt.) of distilled water, under usual experimental conditions (i.e. at 260°C for 1 hour) were about the same as that without catalyst.

	Yield %	Intrinsic viscosity $[\eta]$ dl/g	Viscosity average mol.wt. ($\overline{M}_v$)
without water	92.0	1.00	12300
with water	92.4	1.00	12350

Since there was no appreciable change in polymer yield or mol.wt. further studies on polycondensation of ω-AEA in presence of water were not carried out.

2.3.4 Polycondensation of ω-AEA under closed conditions

The polycondensation reaction was carried out under closed conditions (the closed conditions mean that passing of nitrogen was stopped after flushing the polymerization tube and its contents and during the reaction no byproduct was allowed to escape from the polymerization tube) at 260°C for 1 hour. The yield and mol.wt. of the polymer obtained were:

	Yield %	Intrinsic viscosity $[\eta]$ dl/g	Viscosity average mol.wt. ($\overline{M}_v$)
atmospheric pressure	92.0	1.00	12300
under closed conditions.	93.6	1.00	12250

These results were about the same as that with open conditions. Since neither yield nor mol.wt. was increased further reactions under closed conditions were not carried out (Ref.p. 63).

3.4 Fractionation and molecular weight distribution (MWD) of nylon-7

Mere fractionation does not give any information about the distribution of mol.wt. Hence fractions must be characterized for their mol.wts. Molecular weight distribution (MWD) has great influence on the properties of polymer. In order to study the MWD of nylon-7, it was fractionated into different fractions of different mol.wts. by fractional precipitation method. The principle of fractionation is that when nonsolvent (precipitant) is slowly added to the polymer solution (concentration being about 1%) the highest mol.wt. fraction precipitates out first. Further addition of nonsolvent gives the second highest mol.wt. fraction and so on.

Following different solvent-nonsolvent systems were tried for fractionation.

	solvent		non-solvent
(1)	Phenol	-	water
(2)	Phenol	-	methanol
(3)	m-cresol	-	cyclohexane
(4)	m-cresol	-	pet.ether
(5)	m-cresol	-	benzene
(6)	m-cresol	-	methanol
(7)	formic acid	-	formic acid + water
(8)	sulphuric acid	-	water

Out of these systems, only system formic acid (solvent)-formic acid + water (nonsolvent), was used. Others were rejected for various reasons (Ref.p. 64).

To draw MWD curves, the knowledge of weight fraction (x), integral weight fraction (I) and differential weight fraction (D) was needed. Weight fraction (x) was the ratio of the actual weight 'y' gm. of the polymer fraction, to the total weight 'z' gm. of the recovered polymer after fractionation

$$\text{i.e.} \quad x = \frac{y}{z}$$

The fractions were arranged (Table Nos. VII to X) according to the increasing order of their mol.wts. In this series, an integral weight fraction (I_d) of a particular fraction 'd', was obtained by taking a sum of the weight fractions ($I_a + I_b + I_c + I_d$) of the fractions a, b, c and d. Integral weight fraction of n^{th} fraction was the sum of the weight fractions of a, b, c .... and n.

The data of integral weight fractions thus obtained were plotted against respective mol.wts. and the integral MWD curves were obtained (curves marked 'A' in Figs. IV, V, VI and VII).

On the integral MWD curves, different mol.wts (x-axis) were chosen at fixed intervals e.g. 1000, 2000, 3000 etc. The corresponding integral weight fractions on the curves were noted. Differential weight fraction D_d for fraction 'd' was obtained by dividing (I_e-I_d), the difference between two consecutive integral weight fractions, by (M_e-M_d), the difference between two corresponding mol.wts. The values of D (calculated similarly) were plotted vs. mean mol.wts. and the differential MWDs were obtained (curves marked 'B' in Figs.IV,V,VI and VII). These experimental curves have been compared with the most probable distribution curves, at different extents of reaction (Fig. VIII) (Ref.p. 69).

Corrections (for one polymer sample) for the loss of low mol.wt. fractions during the fractionation procedure, were applied. The corrected integral and differential MWDs are shown in Fig.IV-A' and IV-B' (dotted lines) respectively. Similar corrections can as well be made for other polymer samples.

3.5 End group measurements of nylon-7

End group measurement, being an absolute method, gives number average mol.wt. ($\overline{M}_n$) directly, without involving any constant. In the present work both the end groups viz. amino ($-NH_2$) and carboxyl ($-COOH$) groups of nylon-7 were titrated in benzyl alcohol.

The end groups were calculated as shown in Chapter II (Ref.p. 33). The mol.wts. were calculated therefrom, using the formula[24]:

$$\overline{M}_n = \frac{2 \times 10^6}{\text{Total No.of end groups}}$$

The term 2 in the numerator occurs as the end groups are at both the ends of polymer chain. The results have been tabulated in Table No.XI. Table XI shows that for all the polymer samples the number of $-COOH$ groups was always higher than the number of $-NH_2$ groups (Ref.p. 70).

The decrease of end groups with increase in mol.wt. and with increase in temperature (of polycondensation reaction) has been shown graphically in Fig. IX (Ref. p. 70).

3.6 Relationship between intrinsic viscosity $[\eta]$ and mol.wt. (M) for nylon-7

Mark-Houwink equation[2,42,43]:

$$[\eta] = K\overline{M}_v^{\alpha}$$

for calculating viscosity average mol.wt. of the polymer from intrinsic viscosity involves two constants K and α . For the calculation of these constants for nylon-7, the mol.wts. of different polymer samples were measured by end group measurements and their respective intrinsic viscosities were determined by viscometry. The results have been given in Table No.XII.

Log.$[\eta]$ versus log $(\overline{M}_n)$ has been plotted in Fig.X. The relation seemed to be linear on a logarithmic plot. The slope of the straight line gave α value. By putting this value in the above equation, the value of K was calculated. The values for α and K are 0.6 and 0.9×10^{-2} respectively, for nylon-7, for m-cresol solvent at 25°C (Ref.p. 72).

3.7 Infra red spectrum of nylon-7

Infra red spectra of few samples of nylon-7 were taken in nujol. All the spectra were found to be identical. One of them is shown in Fig.XI.

Fig.XI shows the principal absorption bands at 3194 cm^{-1}

(N-H stretch); 2859 cm^{-1} (CH_2 sym. stretch); 1631 cm^{-1} (amide I); 1550 cm^{-1} (amide II) and 1456 cm^{-1} (CH_2 bending). Some addition absorption bands were also observed. An attempt has been made to distinguish nylon-7 spectrum from those of other resins (Ref.p. 73).

Table No.III

Effect of temperature on polycondensation of ω-ABA (without catalyst)

Monomer = 10 gms.
Time = 1 hr.

No.	Temperature °C	Percent conversion (yield %)	Intrinsic viscosity $[\eta]$ dl/g.	viscosity average mol.wt. ($\overline{M}_v$)
(1)	200	35.6	0.34	1400
(2)	210	93.7	0.51	3250
(3)	220	93.9	0.61	4550
(4)	240	93.1	0.86	9200
(5)	260	92.4	1.00	12300
(6)	280	92.74	1.25	19250
(7)	300	91.75	1.30	21000

Table No.IV

Effect of time on polycondensation of (ω-AEA) (without catalyst)

Monomer = 10 gms.

Temperature = 260°C

No.	Time (hours)	Percent conversion (yield %)	Intrinsic viscosity $[\eta]$ dl/g	Viscosity average mol.wt. ($\bar{M}_v$)
(1)	15 min.	92.6	0.42	2150
(2)	½ hr.	91.9	0.77	7350
(3)	1 hr.	92.0	1.00	12300
(4)	2 hrs.	92.7	1.21	17950
(5)	5 hrs.	90.8	1.49	27550
(6)	7 hrs.	-	2.06	47750

Table No.V

Effect of acidic catalysts on the polycondensation of ω-ABA

Monomer = 10 gms
Temperature = 260°C
Time = 1 hour
Catalyst concentration = 1% (by weight)

No.	Catalyst	Yield %	Intrinsic viscosity $[\eta]$dl/g	Viscosity average mol.wt. ($\overline{M}_v$)
(1)	Without catalyst	92.0	1.0	12300
(2)	Acetic acid	94.4	0.59	4300
(3)	Oxalic acid	92.5	0.53	3500
(4)	Succinic acid	94.1	0.68	5650
(5)	Phthalic acid	93.9	0.84	8750
(6)	Benzoic acid	85.5	0.91	10350
(7)	Phosphoric acid	88.8	1.09	14700
(8)	Boric acid	94.8	1.69	35250

Table No.VI

Effect of alkaline catalysts on polycondensation of ω-AMA

Monomer = 10 gms.
Temperature = 260°C
Time = 1 hour
Catalyst concentration = 1% (by weight)

No.	Catalyst	Yield %	Intrinsic viscosity $[\eta]$ dl/g	Viscosity average mol.wt ($\overline{M}_v$)
(1)	Without catalyst	92.0	1.0	12300
(2)	Sodium hydroxide	93.5	0.65	5250
(3)	Sodium carbonate	91.7	0.62	4650
(4)	Potassium carbonate	93.9	0.70	6050
(5)	Calcium chloride	94.3	0.84	8650
(6)	Ammonium chloride	91.9	0.71	6250
(7)	Potassium hydroxide + phthalic anhydride	94.3	0.55	3700

Table No.VII

Fractionation of nylon-7 by fractional precipitation method

Solvent = formic acid (90% w/w)
Non-solvent = formic acid + water(varying from 50:50 to 0:100)
Nylon-7 of intrinsic viscosity= 1.21
Molecular weight = 17950 (Ref. Table No IV, Expt. 4)
Concentration of solution = 1% (6 gms. in 600 mls.)
Ammonium sulphate = 5 gms. per 100 mls. of nonsolvent
Temperature = 30° ± 0.1°C
Total time for fractionation = 22 days (about 530 hours)

Sr. No.	Fraction No.	Wt. of the fraction in gms.	Weight fraction $x = \frac{y}{z}$	Integral weight fraction (I)	Intrinsic viscosity $[\eta]$ dl/g	Viscosity average mol.wt. ($\bar{M}_v$)
1.	14	0.051	0.0094	0.0094	0.32	1250
2.	13	0.056	0.0103	0.0197	0.43	2300
3.	12	0.100	0.0183	0.0380	0.44	2400
4.	11	0.051	0.0093	0.0473	0.55	3700
5.	10	0.033	0.0060	0.0533	0.64	5000
6.	9	0.281	0.0516	0.1049	0.64	5000
7.	8	0.035	0.0064	0.1113	0.66	5300
8.	7	0.083	0.0152	0.1265	0.76	7200
9.	6	0.740	0.1359	0.2624	0.99	12000
10.	5	0.664	0.1218	0.3842	1.00	12300
11.	4	0.243	0.0447	0.4289	1.02	12900
12.	3	0.780	0.1432	0.5721	1.04	13300
13.	2	1.651	0.3031	0.8752	1.27	19900
14.	1	0.681	0.1249	1.0001	1.39	23950
		z= 5.449				

The polymer recovery was 90.80%

Table No.VIII

Fractionation of nylon-7 by fractional precipitation method

Solvent - formic acid (90% w/w)

Non-solvent -formic acid + water (50:50 to 0:100)

Nylon-7 of intrinsic viscosity = 0.77

Molecular weight = 7350 (Ref.Table IV, Expt.2)

Concentration of solution = 1%(2.5 gms.in 250 mls.)

