I. INTRODUCTION

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I.1 GENERAL :

1(a) POLYMERS :

In day-to-day activities, we come in touch with many materials made up of plastics, rubbers, fibers, foams, etc, which generally fall under the category of polymers i.e. compounds formed by more or less regular repeatition of large number of same atomic groupings joined by chemical bonds into long linear chains with or without side branches or long chains cross-linked into three-dimensional networks. The repeat unit of a polymer is equivalent or nearly equivalent to monomer(s), or starting material(s) from which the polymer is formed. The length of the polymer chain is specified by the number of repeat units in the chain, termed the degree of polymerization (DP). Polymers consisting of identical repeat units are called ''Homopolymers'' and those containing several types of monomeric units are known as ''Copolymers''. Further, polymers may be (i) organic, inorganic or elemento-organic. (i.e. hetero-organic), (ii) polar or nonpolar, (iii) crystalline or amorphous, (iv) thermoplastic or thermosetting, (v) hydrophilic or hydrophobic, (vi) hard and brittle or soft and elastic, etc.

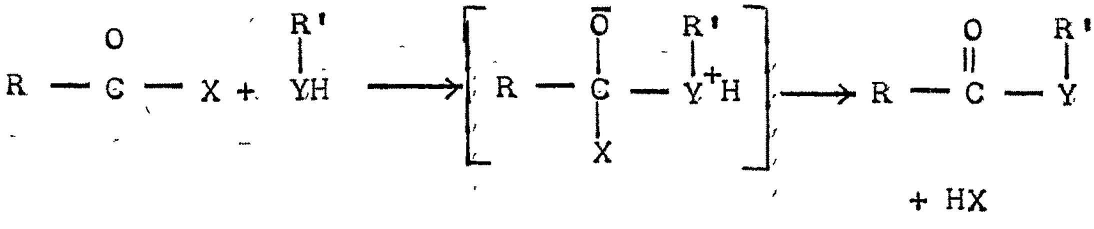
1(b) POLYMERIZATION :

The processes of polymerization are generally divided into two groups known as condensation polymerization and addition polymerization.

Condensation (or step-reaction) polymerization is entirely analogous to condensation in low molecular weight compounds. In polymer formation, condensation takes place between two polyfunctional molecules to produce one large polyfunctional molecule, with the possible elimination of small molecules such as water, ammonia, etc.

Addition (or chain - reaction) polymerization involves chain reactions in which the chain carrier may be an ion or a free radical. Polymers made in chain reactions usually contain only carbon atoms in the main chain (homochain polymers), whereas polymers made in step reactions may have other atoms, originating from the functional groups, as a part of the chain (heterochain polymers).

The preparation of condensation polymers often involves transitory addition and subsequent elimination, say, at the carbonyl double bond of carboxylic acids, and their derivatives. The generalized reaction for carbonyl compounds is



$$R-\overset{O}{C}-X+\overset{R'}{\overset{|}{YH}}\longrightarrow\left[R-\underset{X}{\underset{|}{\overset{\bar{O}}{\overset{|}{C}}}}-\overset{R'}{\overset{|}{Y^{+}H}}\right]\longrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{Y}}+HX$$

where R and R' may be alkyl or aryl groups, X may be OH, OR', NH_2, NHR, $O\overset{\overset{O}{\|}}{C}R$ or Cl, and YH may be OH, NH_2 or COOH.

The reaction of acid halide with a glycol or diamine proceeds rapidly to a high-molecular-weight polymer if carried out at the interface between two liquid phases, each containing one of the reactants. The method has been applied to the formation of polyamides, polyurethanes, polyureas, polysulfonamides, polyphenyl esters, etc.

Copolymerization involves polymerization of two or more different monomers resulting in a copolymer with two or more types of repeat units. (If three repeat units are present, the product is termed ter - copolymer). A polymer can be transformed into a copolymer by partially modifying its functional group. The properties of copolymers can be varied over a wide range by adjusting the ratio of repeat units. Copolymers with long sequences of two repeat units can have two arrangements of chains :

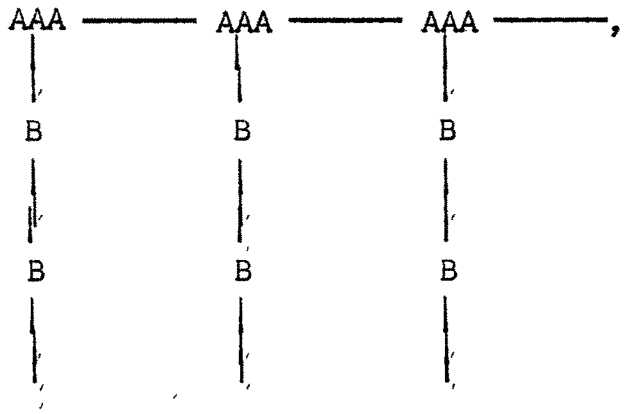
(i) block copolymers and (ii) graft copolymers.