Ammonium sulphate = 5 gms.per 100 mls. of nonsolvent

Temperature = 30° ± 0.1°C

Total time for fractionation = 10 days(about 240 hrs.)

Sr.No.	Fraction No.	Wt.of the fraction in gms.	Weight fraction (x)	Integral weight fraction (I)	Intrinsic viscosity $[\eta]$dl/g	Viscosity average mol.wt ($\overline{M}_v$)
1.	5	0.341	0.2280	0.2280	0.66	5400
2.	4	0.249	0.2280	0.4560	0.67	5500
3.	3	0.289	0.1930	0.6490	0.83	8450
4.	2	0.277	0.1850	0.8340	0.87	9400
5.	1	0.340	0.1660	1.0000	0.92	10500

The recovery of the polymer was 60%

Table No.IX

Fractionation of nylon-7 by fractional precipitation method

Solvent = formic acid(90% w/w)
Non-solvent = formic acid + water(varying from 50:50 to 0:100)
Nylon-7 of intrinsic viscosity = 0.65
Molecular weight = 5250 (Ref.Table VI, Expt.2)
Concentration of solution = 1% (4 gms.in 400 mls.)
Ammonium sulphate = 5 gms.per 100 mls.of nonsolvent
Temperature = 30° ± 0.1°C
Total time for fractionation = 18 days(about 430 hours)

Sr.No.	Fraction No.	Wt.of the fraction in gms.	Weight fraction (x)	Integral weight fraction (I)	Intrinsic viscosity $[\eta]$ dl/g	Viscosity average mol.wt. ($\bar{M}_v$)
1.	8	0.103	0.0286	0.0286	0.34	1400
2.	7	0.185	0.0514	0.0800	0.37	1700
3.	6	0.094	0.0261	0.1061	0.56	3800
4.	5	1.191	0.3309	0.4370	0.63	7650
5.	4	0.028	0.0078	0.4448	0.82	8250
6.	3	1.911	0.5308	0.9756	0.83	8500
7.	2	0.071	0.0197	0.9953	0.94	10950
8.	1	0.013	0.0035	0.9988	-	-

The polymer recovery was 89.9%

Table No.X

Fractionation of nylon-7 by fractional precipitation method

Solvent = formic acid (90% w/w)
Non-solvent = formic acid + water (50:50 to 0:100)
Nylon-7 of intrinsic viscosity = 0.61
Molecular weight = 4550 (Ref.Table III, Expt.3)
Concentration of solution = 1% (3 gms.in 300 mls.)
Ammonium sulphate = 5 gms. per 100 mls. of nonsolvent
Temperature = 30° ± 0.1°C
Total time for fractionation = 12 days(about 288 hrs.)

Sr.No.	Fraction No.	Wt.of the fraction in gms.	Weight fraction (x)	Integral weight fraction (I)	Intrinsic viscosity $[\eta]$dl/g	Viscosity average mol.wt. ($\overline{M}_v$)
1.	6	0.423	0.1700	0.1700	0.60	4500
2.	5	0.466	0.1740	0.3440	0.61	4600
3.	4	0.476	0.1690	0.5130	0.61	4650
4.	3	0.461	0.1626	0.6756	0.62	4750
5.	2	0.465	0.1706	0.8462	0.63	4850
6.	1	0.444	0.1546	1.0008	0.65	5240

The polymer recovery was 91.1%

Table No.XI

End group measurements of nylon-7

Polymer dissolved in benzyl alcohol (1% solution)

Titrant for -COOH groups = alcoholic KOH (0.03 N approx.)
Titrant for $-NH_2$ groups = aqueous HCl (0.03 N approx.)
Indicator for-COOH groups = phenol-phthalein
Indicator for $-NH_2$groups = thymol blue

No.	No. of $-NH_2$ groups	No.of -COOH groups	Total No.of end groups	Number average mol.wt. by end group measurements ($\overline{M}_n$)	Viscosity average mol.wt. ($\overline{M}_v$)
1.	621	877	1498	1350	1400
2.	318	513	831	2400	2150
3.	263	445	708	2850	3250
4.	215	331	546	3650	4550
5.	107	223	330	6050	7350

The above table shows that for all the polymer samples, the number of -COOH groups was always higher than the number of $-NH_2$ groups(Ref.p 70).

Table No.XII

Intrinsic viscosity $[\eta]$ - molecular weight (M) relationship for nylon-7 polymer

No.	Intrinsic viscosity $[\eta]$	Log $[\eta]$	Number average mol.wt. by end group measurements ($\bar{M}_n$)	Log ($\bar{M}_n$)
1.	0.34	$\bar{1}.5321$	1350	3.1255
2.	0.42	$\bar{1}.6185$	2400	3.3819
3.	0.51	$\bar{1}.7110$	2850	3.4510
4.	0.61	$\bar{1}.7831$	3650	3.5639
5.	0.77	$\bar{1}.8867$	6050	3.7825

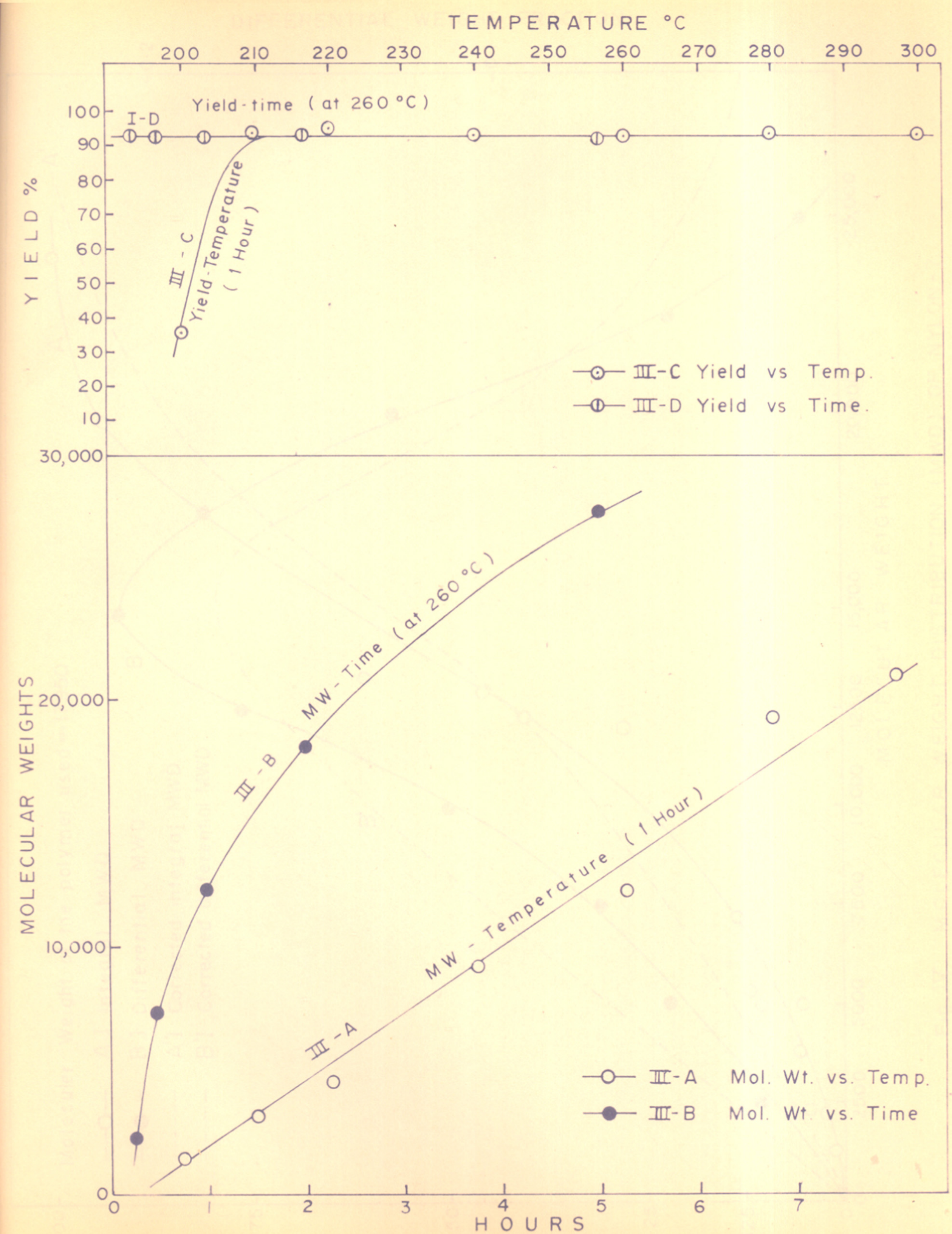


Fig. III EFFECT OF TEMPERATURE & TIME ON MOLECULAR Wt. & PERCENT CONVERSION (yield) OF NYLON-7

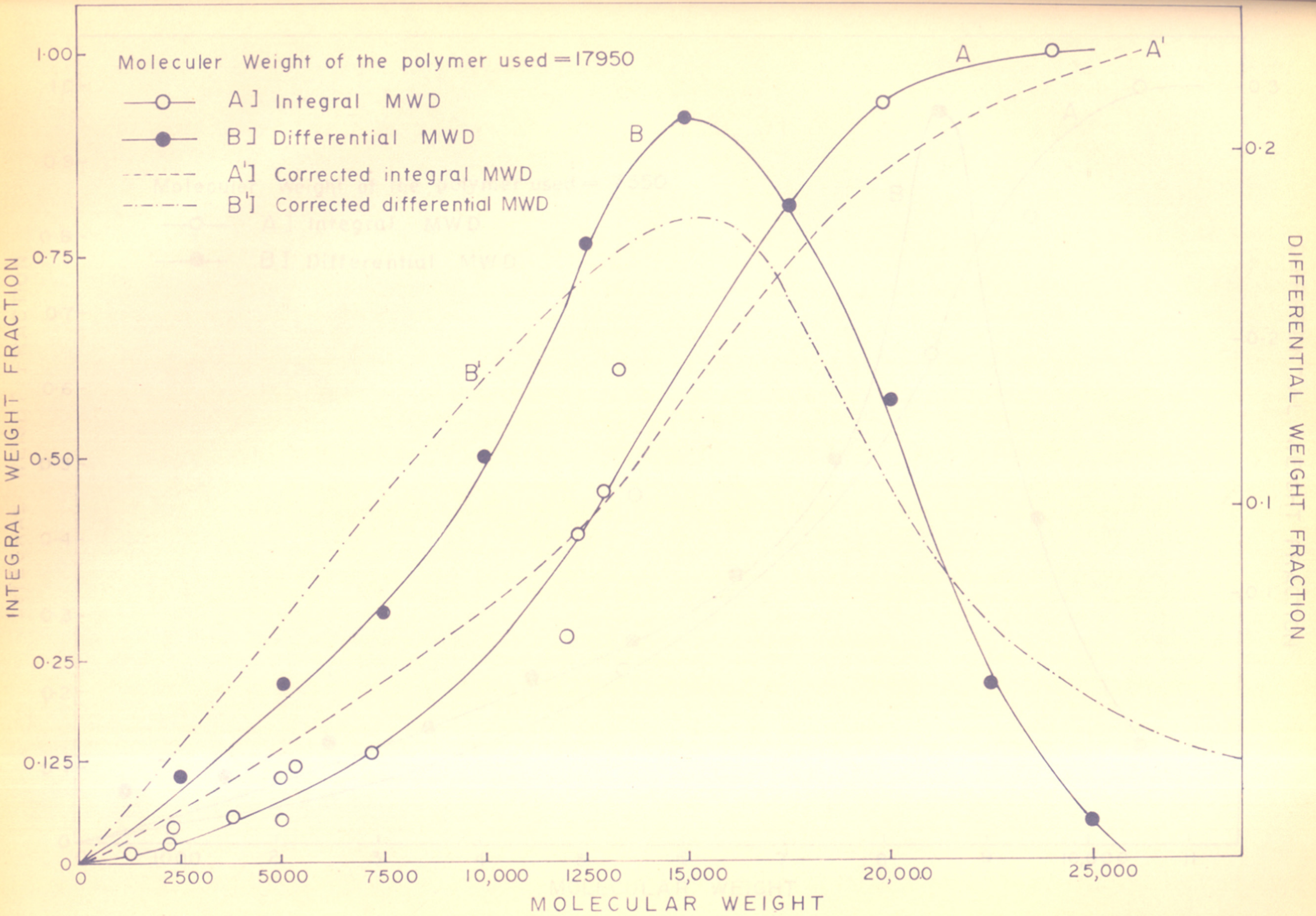


Fig. IV: MOLECULAR WEIGHT DISTRIBUTION (MWD) OF NYLON-7

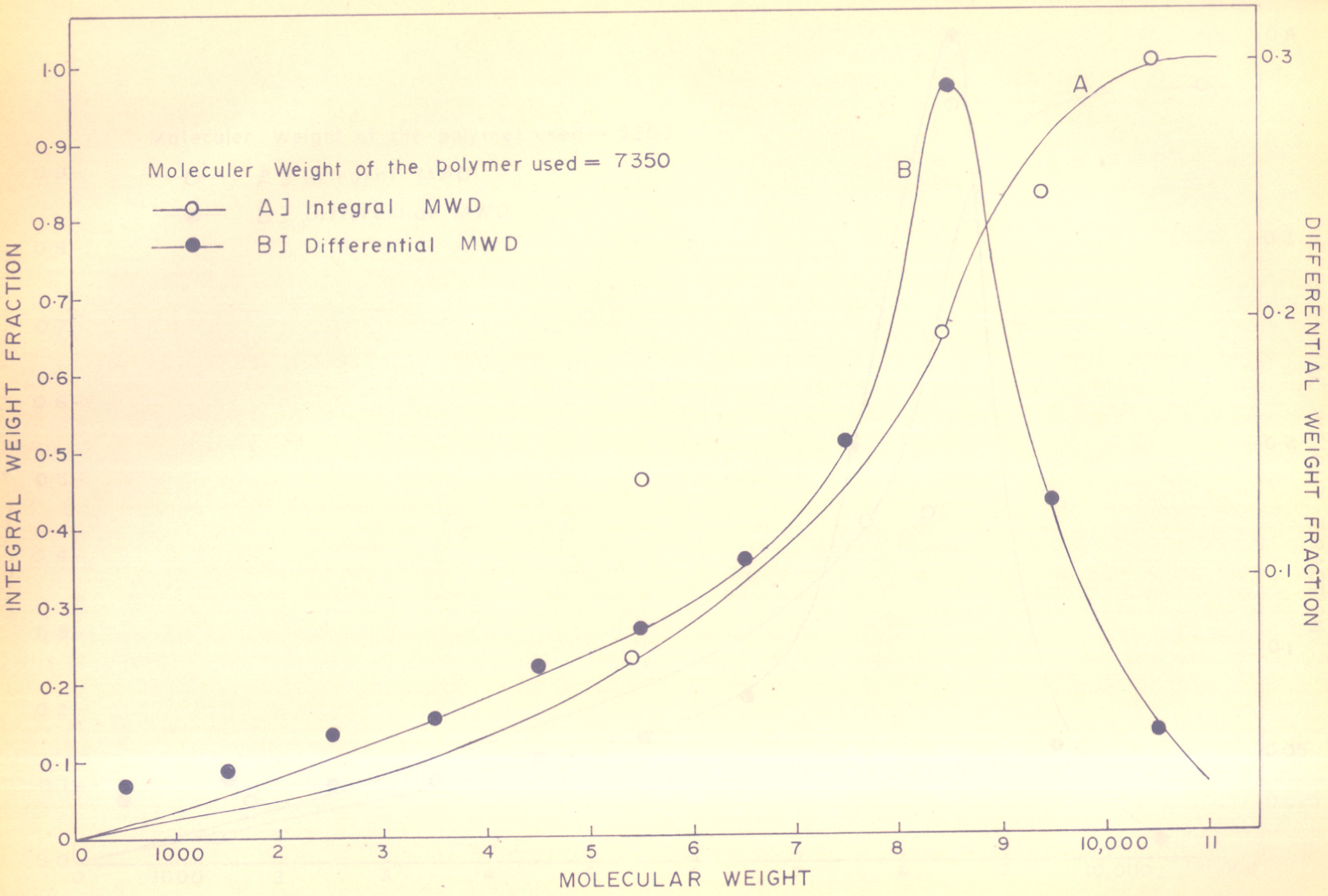


Fig. V: MOLECULAR WEIGHT DISTRIBUTION (MWD) OF NYLON-7

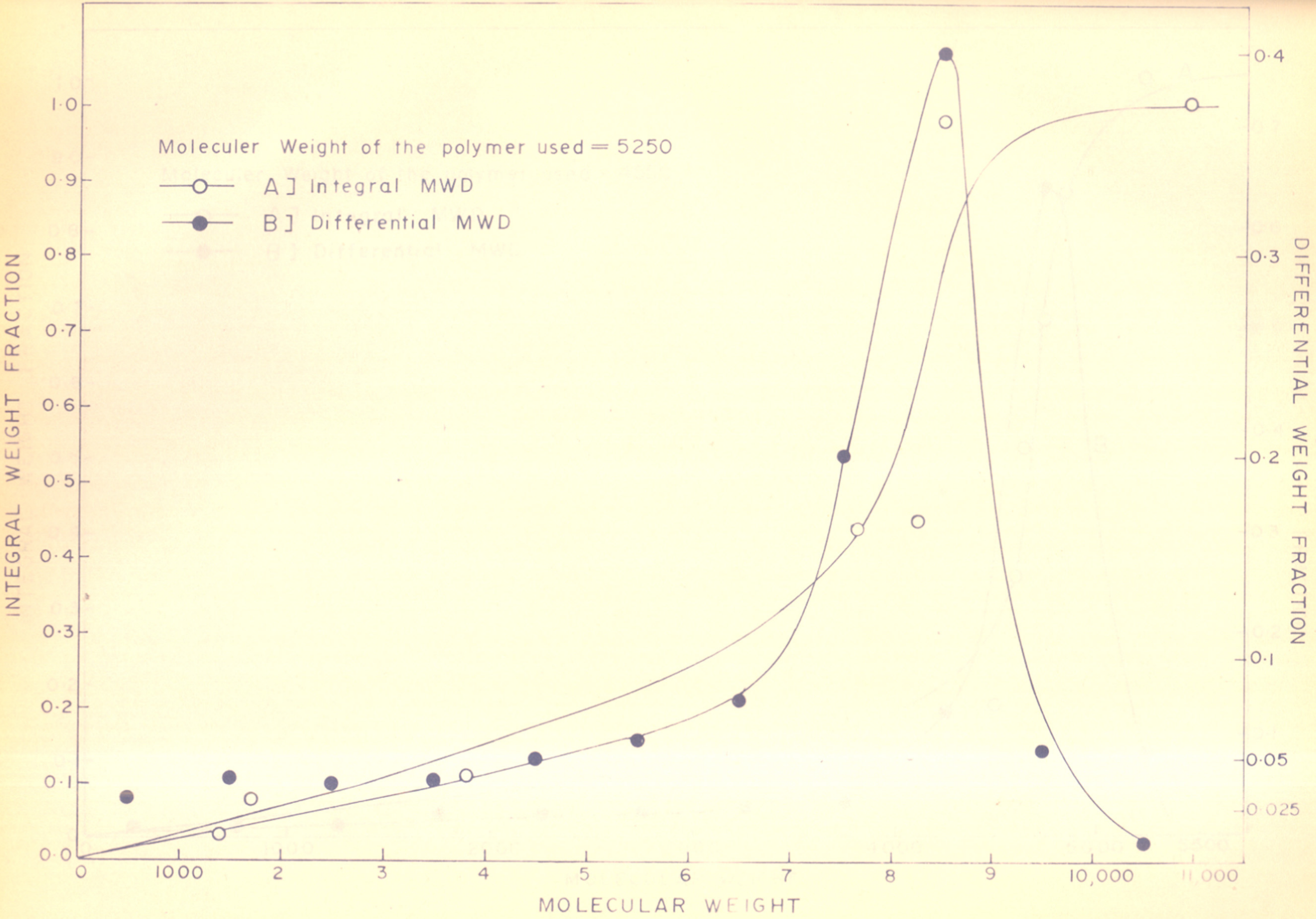


Fig. VI: MOLECULAR WEIGHT DISTRIBUTION (MWD) OF NYLON-7

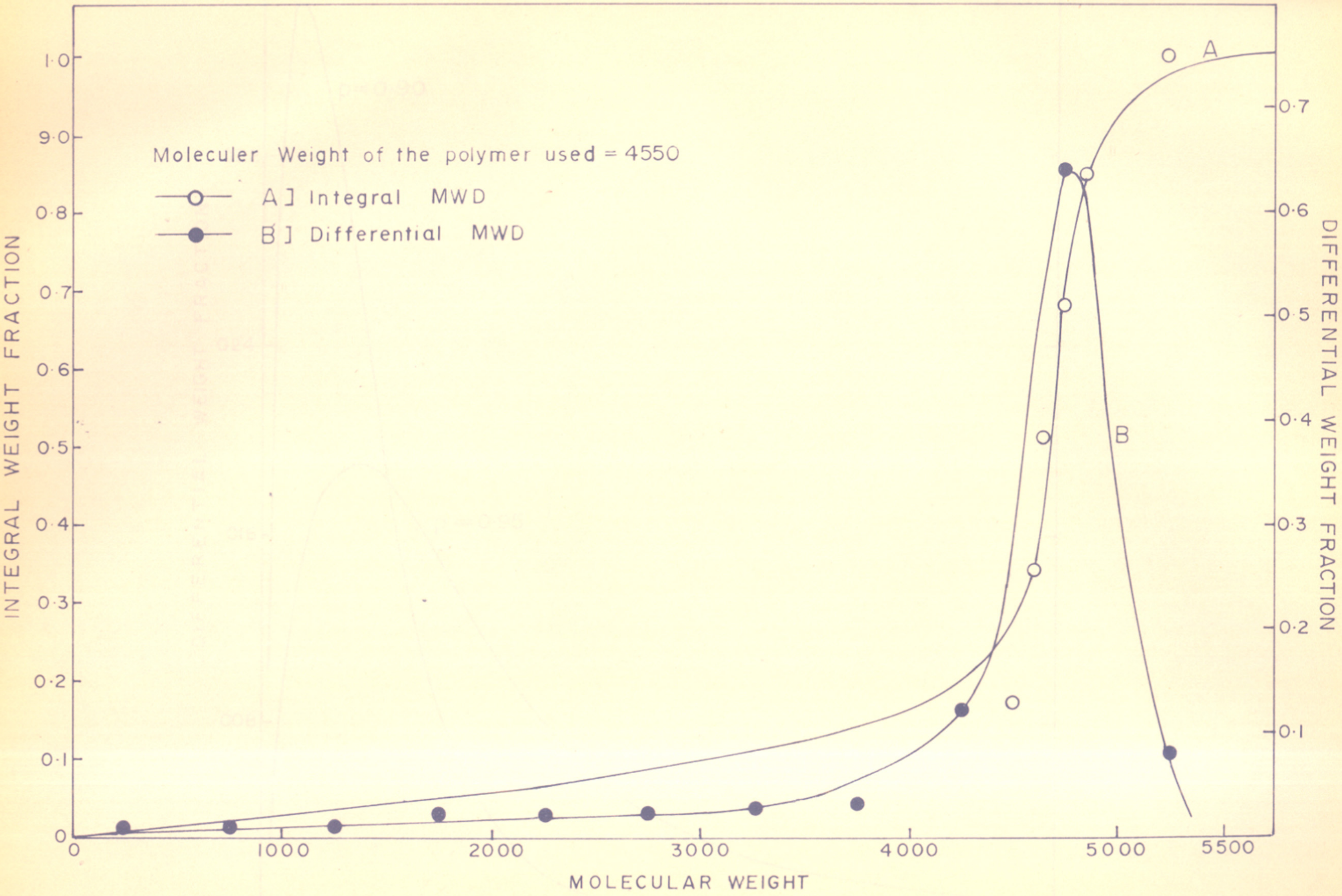


Fig. VII : MOLECULAR WEIGHT DISTRIBUTION (MWD) OF NYLON-7

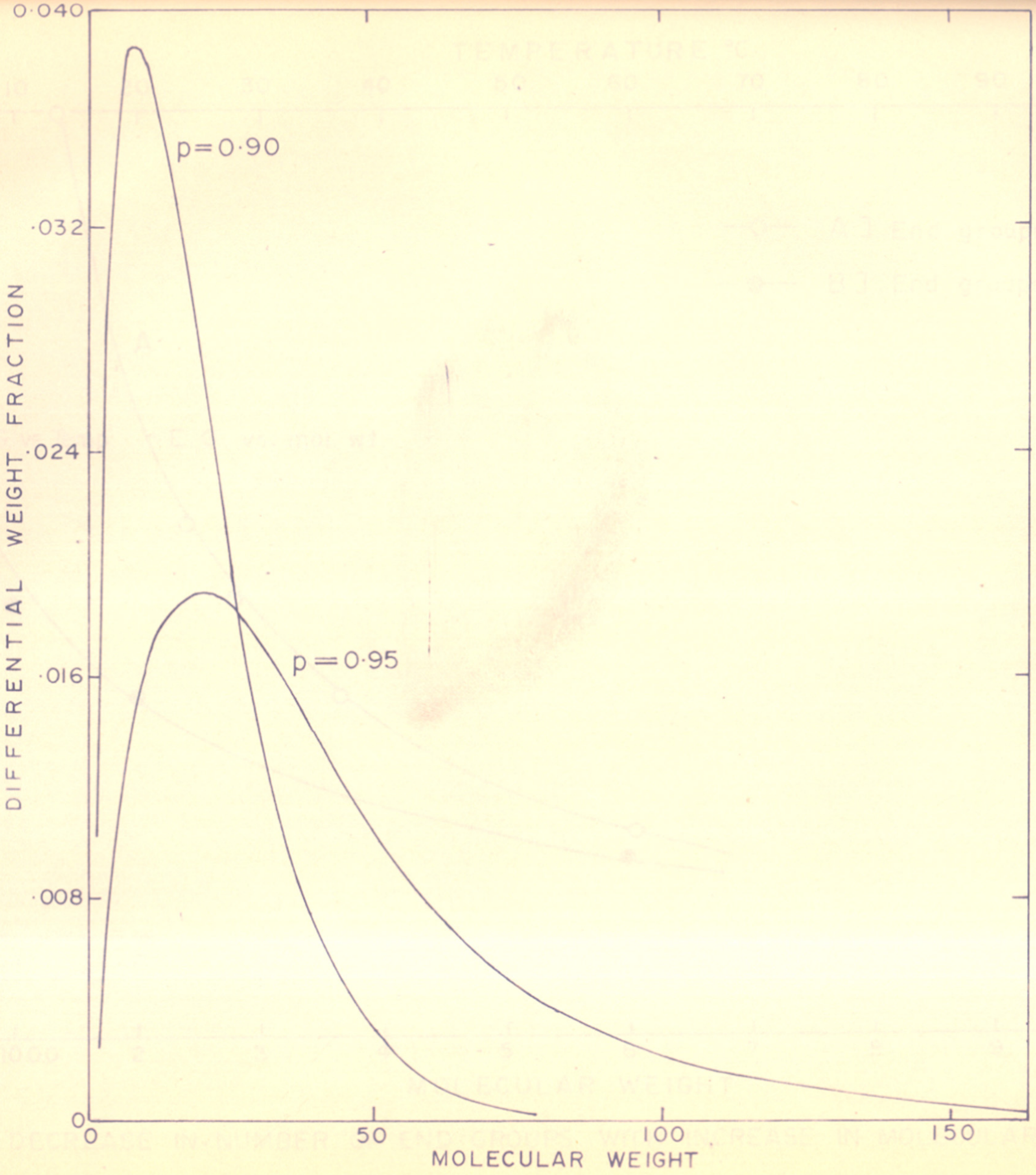


Fig. VIII MOST PROBABLE DISTRIBUTION

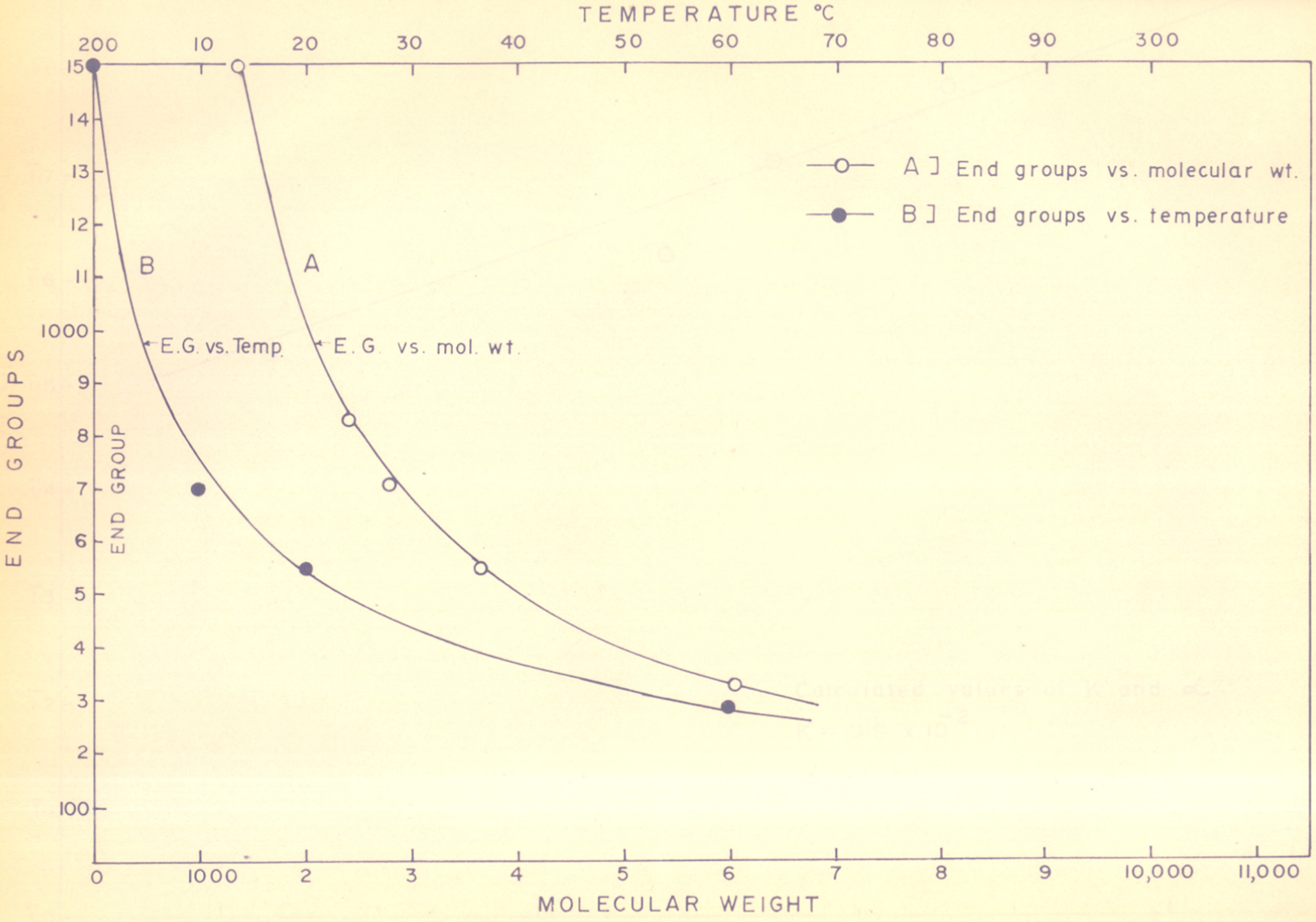
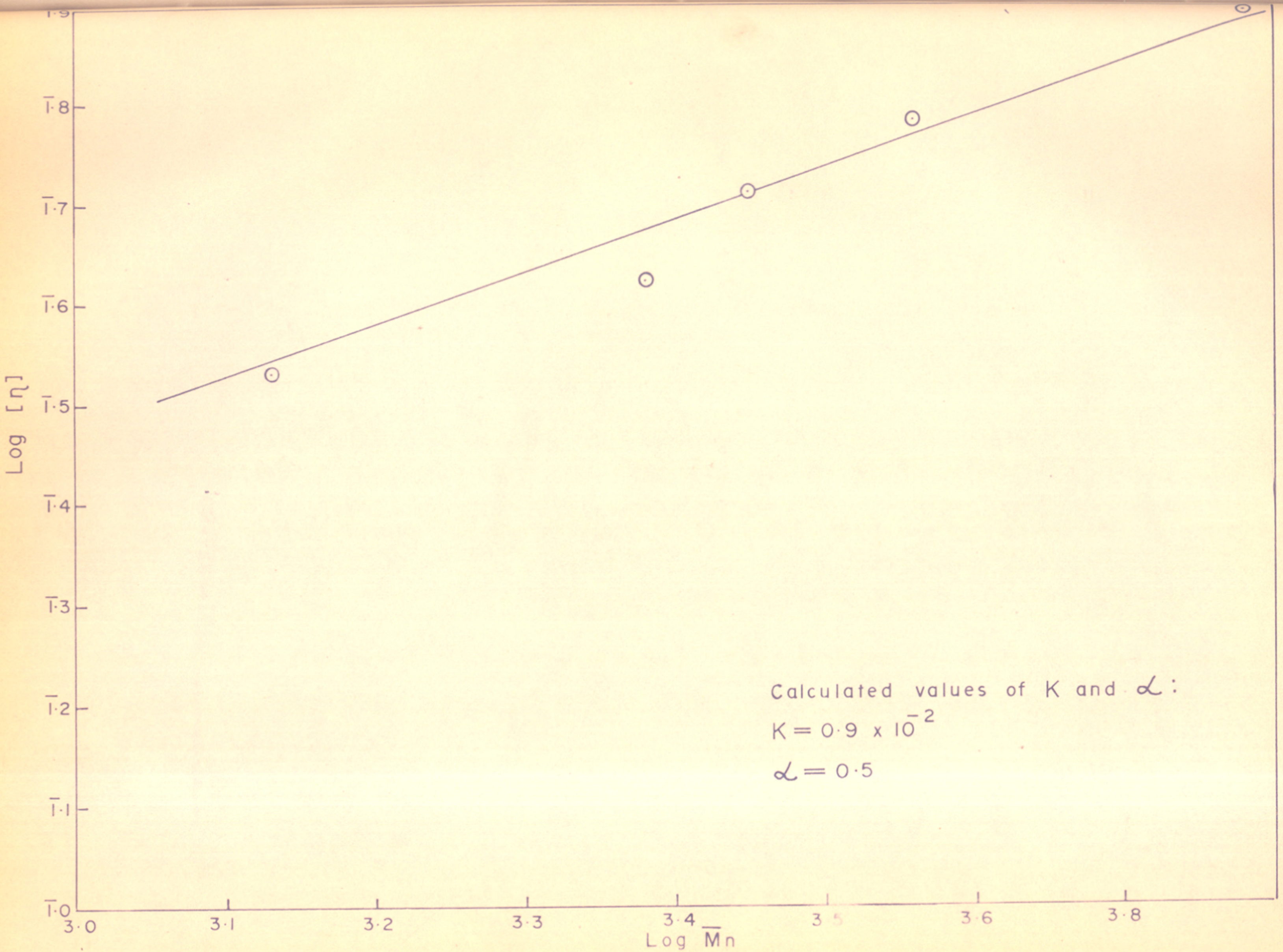


Fig. IX: DECREASE IN NUMBER OF END GROUPS WITH INCREASE IN MOLECULAR Wt. & TEMPERATURE.



Calculated values of K and α:

$K = 0{\cdot}9 \times 10^{-2}$

$\alpha = 0{\cdot}5$

Fig. X : LOG-LOG PLOT OF INTRINSIC VISCOSITY [η] Vs. NUMBER AVERAGE MOL. WT ($\overline{M}n$, BY END GROUP MEASUREMENTS)

CHAPTER-IV

DISCUSSION

4.1 Polycondensation reactions of ω-AEA with probable mechanism