In block copolymers, the sequences follow one another along the main polymer chain,

$$\text{— AABB — BBAA — AABB —}\ ,$$

The usual method of preparing block copolymers utilizes polymers with definite and groups to react under specific conditions.

In graft copolymers sequences of one monomer type are ''grafted'' onto a ''backbone'' of a second monomer type,



Graft copolymerization results from the formation of an active site at a point on a polymer molecule other than its end, and exposure to the second monomer.

1(c) PLASTICS (RESINS) :

Plastics are divided into two categories : (i) thermoplastic resins and (ii) thermosetting resins.

In the category of thermoplastic resins fall such prominent materials are cellulosics, nylons, polyesters, polyethylene, polyvinyls, polyacrylates, etc. In these polymers softening-hardening cycle (heating-cooling cycle) can be repeated. Most thermoplastics are soluble in specific solvents and their softening temperatures vary with polymer type and grade.

Thermosetting resin is one which changes irreversibly under the influence of heat from a fusible, soluble material into a infusible, insoluble material through the formation of a cross-linked, thermally stable network. The important thermosetting resins are phenolic resins, amino resins, epoxy resins, alkyd resins, etc.

I.2 POLYVINYL ALCOHOL :

2(a) GENERAL :

Polyvinyl alcohol was the first totally synthetic colloid prepared from polyvinyl esters in 1924. Today, it is available in many different grades, varying in the degrees of polymerization and hydrolysis.

The starting material for the production of polyvinyl alcohol is its polymerized ester and not its monomer. Alkaline saponification of the polyvinyl ester was the first method studied for the production of polyvinyl alcohol. It is considered to have 1,3 glycol structure.

2(b) COMMERCIAL GRADES :

The first industrial production of polyvinyl alcohol took place in 1926 for use as a textile size and it has remained a major application today; however many other uses have been found, leading to great expansion of the industry. The commercial applications of polyvinyl alcohol are many and varied depending on degree and ease of solubility, stability of aqueous solutions, etc. There is, therefore, a demand of various grades of polyvinyl alcohol exhibiting a range of properties.

Commercial grades produced by different manufacturers(1) are listed in Table I.1.

These grades fall into (i) a fully hydrolysed group with a degree of hydrolysis above 98 % and (ii) a partly hydrolysed group with 87 to 89 % hydrolysis. The partly hydrolysed group includes a subgroup with about 80 % hydrolysis. In terms of degree of polymerization based on the viscosity, at 20°C, of 4 % aqueous solution of polyvinyl alcohol, the major groups are : (i) a low viscosity group of approximately 5 cP, (ii) a medium viscosity group of 20 to 30 cP, and (iii) a high viscosity group of 40 - 50 cP(with a subgroup of 60 cp). From the view-point of the degree of polymerization (DP) of the chains, the major groups have DP of approximately (i) 500, (ii) 1700, and (iii) 2400 with subgroups

Table - I.1

Trade name	Manufacturer
Alcotex	Revertex
Elvanol	du Pont
Gelvatol	Shawinigan
Gohsenol	Nippon Gohsei
Lemol	Borden
Moviol	Hoechst
Polyviol	Wacker
Poval	Kuraray
Rhodoviol	Rhone-poluene
Vinol	Airco Chemical

having DP of 1000, 2000 and 3200. These grades have broad specificity of applications :

(i) As emulsion stabilizers, partly hydrolysed grades are normally used ;

(ii) In remoistenable adhesives, partly hydrolysed grades, mixed with various other adhesives, are used ;

(iii) In textile warp sizes, fully hydrolysed grades are used for hydrophilic cotton and staple yarns, and partly hydrolysed grades are used for filament yarns ; polyvinyl alcohol with DP of 1700 is used for spun yarns, and one with DP of 500 is used for filaments.

(iv) In papermaking, fully hydrolysed grades are generally used.

2(c) PHYSICAL PROPERTIES :

Its solubility in water depends on its degree of polymerization and degree of hydrolysis. Its many hydroxyl groups cause it to have high affinity for water, with strong hydrogen bonding between the intra and intermolecular hydroxyl groups ; on the other hand, the residual acetate groups in partly hydrolysed polyvinyl alcohol are essentially hydrophobic, and weaken the intra and intermolecular hydrogen bonding of adjoining hydroxyl groups. Aqueous solutions of polyvinyl alcohol of high degree of hydrolysis increase in viscosity with time, and may finally gel. The rate of increase in viscosity increases with concentration and decreases with temperature. However, the viscosity of 88 % hydrolysed grade is virtually stable with time. Boric acid and borax cause thickening and gelation of polyvinyl alcohol by chemical bonding with polyvinyl alcohol. Aqueous solution of polyvinyl alcohol forms a thermoplastic gel with certain organic compounds(2).

On heating, polyvinyl alcohol undergoes glass, structural and melting transitions, and eventually decomposes at elevated temperatures. Heat capacity of polyvinyl alcohol was studied by Sochava and Trapenikova(3).

2(d) CHEMICAL PROPERTIES :

The polyvinyl alcohol molecule is a linear polymer chain with pendant secondary - alcohol groups(4-6). Esterification, etherification, and acetal formation are the reactions of importance. Esterification reactions are breifly mentioned below.

Esterification Reactions :

(i) Formation of inorganic esters -

Reactions with inorganic acid compounds lead to the formation of sulphate, sulphonate, nitrate, phosphate, etc (Table I.2)(7-20). Two polymers, with distinctly different solubilities, were obtained by reaction with hydrogen isocyante and cyanamide(20). A molecular complex is reported to be formed by polyvinyl alcohol with sodium hydroxide(21).

(ii) Formation of organic esters -

The formate, acetate, acetoacetate, chloracetate, cinnamate, etc, have been prepared(22-25), and studied for photographic uses. These and other esters (except carbamates and esters of long chain fatty acids) are shown in Table I.3(26-39).

(iii) Formation of long-chain acid esters and related compounds -

Reactions of acid chlorides of long - chain fatty acids, and related compounds with polyvinyl alcohol have been prepared (Table I.4)(40-44) and studied for use in surface coating and for photographic systems(43,45).

(iv) Formation of Carbamate esters -

The reaction of isocyanates and urea with polyvinyl alcohol has been used to obtain substituted carbamates (Table I.5)(46-51).

Table I.2

Formation of inorganic esters.

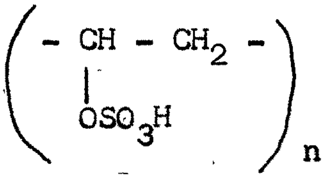
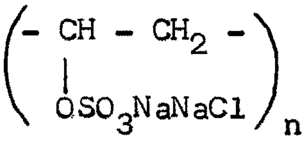
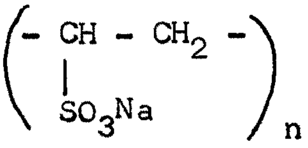
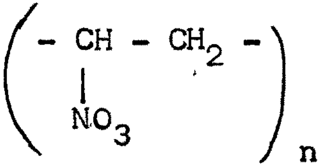
No.	Reagent	Product	References
1	2	3	4
(1)	SO_3	 $\left(-\underset{\substack{\mid\\ OSO_3H}}{CH}-CH_2-\right)_n$	7-10
(2)	$SO_3+C_5H_5N$ + $ClSO_3Na$	 $\left(-\underset{\substack{\mid\\ OSO_3NaNaCl}}{CH}-CH_2-\right)_n$	11
(3)	$COCl_2 + C_5H_5N$ $H_2SO_4 + CH_3OH$	As with SO_3	12
(4)	$ClSO_3H - C_5H_5N$	 $\left(-\underset{\substack{\mid\\ SO_3Na}}{CH}-CH_2-\right)_n$	13
(5)	HNO_3	 $\left(-\underset{\substack{\mid\\ NO_3}}{CH}-CH_2-\right)_n$	14

Table I.2 (Continued)

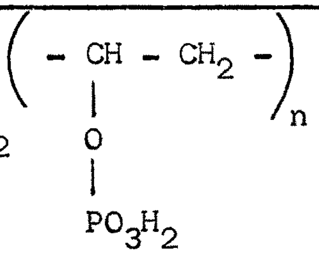
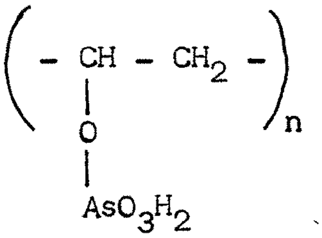
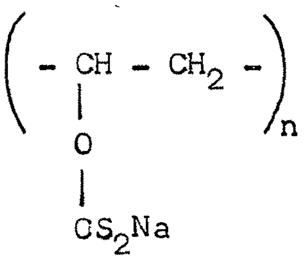
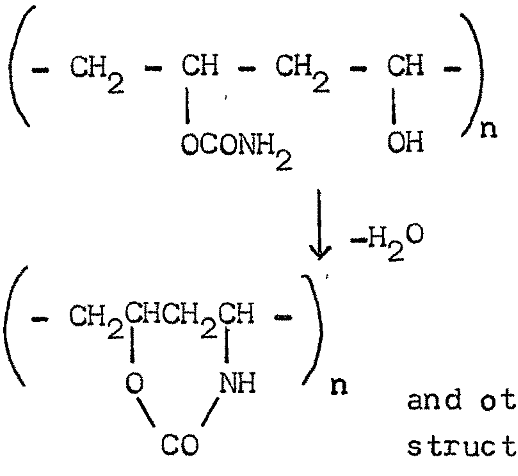
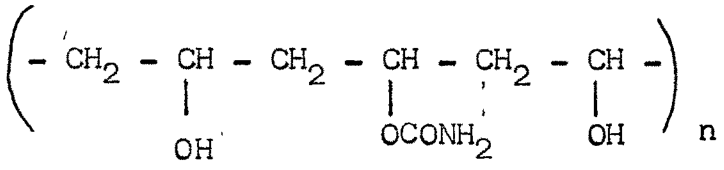
1	2	3	4
(6)	P_2O_5 or $H_3PO_4 + CO(NH_2)_2$	 $(-CH(OPO_3H_2)-CH_2-)_n$	15,16
(7)	H_3AsO_4 $CO(NH_2)_2$	 $(-CH(OAsO_3H_2)-CH_2-)_n$	16,17
(8)	$NaOH + CS_2$	 $(-CH(OCS_2Na)-CH_2-)_n$ (Xanthate)	18,19
(9)	HNCO	 and other structures.	20
(10)	$H_2NCN + HCl$	 $(-CH_2-CH(OH)-CH_2-CH(OCONH_2)-CH_2-CH(OH)-)_n$	20