The results of the polycondensation reactions of ω-AEA to nylon-7, at 200-300°C, for 15 minutes to 7 hours with and without catalysts have been discussed in this Chapter.

Probable mechanism

The mechanism, neither for polycondensation of ω-AEA nor that for other ω-amino acids, is clearly described in the literature. However, from a knowledge of the well known mechanism of esterification reaction, the mechanism of polycondensation of ω-AEA may be described as follows:

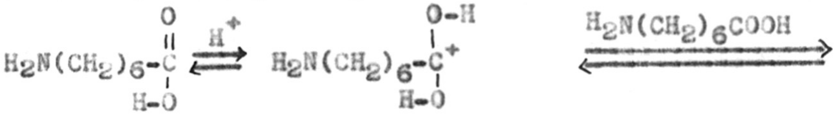
The polycondensation reaction,

$$n\ H_2N(CH_2)_6COOH \longrightarrow [-HN(CH_2)_6CO-]_n + nH_2O$$

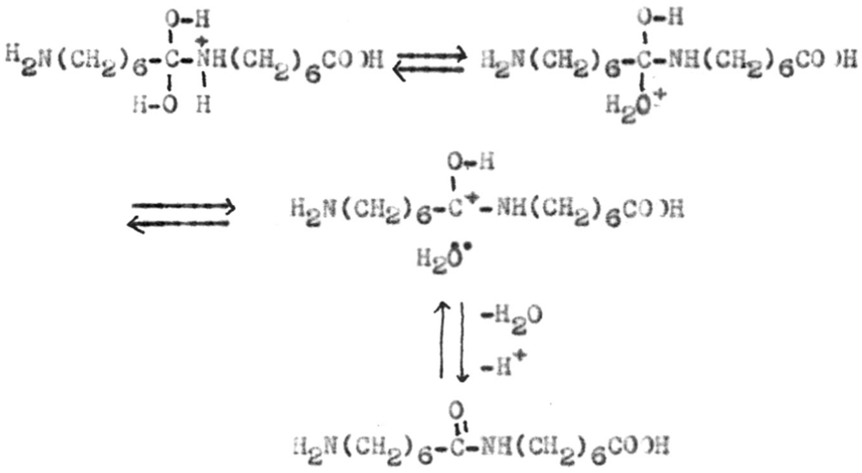
is autocatalytic[12,40,41] in nature. The monomer ω-AEA is in equilibrium as:

$$H_2N(CH_2)_6COOH \rightleftharpoons H^+H_2N(CH_2)_6COO^-$$

The proton H^+ from -COOH group is responsible for the reaction, the way being shown as follows[44]:



$$H_2N(CH_2)_6-\overset{\overset{O}{\|}}{\underset{\underset{H-O}{|}}{C}} \overset{H^+}{\rightleftharpoons} H_2N(CH_2)_6-\overset{\overset{O-H}{|}}{\underset{\underset{H-O}{|}}{C^+}} \xrightleftharpoons{H_2N(CH_2)_6COOH}$$



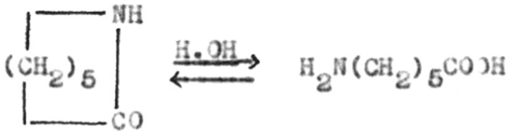