Table I.3

Formation of organic esters

(except long-chain acid esters and carbamates)

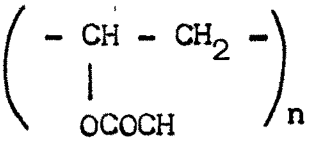
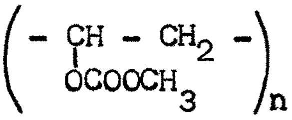
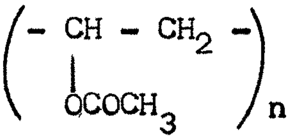
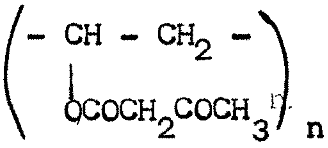
No.	Reagent	Product	References
1	2	3	4
(1)	$HCOOH$	 $\left(-\underset{\mathrm{OCOCH}}{\underset{\mid}{\mathrm{CH}}}-\mathrm{CH_2}-\right)_n$	-
(2)	$ClCOOCH_3$ $(+ C_5H_5N)$	 $\left(-\underset{\mathrm{OCOOCH_3}}{\underset{\mid}{\mathrm{CH}}}-\mathrm{CH_2}-\right)_n$	26
(3)	$(CH_3CO)_2O$ + $NaOCOCH_3$	 $\left(-\underset{\mathrm{OCOCH_3}}{\underset{\mid}{\mathrm{CH}}}-\mathrm{CH_2}-\right)_n$	27
	$(CH_3CO)_2O$ + C_5H_5N		
(4)	$(CH_2CO)_2O$ + CH_3COOH	 $\left(-\underset{\mathrm{OCOCH_2COCH_3}}{\underset{\mid}{\mathrm{CH}}}-\mathrm{CH_2}-\right)_n$	28

Table I.3 (Continued)

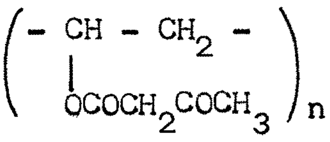
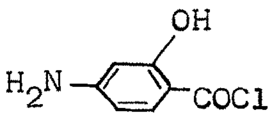
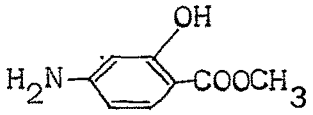
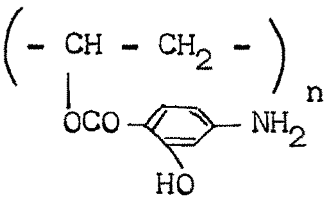
1	2	3	4
(5)	$CH_3COCH_2COOC_2H_5$	 $\left(\underset{OCOCH_2COCH_3}{\underset{\vert}{-CH}}-CH_2-\right)_n$	29
(6)	 $+ C_5H_5N$ or $HCON(CH_3)_2$ or  $+ NaOCH_3 + HCON(CH_3)_2$		30, 31

Table I.3 (Continued)

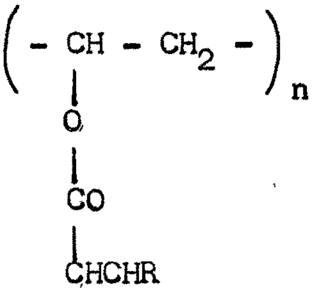
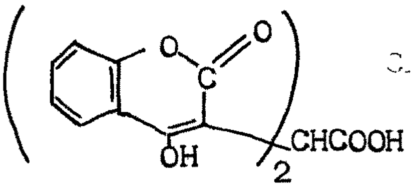
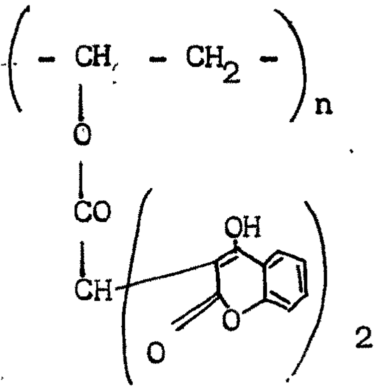
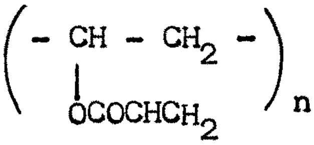
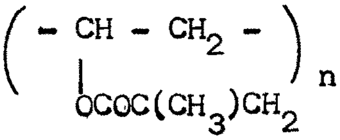
1	2	3	4
(7)	RCHCHCOCl with + NaOH in organic solvent (R = C_6H_5 or substituted C_6H_5)	 $\left(-\underset{\substack{\vert\\O\\\vert\\CO\\\vert\\CHCHR}}{CH}-CH_2-\right)_n$	32, 33
(8)	 + C_5H_5N		34
(9)	$(CH_2CHCO)_2O$	 $\left(-\underset{\substack{\vert\\OCOCHCH_2}}{CH}-CH_2-\right)_n$	35
(10)	$(CH_2C(CH_3)CO)_2O$	 $\left(-\underset{\substack{\vert\\OCOC(CH_3)CH_2}}{CH}-CH_2-\right)_n$	36

Table I.3 (Continued)

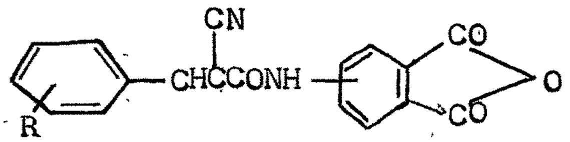
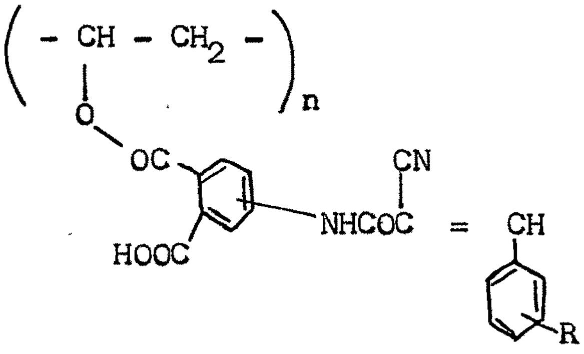
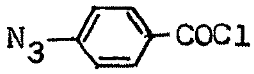
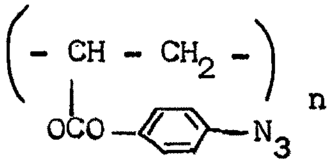
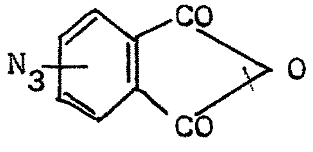
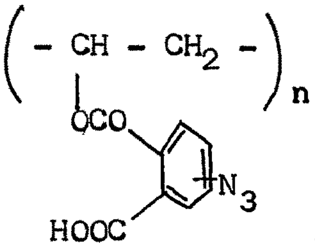
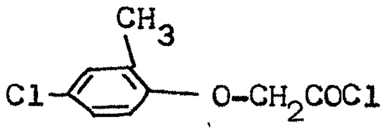
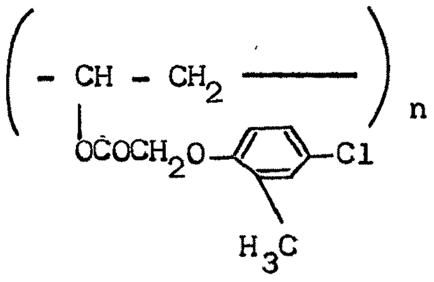
1	2	3	4
(11)			37
(12)			38
(13)			38
(14)			39

Table I.4

Formation of long-chain esters and related Compounds

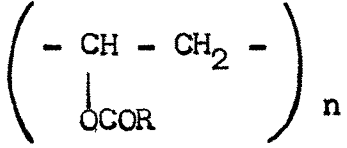
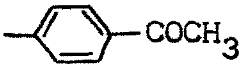
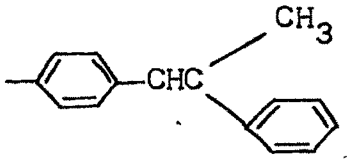
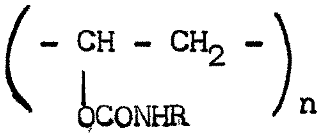
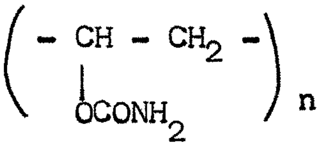
No.	Reagent	Product	References
(1)	RCOCl R = C_6H_5 R = stearyl R = oleoyl R = lauryl (i) RCOCl followed by (ii) $(RCO)_2O$ or Phthalic anhydride	 $\left(-\underset{OCOR}{\underset{\vert}{CH}}-CH_2- \right)_n$	40–42
(2)	Linseed acids	Polymeric drying oils	43, 44
	C_{14}–C_{24} unsaturated acids in C_6H_5OH	Linear polymers.	
	$CO(NH_2)_2$ + NH_2SO_2H + NaOH on R – Substituted polyvinyl alcohol (R = C_{12}, C_{16})	R – Substituted poly (sodium vinyl sulphate)	