$$H_2N(CH_2)_6-\underset{\underset{H-O}{|}}{\overset{\overset{O-H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{+}{N}}H(CH_2)_6COOH \rightleftharpoons H_2N(CH_2)_6-\underset{\underset{H_2O^+}{|}}{\overset{\overset{O-H}{|}}{C}}-NH(CH_2)_6COOH$$

$$\rightleftharpoons H_2N(CH_2)_6-\underset{H_2O^{\bullet}}{\overset{\overset{O-H}{|}}{C^+}}-NH(CH_2)_6COOH$$

$$\Big\uparrow\Big\downarrow \begin{matrix}-H_2O\\ -H^+\end{matrix}$$

$$H_2N(CH_2)_6-\overset{\overset{O}{\|}}{C}-NH(CH_2)_6COOH$$

In case of hydrolytic polymerization[63] of caprolactam, the scission of lactam ring takes place first, thus creating two functional groups viz. $-NH_2$ and $-COOH$ at the two ends of the monomer unit.



$$(CH_2)_5\ \text{NH}\ \text{CO} \underset{}{\overset{H.OH}{\rightleftharpoons}} H_2N(CH_2)_5COOH$$

caprolactam **ε-amino caproic acid**

The newly created acid, either accepts one more molecule of caprolactam on its $-NH_2$ side (the acceptance being catalyzed by $-COOH$ group), or it condenses with a similar molecule of acid formed, thus giving rise to a dimer molecule. This continues till a high mol.wt. nylon-6 polymer is formed. In case of alkaline catalysts, salt formation of caprolactam is the first step, which is then followed by polymerization.

Coming back to the polycondensation of ω-AEA, it is assumed that each successive addition of a monomer unit to a polymeric chain formed, involves amidation reaction. In the initial stages of polycondensation reaction, random combinations of two monomer units occur to form dimer molecules. These dimer molecules then combine with equal reactivity, either with a monomer unit or with another dimer unit to form trimers or tetramers respectively. Thus all polymer chains start growing at approximately the same time and continue to grow with relatively slow but steady rate with one step at a time, to give a polymer molecule.

In case of acid catalyzed reactions, the hydrogen ion H^+ is furnished by the external acid by its ionization and it helps in polycondensation. The polycondensation reactions in the present investigations, did not take much time but further processing i.e. purification and drying of the polymer was time consuming. It required a week or so, just to dissolve the crude polymer in sulfuric acid. (m-cresol, in trial experiment, could dissolve hardly 10% of the polymer within a pretty long period of one month). The long period required might be because the polymer was very hard and tough.

Another time consuming stage was the separation of the polymer from liquid phase, after reprecipitation of it into water from its solution in sulfuric acid. It took another week to separate the polymer. It was, ofcourse, due to the hydrogen bonding nature of the polymer (Ref.p. 64).

Polymer recovery on G-4 sintered disc, by filtration, then washing with distilled water till acid free and vacuum drying to a constant weight required 4-5 days.

The total time for one experiment from polycondensation reaction to vacuum drying of the polymer, was about 20 days. The experimental conditions and effect of catalysts have been discussed below.

4.2 Effect of variation in experimental conditions

4.2.1 Reaction temperature (200-300°C)

The temperature studies of these reactions are shown in Table No.III. At the lower reaction temperature (200°C), the percent conversion of monomer to polymer was considerably less (35.6%) because this temperature is very near to the melting point of the monomer (195°C). At such a low temperature, the rate of conversion is slow and hence the yield is low. Moreover, the oligomers formed (which seemed to be more than 50% in this case) were soluble in water and during purification of the polymer (Ref.p 32) they remained in solution only and were not precipitated.

The high and constant conversion (90-93%) at 210°C and above is probably explained by the fact that, though the polycondensation reaction of ω-AEA is reversible like other esterification reactions, the forward reaction (condensation of monomer unit) predominates over the backward reaction (depolymerization). This is clear from the fact that mol.wt. increases with time and hence the extent of reaction and polycondensation proceeds upto about 90-93% conversion.

Cubbon[40] ends up with a similar reason for the higher conversion of enantholactam $\overline{HN(CH_2)_6CO}$ and capryllactam $\overline{HN(CH_2)_7CO}$ against only 70% conversion of caprolactam $\overline{HN(CH_2)_5CO}$, when polymerized under similar conditions. He points out that polymerization of caprolactam proceeds to about 70% conversion and then it is slowed down as the depropagation reaction becomes increasingly important. On the contrary, enantholactam and capryllactam polymerize to almost complete conversion and the depolymerization reaction is evidently insignificant for these lactams.

The present writer finds that the mol.wt. of nylon-7 polymer is unaffected by the non-exclusion of water liberated during the polycondensation reaction under the applied experimental conditions. In other words, water does not hydrolyze nylon-7 to any appreciable extent. This also provides evidence for the fact that depolymerization reaction is negligible compared to the polycondensation reaction (Ref.p. 63). The monomer ω-AEA is quantitatively[16] converted into nylon-7 which hardly contains any monomer molecule.

The second observation from Table No.III and Fig.III-A was that the mol.wt. of the polymer increased with temperature. The low mol.wt. at 200°C, 210°C and 220°C was probably due to the fact that, when the oligomers reached a certain chain length, they became insoluble in monomeric amino acid (m.p. of nylon-7 being 225°C) and crystalized out.

As the temperature is raised, the viscosity of the medium decreases and the mobility of the molecules increases. Hence the number of collisions between polymer chain ends are more at higher temperatures, thus giving rise to the higher mol.wt. products.

Figs. III-C and III-A show the effect of temperature on the yield of the polymer and its mol.wt. The yield increased very fast between 200°C and 210°C. It attained a steady value between 210°C and 220°C and remained constant upto 300°C. Increase in mol.wt. seemed to be a linear function of temperature.

4.2.2 Reaction time (15 minutes to 7 hours)

Even a short period of 15 minutes (Table No.IV) was found enough to convert about 92.6% of the monomer into polymer. This conversion was almost constant (90-93%) for different time durations upto 7 hours, because of the similar reasons explained earlier. (Ref.4.2.1 p.58).

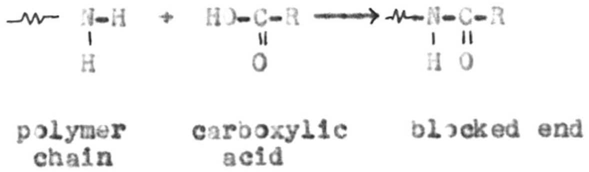
Further, it was observed that the mol.wt. of the polymer increased with the time. This is explained by the fact that, the polymer chains, (short or long), have free $-NH_2$ and $-COOH$ groups. Long period provides chances for more number of collisions between polymer ends leading to further condensation. From the theory, of classical reactions, it is known that the rate of reaction increases with the increase of collisions and gives rise to a high mol.wt. product.

Fig.III-D shows the constant yield of the polymer and Fig.III-B shows the increase in mol.wt. of the polymer with time within the range 15 minutes to 7 hours. The increase, however, was not linear, as that with temperature. In the initial stages (Fig.III-B) say upto 1 hour, the mol.wt. increased rapidly because more end groups were available for condensation. After 1 hour the rate of increase in mol.wt. was slightly diminished as the concentration of the end groups was decreased.

4.2.3 Acidic catalysts in polycondensation of ω-AEA

Under the usual experimental conditions (Ref.p. 31) the acids used (1% by weight) gave the polymer yield between 90-94% except benzoic acid (85.5%) and phosphoric acid (88.8%)(Table No.V).

It was also observed that the inorganic acid catalyzed polymers were of higher mol.wts. than those catalyzed by organic acids. The organic acids gave low mol.wt. polymers (even lower than that without catalyst) because they acetylate, as is well known, the $-NH_2$ group of the monomer ω-AEA or of the linear polymer chain.



$$\sim\!\sim \underset{H}{\underset{|}{N}}{-}H \; + \; HO{-}\underset{O}{\underset{\|}{C}}{-}R \longrightarrow \sim\!\sim \underset{H}{\underset{|}{N}}{-}\underset{O}{\underset{\|}{C}}{-}R$$

Thus one end of the chain is blocked and no further condensation on this end is possible. The presence of an amide forming reactant limits the degree of polymerization (DP) to some value lower than that in the absence of such reactant. The balance of functionality is disturbed by blocking one end of the growing polymer chain. Because of this property, the carboxylic acids[2,47,48,50,52,55] are used to control the mol.wt. of the polymer when high mol.wt. polymer is not desirable for spinning.

The inorganic acids, being strong acids, as compared to the organic weak acids, ionize very fast giving rise to more hydrogen ions H^+, which in their turn polymerize the monomer as shown under (4.1) (Ref.p. 55). Among inorganic acids, boric acid gave the highest yield (95%) and highest mol.wt. polymer (35,250). Boric acid is very little effective as a stabilizing agent[50] for the polyamide macromolecule while phosphoric acid stabilizes the mol.wt. more effectively than boric acid and hence the latter gave lower mol.wt. polymer. Phosphoric acid catalyzed nylon was bright white and had a shining appearance too.

Similar catalytic action of boric acid[48-50,52] and phosphoric acid[53,54] was observed by some workers. The most effective catalyst found was 1% of boric acid used by weight of ω-ASA. Boric acid produced polymers were of higher mol.wt. than those produced by other catalysts under the same conditions.

4.2.4 Alkaline catalysts for polycondensation of ω-ASA

Table No.IV shows that there is no significant variation in the percent conversion of the monomer to polymer, with different alkaline catalysts, under the usual experimental conditions. The conversion was nearly the same, with all the alkaline catalysts, and it was 92-94%. However, the mol.wts. were much lower as compared to the polymer obtained without any catalyst. Though the alkaline polymerization of[9,32,36,48,54,56-62] ε-caprolactam is well acknowledged as it gives polymer within several minutes, the use of alkaline catalysts for the polycondensation of ω-AEA in the present work, did not prove any increase in mol.wt. of the polymer nor in the percent conversion of the monomer. The reasons however are not known. More extensive studies are required for clarification.

4.2.5 Water for polycondensation of ω-AEA

Under the usual experimental conditions, addition of water (1% by weight of ω-AEA) had effect neither on yield of the polymer nor on its mol.wt.

	Yield	mol.wt.
with water	92.4%	12,350
without water	92.0%	12,300

The above results mean that water did not catalyze the polycondensation of ω-AEA. In case of caprolactam polymerization[9,51,63-67], water helps to open the lactam ring to produce the condensable reactive functional end groups $-NH_2$ and $-COOH$. But in case of ω-AEA, the end groups are already present[20,31,68]. Since neither polymer yield nor mol.wt. of it was improved by the use of water, it was not used any further.

4.2.6 Polycondensation of ω-AEA under closed conditions

In these experiments, the stream of nitrogen was not passed throughout the experiment but was stopped after flushing the polymerization tube and the monomer in it. The outlet of the polymerization tube was stopped. The inlet of nitrogen was also stopped. No volatile byproduct such as water was allowed to escape and hence the conditions were called 'closed conditions'. Some experiments were planned under closed conditions. The results were:

	yield	mol.wt.
closed conditions	93%	12250
usual conditions	92%	12300

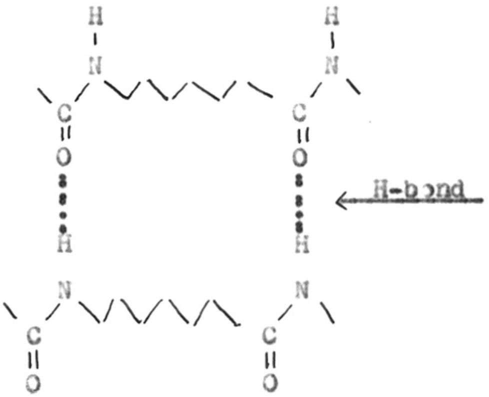
This leads one to conclude that the water liberated during condensation does not hydrolyze the polymer formed. Since the reactions under closed conditions were by no way advantageous, further studies on these lines were not carried out.

4.3 Fractionation and molecular weight distribution of nylon-7

Fractionation of the polymer was carried out in order to determine its molecular weight distribution (MWD).