Table I.5

Formation of Carbamate esters.

No.	Reagent	Product	References
(1)	RNCO R = C_6H_5 R = 6 - Ureido - n - hexyl R =  R = $(CH_2)_2Cl$ R =  R = 	 $\left(- \underset{\mathrm{OCONHR}}{\mathrm{CH}} - \mathrm{CH_2} - \right)_n$	5,46-49
(2)	$CO(NH_2)_2$	 $\left(- \underset{\mathrm{OCONH_2}}{\mathrm{CH}} - \mathrm{CH_2} - \right)_n$	50, 51

2(e) APPLICATIONS OF POLYVINYL ALCOHOL :

Polyvinyl alcohol adheres strongly to cellulosic materials, and is used for bonding paper to paper. The applications of polyvinyl alcohol in this field are as (i) general adhesives for paper, (ii) remoistenable adhesives and (iii) adhesives for plywood(52).

The polyvinyl alcohol used for emulsion polymerization fulfils the dual function of emulsifying the monomer and stabilizing the polymer particles formed during the process(53). Polyvinyl alcohol is often used in conjunction with micelle-forming surfactants(54-56).

Photosensitized reactions of polyvinyl alcohol are used in printing technology, etc (57). An important application of the photochemical insolubilization of dichromated polyvinyl alcohol is in the production of screens for colour-television receivers. Similarly polyvinyl cinnamate is used as photosensitive material. Dichromated polyvinyl alcohol has also found use in the manufacture of printed Circuits(58), and in preparing lithographic plates, photoresists for printing and Silk Screens(59,60).

I.3 POLYESTERS :

3(a) GENERAL :

Polyesters, a large important family of synthetic resins initially developed in 1938, led to entirely new processing techniques in molding and laminating large and often complex structural products. The introduction of unsaturated polyesters that could polymerize quickly at room temperature without external pressure brought about wholly new industries and opened new market for plastic products. The reasons for stedily increasing uses of polyesters by industry are numerous, e.g.

(i) low cost,
(ii) ease of production from abundant raw materials,
(iii) wide range of formulations to meet a variety of requirements,
(iv) crystal clarity to light straw color and can be pigmented to any desired hue,
(v) available as liquids, pastes, or flakes,
(vi) adaptability to many molding and laminating methods,
(vii) ability to be polymerized with a variety of catalysts,
(viii) permit passage of microwaves for radar applications,
(ix) resist deterioration by sunlight, oxidation, saltwater, fungus and many chemicals,
(x) excellent mechanical, thermal and electrical properties, etc.

Polyesters are produced in thermoplastic varieties as transparent film or as textile fiber. The importance of thermosetting type is derived from the nature of the curing process. It does not produce gaseous by-products commonly associated with condensation - type polymerization.

By comparison, unsaturated polyesters undergo a chain formation process called addition polymerization, in which no condensate is formed during the cure; for this reason they are termed low-pressure resins since no external pressure is necessary for casting or laminating, and only low pressures (50 to 200 psi) are needed for many compression-moldings.

3(b) UNSATURATED POLYESTER RESINS :

Polyesters of several diverse types are useful. Unsaturated polyesters have come to be associated with glass fibers in the production of reinforced plastics. The chemical inertness, great strength, and good temperature resistance of glass fibers have always made them attractive as reinforcing material for laminated plastics in place of cloth and paper. The outstanding advantage of unsaturated polyester is that the cross - linking reaction is essentially an addition polymerization, which takes place without elimination of water or other small molecules. The average cross - linking length, i.e. the number of chain links between two cross - links can be derived from both the chemical structure of linear unsaturated polyester and the number of groups that have not reacted during the cure.

The most important properties of unsaturated polyester systems include ease of handling, rapid curing with no volatiles evolved, light color, dimensional stability, and generally good physical and electrical properties. The major applications of glass - reinforced polyester resins fall in the following categories : boat hulls, transportation, including passenger car parts and bodies and truck cabs, consumer products such as chairs, fishing rods, trays, pipes and ducts, electrical appliances, construction applications largly as sheets and panels, etc.