4.3.1 Different systems used and difficulties observed

Different solvent-nonsolvent systems were tried for the fractionation (Ref.p. 41). The inherent difficulty in fractionating crystalline and semi-crystalline polymers, like nylon-7, has been well reviewed in literature. In the case of these polymers, fractional precipitation involves inherent difficulties due to the lack of liquid-liquid separation. Fractionation above the melting point of the polymer overcomes this difficulty but it is not practicable. Nylon-7 is semi-crystalline and the hydrogen-bonds (H-bonds) between $-\underset{\underset{O}{\|}}{C}-$ and $-\underset{\underset{H}{|}}{N}-$ groups of the two neighbouring chains in the structure as shown below, should be overcome to achieve a meaningful separation of the individual fraction.



structure of nylon-7

The systems phenol-methanol, phenol-methanol + water, m-cresol-benzene, m-cresol-ether, m-cresol-cyclohexane presented serious difficulties. Non-solvent added to the system just to make it turbid, when left overnight, resulted in complete precipitation and no polymer was left in solution for further fractionation. This might be due to the H-bonding nature of the polymer. In addition to that extra precaution to avoid excessive loss of ether (due to its fast evaporation) was necessary in case of m-cresol-ether system. Benzene being very poor nonsolvent, large amounts of benzene required for precipitation from m-cresol-benzene system, and thus created handling difficulties.

The choice of phenol-water system required temperatures higher than 66°C, which is a critical consolute temperature for phenol-water mixture. Below it phenol and water are not miscible. Polymer had a tendency to go to the phenol rich phase and hence the precipitated polymer fraction redissolved in the phenol rich phase. At high temperatures fractionation was likely to be efficient as the H-bonds are easily overcome at higher temperatures, but this system was not used in order to avoid high temperatures, which were difficult to maintain.

Apart from high temperatures, H-bonding can as well be overcome by the use of strong electrolytes[69] such as ammonium sulphate or sodium chloride. Successful fractionation of nylon-7 was achieved by using formic acid (solvent) and formic acid + water (50:50 to 0:100) mixture containing about 5% of ammonium sulphate in it as the non-solvent.

The fractionation process was found to be time consuming. It took several days (10 to 22 days) to fractionate one polymer sample. After precipitating one fraction in the experiment, it took about 1-2 days, just for the separation of the precipitated polymer fraction from solution phase, even after adding an electrolyte to break the H-bonds.

4.3.2 Fractionation results

Table Nos.VII - X show the actual weights of the fractions, their weight fractions and corresponding mol.wts.

It was observed that the fractions obtained in all the cases were not uniform. Because the control of the fractionation was very difficult due to the H-bonding nature of the polymer. Inspite of excessive care excercised during fractionation, some reversal of the mol.wt. in the early fractions was noticed due to factors which were not apparent. One of them might be the reverse[70] order fractionation, which is explained by the decrease in polymer concentration during fractionation process. The fractionation of higher mol.wt. portions is carried out at higher concentrations than lower mol.wt. portions. Because the concentration of the polymer decreases by successive addition of non-solvent and by removal of preceding fractions.

4.3.3 Most probable distribution curve

The MWD resulting from condensation of bifunctional monomers has been obtained by Flory[18]. In a linear condensation polymer formed from a difunctional monomer, say ω-amino acid, the probability that a molecule is composed of' x'units can be found out as follows:

H-HN R CO ——— HN R CO —·····HN R CO - OH

1 2 x-1 x

The probability that the -COOH group of the first unit is condensed, is equal to p. Or p may be defined as the probability that a given functional group has reacted, which is equal to the fraction of all functional groups of the same type, which have been condensed. The probability that the -COOH of second unit has undergone amidation is also equal to p. For x-1 linkages in series, the probability is the product of their separate probabilities i.e. (p) (p) (p).... upto (x-1) times which is equal to p^{x-1}. The probability of the x^{th} -COOH group is 1-p. Hence the probability (N_x) of the molecule of 'x' units is:

$$N_x = p^{x-1} (1-p) \qquad \ldots(1)$$

The total number of x-mers is given by:

$$N_x = N(1-p)p^{x-1} \qquad ...(2)$$

where N = total number of molecules of all sizes. But $N = N_o(1-p)$, where N_o = total number of units. Putting this value of N in equation (2):

$$N_x = N_o(1-p)^2 . p^{x-1} \qquad ....(3)$$

The mol.wt. of each species (x-mer) is directly proportional to 'x', if the weight (H + OH) for each molecule is neglected. Hence the weight fraction can be written as:

$$W_x = \frac{x\ N_x}{N_o}$$

For low mol.wt. tails, the error is more. Substituting the value of $\frac{N_x}{N_o}$ from equation (3):

$$W_x = x(1-p)^2\ p^{x-1} \qquad ...(4)$$

The same derivation holds for the polymers formed by condensation of two functional units of the type A-A and B-B.

The most probable weight distribution curves calculated by Flory from equation (4) are shown in Fig. VIII.

In these distributions, the proportion of very low mol.wt. polymers is small and is diminished as the average mol.wt. is increased. Maxima occurs very near the number average value of 'x' i.e.

$$x = \bar{x}_n = \frac{1}{(1-p)}$$

Cubbon[40] ends up with a similar reason for the higher conversion of enantholactam $\overline{HN(CH_2)_6CO}$ and capryllactam $\overline{HN(CH_2)_7CO}$ against only 70% conversion of caprolactam $\overline{HN(CH_2)_5CO}$, when polymerized under similar conditions. He points out that polymerization of caprolactam proceeds to about 70% conversion and then it is slowed down as the depropagation reaction becomes increasingly important. On the contrary, enantholactam and capryllactam polymerize to almost complete conversion and the depolymerization reaction is evidently insignificant for these lactams.

The present writer finds that the mol.wt. of nylon-7 polymer is unaffected by the non-exclusion of water liberated during the polycondensation reaction under the applied experimental conditions. In other words, water does not hydrolyze nylon-7 to any appreciable extent. This also provides evidence for the fact that depolymerization reaction is negligible compared to the polycondensation reaction (Ref.p. 63). The monomer ω-AEA is quantitatively[16] converted into nylon-7 which hardly contains any monomer molecule.

The second observation from Table No.III and Fig.III-A was that the mol.wt. of the polymer increased with temperature. The low mol.wt. at 200°C, 210°C and 220°C was probably due to the fact that, when the oligomers reached a certain chain length, they became insoluble in monomeric amino acid (m.p. of nylon-7 being 225°C) and crystalized out.

As the temperature is raised, the viscosity of the medium dryness to recover low mol.wt. material. But it was not done as the presence of very low mol.wt. material was not suspected. As a test case, in one of the fractionations ($p = 0.99$), the loss of unrecovered polymer was assumed to be entirely due to the loss of soluble low mol.wt.fraction, whose mol.wt. is lower than the last recovered fraction. The MWDs calculated on this basis are shown as dotted lines in Fig. IV-A' and B'. The corrected distribution bears greater resemblance to the expected distribution, particularly in the low mol.wt.range. This lends support to the assumption that the major error in the determination of the MWDs has been the inefficient recovery of the low mol.wt. fractions.

In view of this, the narrow[71-74] distributions obtained for polyamides by fractional precipitation method are most probably due to the inefficient fractionation achieved by fractional precipitation method. The two phase extraction method gives flat curves while precipitation method usually gives[71] sharp curves. The use of ammonium sulphate to obtain liquid-liquid separation during fractionation in this investigation partly overcome such separation difficulties but required efficiency at the low mol.wt. end could not unfortunately be achieved.

4.4 End group measurements of nylon-7

Both amino ($-NH_2$) and carboxylic ($-COOH$) groups were titrated in the same solvent i.e. benzyl alcohol, using thymol blue and phenolphthalein indicators respectively.

Table No.XI shows that in all the cases, the carboxylic groups were always more in number than amino groups. Or in other words, the mol.wts. calculated from amino groups were always higher than those calculated from carboxylic groups. The higher number of -COOH groups is explained by the fact that benzyl alcohol oxidizes[75] to benzoic acid by atmospheric oxygen. The newly oxidized alcoholic groups are also counted in the carboxylic group measurements. Larger deviations[37] between the numbers of two end groups might as well be due to prolonged heating or due to the presence of some impurities in the starting materials. The difference was, however, overcome by averaging the two numbers.

Similar results were observed by some workers[69,76-78] in this field. Some contradictory results were observed by Yumoto[79]. He found that -COOH groups were one third of $-NH_2$ groups.

Fig.IX shows the decrease in concentration of end groups along with time and mol.wt. As the time increases, more and more groups are condensed giving rise to higher and higher mol.wt. products i.e. their concentration decreases. The curves should overlap one another, according to the equal reactivity theory (at a time one $-NH_2$ and one -COOH group get condensed). But because of some experimental errors and inefficient measurements due to difficult judgement of end point, two different curves are observed[63].

4.5 Viscosity measurements

Since many viscosity measurements had to be made in the present work, a single viscosity measurement was made to calculate intrinsic viscosity $[\eta]$ (it is a limiting value of η_{sp}/C, at infinite dilution).

The widely used equations[80] to determine $[\eta]$ from single viscosity measurements are:

$$\eta_{sp}/C = [\eta](1 + k' \eta_{sp}) \qquad \text{by Huggins,}$$

$$[\eta] = \frac{a}{c} (\eta_r^{1/a} - 1) \qquad \text{by Baker, and}$$

$$\eta_{sp}/C = [\eta]e^{k [\eta] C} \qquad \text{by Martin.}$$

But all these equations have their own unknown constants that have to be calculated before use.

Soloman[39] and Guita proposed an equation:

$$[\eta] = \frac{\sqrt{2}}{C} \sqrt{\eta_{sp} - \ln \eta_r}$$

and verified for different polymer solution systems. The values of $[\eta]$ were in accord with those obtained by extrapolation. The above equation has no unknown constant and could be used readily.

4.6 Relationship between $[\eta]$ and $[M]$

The log values of ml.wts. by end group measurements vs. log values of $[\eta]$ by single point measurement have been plotted in Fig.X. The plot is a straight line indicating some relation between $[\eta]$ and $[M]$.

The Mark-Houwink equation:

$$[\eta] = K \overline{M}_v^{\alpha}$$

for the calculation of $\overline{M}_v$ from $[\eta]$, can be written as:

$$\log [\eta] = \log K + \alpha \log \overline{M}_v ,$$

which is of the form $y = mx + C$, where m is a slope of the straight line and C is the intercept on y axis.

From Fig.X, the slope of the straight line gave the value from which the K value was calculated by putting the value of α in Mark-Houwink equation. The values are: $\alpha = 0.5$; $K = 0.9 \times 10^{-2}$, for nylon-7 in m-cresol at 25°C.