3(c) POLYESTERS FROM POLYHYDRIC ALCOHOLS AND POLYACIDS :

Water soluble monoesters of PVA with di and tribasic acids (maleic, succinic, glutaric, tartaric, malic, glutaconic, phthalic, citric, etc.) have been reported and used as dispersing agents for silver halides(61). Polyesters from polyhydric alcohol, unsaturated oil and unsaturated dicarboxylic acid were copolymerized with ethylenic monomers. These copolymers were useful as surface coating agents(62). Polymer from amino acetic acid and polyvinyl alcohol was prepared in a closed vessel in presence of water and catalyst at 140 - 80°C (63). Soluble copolymers of unsaturated alcohols and acrylic esters have been prepared(64).

Polyesters from bisphenols and dicarboxylic acid chlorides (isophthalic or fumaric) were prepared and their mechanical properties were studied by Conix(65), Discoloration of polyesters was inhibited by the use of salicylic acid esters (66).

Cotton cellulose was esterified with acid chlorides in DMF and pyridine yielding products having degree of esterification 2.4 - 2.6 acyl groups/glucose unit and having degree of polymerization varying with pyridinic amount(67).

Kinetic studies of melt polyesterification of dibasic acids such as maleic, fumaric, phthalic, succinic, adipic and sebacic with glycols led to the classification of acids into two groups having large and small differences between the first and second dissociation constants of these acids(68).

Properties :

Physical and mechanical properties of polyester resins (maleates, acrylates, etc) have been reported by Zhelyazko(69).

Esters of PVA with polybasic acids were studied as dispersing agents for silver halides(61). Copolyesters from unsaturated oils, unsaturated acids and ethylenic monomers were prepared for use as surface coating(62). Acrylic ester resins were studied for the fractionation of miscible liquid mixtures(70).

Applications of Polyesters :

A mixture of polyvinyl ester, polymethyl methacrylate in monomer and urea - CH_2O gave a decorative binder which can be cut or ground(71). Polyvinyl esters are reviewed for application as surface coatings(72). Polyvinyl esters of Cinnamic acid and p-nitrobenzoic acid were prepared for use as photocopier layers(73). Polyesters from adipic acid and diols have been prepared for use as plasticizers(74). Esters of polyvinyl alcohol with phosphoric acids were prepared for using them in aerosols to prevent moisture fogging on glass, plastics, metals, etc (75).

Fibres, obtained from polypropylene mixed with PVA were dyed with disperse dyes(76). Halogenated maleate and fumarate polyesters cross - linked with styrene were flame - resistant and could be used in fibre - reinforced panels(77).

I.4 SWELLING OF POLYMERS :

4(a) GENERAL :

Monomers of different chemical structures would lead to different polymers, each having its own characteristics. Obviously as the chemical constituents of the polymer change, so do the properties of the polymer. Swelling due to sorption of vapours, gases or liquids is one such property. Swelling of a polymer is associated with sorption of a low molecular - weight fluid by a polymer and is often accompanied with a change in polymer structure. At very low thermodynamic affinity when the vapours are sorbed by a polymer, the latter is perturbed to a small extent and its volume swelling is practically nil. When the thermodynamic affinity of a sorbate for a polymer is sufficiently high, the changes in the specific features of the latter begin to be exhibited : a polymer swells in volume and changes its structure. Before the formation of a solution, the polymer ''Swells'' . It is a characteristic feature in formation of solution of polymers. Polymer gains weight and increases in volume. Swelling is not merely the penetration of small solvent molecules into the polymer phase, but it inevitably involves a change in polymer structure, which sharply increases its volume. Swelling may be limited or unlimited. Unlimited swelling is swelling that passes spontaneously into dissolution. It is analogous to complete miscibility of liquids. In liquids molecules are small and mobile, they penetrate into each other at equal rates and the liquids mix. The specific feature of dissolving of a polymer is that the molecules of mixing components differ in size by thousands of times and have different mobilities. The mobility of the molecules of low-molecular weight liquid is very high and that of macromolecules is very inconsiderable. Therefore, large macromolecules do not have time to pass over to a solvent phase ; before dissolving, a polymer absorbs a large amount of liquid, i.e. it swells. Swelling is one - directional mixing due to the large size of the polymer molecules. This is supported by the fact that degraded polymers dissolve without preliminary swelling. The swollen polymer, which is a solution of a low-molecular weight liquid in the polymer, coexists for some time with the layer of pure low-molecular weight liquid. After sometime, when the polymer chains have moved apart to a sufficient extent, they begin to diffuse slowly into the solvent. There appears a layer of more dilute solution, coexisting with the layer of more concentrated solution. After some more time has passed, the concentrations of these two layers become equal and they merge into a one-phase homogeneous system.