A survey of the existing literature to the best of the knowledge of the writer, prevails that the constants K and α for nylon-7 in Mark-Houwink equation are not reported so far. This is the first time they have been determined in this work.

These values are well in theoretical limits[2,10,18,22] (α between 0.50 and 1.00 and K between 0.5×10^{-4} and 5×10^{-4}).

4.7 Infra red spectrum of nylon-7

The infra red absorption spectrum of nylon-7 prepared in the present work, was studied to have a comparison with the spectra of other nylons and resins, and to see whether the polymers prepared were crystalline.

The infra red absorption spectrum of nylon-7 recorded on Perkin-Elmer Infracord Spectrophotometer No.137-B, in nujol mull, is shown in Fig.XI. The spectrum shows absorption at

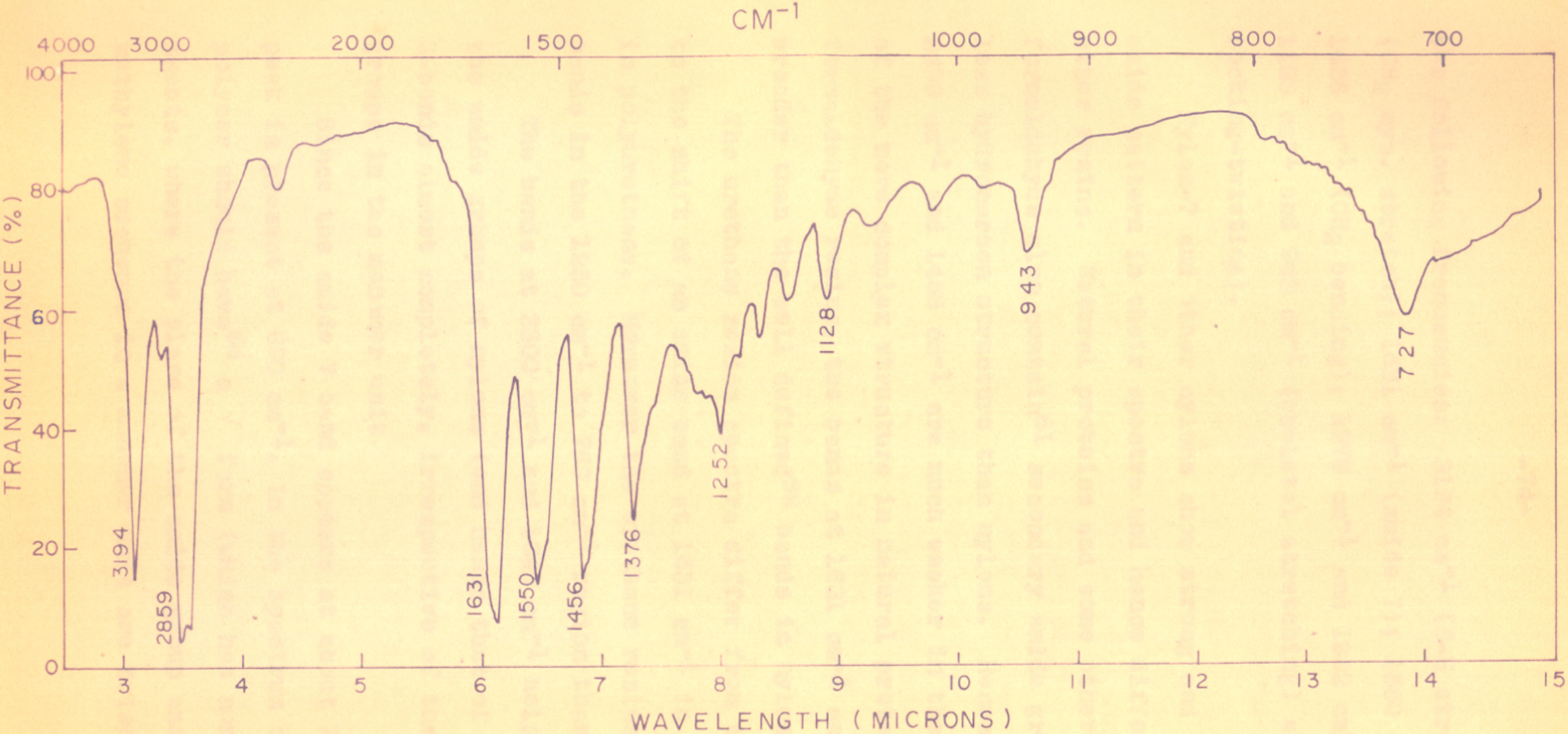


Fig. XI INFRARED SPECTRA OF NYLON-7

the following frequencies: 3194 cm^{-1} (N-H stretch); 2859 cm^{-1} (CH_2 sym. stretch); 1631 cm^{-1} (amide I); 1550 cm^{-1} (amide II); 1456 cm^{-1} (CH_2 bending); 1376 cm^{-1} and 1252 cm^{-1} (CH_2 wagging); 1128 cm^{-1} and 943 cm^{-1} (skeletal stretching) and 727 cm^{-1} (CH_2 rocking-twisting).

Nylon-7 and other nylons show strong and invariant secondary amide pattern in their spectra and hence differ from almost all other resins. Natural proteins and some other resins like urea-formaldehyde also contain[81] secondary amide groups, but have less hydrocarbon structure than nylons. Hence the bands at 2899 cm^{-1} and 1456 cm^{-1} are much weaker in the former. Because of the more complex structure in natural proteins and urea-formaldehyde resins, the bands at 1631 cm^{-1} and 1550 cm^{-1} are broader than the well defined[82] bands in nylons.

The urethane resins spectra differ from that of nylons due to the shift of an amide band at 1631 cm^{-1} in nylon to 1695 cm^{-1} in polyurethane. Moreover the urethane resins have much stronger bands in the 1250 cm^{-1} to 769 cm^{-1} region than nylons.

The bands at 3300 cm^{-1} and 1640 cm^{-1} help[83] to prove that the amide groups of nylons (and hence that of nylon-7) form H-bonds almost completely, irrespective of the number of $-CH_2$ groups in the monomer unit.

Since the amide V band appears at about 725 cm^{-1} and no peak is present at 690 cm^{-1}, in the spectrum of nylon-7, the polymer should have[84] a γ form (which has non-planar pleated sheets, where the plane of the amide group and the plane of the methylene sequence in a monomer unit are twisted by a certain angle). Hence the polymer must be crystalline one (amide V in amorphous polymer appears below 680 cm^{-1}).

4.8 Conclusion

By the detailed study of the polycondensation of ω-ABA to nylon-7, it has been possible to establish the optimum conditions to get the required mol.wt. polymer. Though the convincing evidences have been presented in the literature for the use of alkaline catalysts for the polymerization of ϵ-caprolactam, the said catalysts were found to be unsuitable for the polycondensation of ω-ABA. Organic acids also did not yield higher mol.wt. polymers as they blocked the $-NH_2$ end of the polymer chain, after reaching a certain chainlength, by acetylation. The use of the organic acids as stabilizers has thus been confirmed. Inorganic acids viz. boric acid and phosphoric acid gave higher mol.wt. polymers, boric acid being the most effective among the catalysts series used in doing so.

Fractionation procedure has been standardised with the system formic acid (solvent) - formic acid + water (nonsolvent) by fractional precipitation procedure. The molecular weight distribution curves obtained had a narrow distribution of Poisson or Gaussian type.

The constants K and α in Mark-Houwink equation are not reported so far in the literature. They have been computed from the viscosity and mol.wt. data obtained for the first time and the constants are within the limits theoretically suggested. The constants can be used henceforth to calculate mol.wt. of nylon-7 viscometrically.

More extended studies of the polycondensation reactions of ω-AEA with certain useful catalysts such as phosphoric acid and boric acid, for different monomer-catalyst ratios will widen the scope of this work. The molecular weight distribution can be derived by some novel technique like gel permeation chromatography, which remains to be worked out.

CHAPTER-V

SUMMARY

The discovery of synthetic fibre nylon-66 by Carothers and the intensive researches later on by some other workers in the field, have helped us to overcome the scarcity of natural fibres. Nylon-7 is one of the members of the polyamide family, which has got better thermal and light stability and better elasticity than nylon-66 or nylon-6. Its properties are most suited for its use as a tyre cord material. The monomer ω-amino enanthic acid (ω-AEA) for nylon-7 is produced nowadays by a novel technique known as telomerization.

In the present work, the polycondensation reactions of ω-AEA to nylon-7 were studied first without catalysts and then with acid and alkaline catalysts. The polymer thus obtained was characterized by its molecular weight distribution (MWD). The studies were carried out on the following lines:

(i) The polycondensation reactions were carried out at 200°-300°C in an inert atmosphere of nitrogen, first without any catalyst and then with catalyst. It was observed that the molecular weight of the polymer (without any catalyst) increased with temperature as well as with time within the ranges 200°-300°C and 15 minutes to 7 hours respectively.

This observation confirmed the theoretical assumption that in polycondensation reactions, the molecular weight increases with temperature and time.

Amongst the catalysts used, inorganic acids were found to be more effective than the organic acids as they gave higher molecular weight polymers. Boric acid was found to be the most effective in the series studied. Though alkaline catalysts are reported to be quite popular in polymerizing ϵ-caprolactam to nylon-6, they have been proved by the present studies to be ineffective to catalyze polycondensation of ω-AEA. The H-bonding and crystalline nature of nylon-7 have been proved and confirmed by IR.

(ii) To study the MWD of nylon-7, the polymer obtained was fractionated by fractional precipitation method by progressive addition of non-solvent to the dilute polymer solution. Many solvent-nonsolvent systems were tried amongst which formic acid (solvent) - formic acid + water (nonsolvent) was found to be the most practical. The integral and differential MWD curves were constructed and the curves were compared with most probable distribution curves by Flory. The experimental distributions proved the postulated identity of the theoretical curves.

(iii) End group measurements of some of the polymer samples were carried out in one and the same solvent and the molecular weights were calculated therefrom. The intrinsic viscosities of the same polymer samples were determined with Ostwald Viscometer. Making use of these values of molecular weights by end group measurements and intrinsic viscosities by viscometry, the constants K and α in Mark-Houwink equation $[\eta] = K\overline{M}_v^{\alpha}$, were calculated. These values for nylon-7 are not so far recorded in the literature. The molecular weights of the remaining polymers were determined viscometrically using these constants.

It may be concluded that the optimum experimental conditions for the polycondensation of ω-ABA to nylon-7, need inorganic acids to catalyze the reaction, if higher molecular weight polymers are desired.

CHAPTER-VI

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