Limited swelling is the interaction of polymers with low molecular weight liquids, when it is limited to the stage of sorption of the latter by polymer ; spontaneous solution of the polymer does not occur, i.e. the polymer chains do not separate completely from one another. As a result, two coexisting phases are formed, one of them being a solution of low-molecular weight liquid in polymer and the other, the pure low-molecular weight liquid (if the polymer is completely insoluble) or a dilute solution of polymer in low-molecular weight liquid. These phases are separated by a clearly visible interface and are in equilibrium.

Swelling of linear and cross - linked polymers should be distinguished. In case of linear polymers the process is analogous to partial mixing of liquid : under definite conditions of temperature and concentration of components, swelling is limited, but if the conditions are changed appropriately, unlimited swelling may ensure. Limited swelling of linear polymers may be accounted for by the fact that the energy of interaction of chains with one another is higher than the energy of their interaction with the solvent molecules, so that the chains do not separate completely. Raising the temperature favours disturbance of the bonds between chain molecules, and limited swelling becomes unlimited e.g. swelling of gelatine in water. If the polymer has spatial network composed of chemical bonds, the chains cannot be separated at any temperature (below the decomposition temperature of the polymer). Hence cross - linked polymers are inherently insoluble, but they may swell, forming gels.

4(b) DEGREE OF SWELLING :

From a practical point of view it is very important to know the capacity of cross-linked polymers for swelling in various liquids and vapour media. This capacity is assessed by the degree or amount of swelling, expressed as the amount of liquid (or its vapour) sorbed by unit mass or volume of polymer. Degree of swelling can be determined only for polymers with limited swelling, because upon unlimited swelling, the polymer itself begins to dissolve and the mass of the sample decreases. The degree of swelling changes with time. After certain time the degree of swelling becomes constant. After certain time equilibrium is reached beyond which swelling does not proceed. Different polymers take different periods of time to reach their equilibrium degree of swelling and this is of great importance.

Polymer may absorb low-molecular weight substances not only from the liquid, but also from the gaseous phase ; if the polymer swells in liquid, it will swell in its vapour as well. The rate of swelling in vapours is much lower, but the maximum or equilibrium degree of swelling is the same.

Sometimes a phenomenon called negative swelling is observed in polymers, involving decrease rather than increase of cross-linked structure owing to washing out of soluble fractions from them.

4(c) FACTORS AFFECTING SWELLING :

The ability of a polymer to swell is determined by many factors such as,

(1) chemical nature of a polymer and of a solvent,
(2) molecular mass of a polymer,
(3) flexibility of a polymer chain,
(4) packing density of macromolecules,
(5) phase state,
(6) inhomogeneity of the chemical composition of a chain,
(7) presence and density of a spatial network,
(8) temperature, etc.

The mutual solubility of substances depends on their chemical composition.

4(d) METHODS OF DETERMINATION OF SWELLING :

Degree of swelling can be determined by the

(1) Gravimetric or
(2) Volumetric methods.

Gravimetric method consists of weighing the sample before and after swelling and calculating the amount of swelling from the formula,

$$DS_w = \frac{M = Mo}{Mo}$$

Where Mo = Mass of polymer system, initially

M = Mass of polymer system after swelling

Volumetric method is based on measuring the volume of polymer before and after swelling.

$$DS_v = \frac{V - Vo}{Vo}$$

Where Vo = Volume of polymer system initially

V = Volume of polymer system after swelling

Determination of degree of swelling is used in practice for testing finished polymer articles intended for service in liquid and gaseous media.

The determination of degree of swelling serves as a promising method of assessing the degree of cross - linking, the degree of hydration, etc. The ability of an ion exchange resin to swell was found to depend on the degree of hydration of its ionogenic groups, which determines the affinity of the resin for water. The higher the degree of hydration, the more the resin was found to swell. The degree of swelling was also affected by the nature of electrolyte ions in the solution.

The degree of swelling of the ion-exchange resin was also found to depend on the number of cross - links in the polymer. The larger the number of cross - links, the lower the degree of swelling.

The swelling of the ion exchange resins determines, to a considerable extent, the selectivity of the resin. Strongly swelling ion exchangers take up ions of all types, i.e. their selectivity is very low. Weakly swelling ion exchangers possess a high capacity for smaller ions and a low capacity for larger ones. This is the basic principle of the ion exchange sieves, by means of which like-charged ions of different sizes can be separated, e.g. by using weakly swelling ion exchangers metal ions can be separated from ions of macromolecular compounds, such as proteins, which are not practically sorbed. Complete demieralization of streptomycin is accomplished by means of ion-exchange sieves.

4(e) SWELLING OF PVA AND ITS DERIVATIVES :

PVA cross-linked with HIO_4 and spun has high water sorption and swelling(78). PVA cross-linked with P-containing di acid chlorides has its stability decreasing in order neutral > base > acid(79). Studies in formalation of PVA films indicated simultaneous cross-linking and de-crosslinking in the heterogeneous reaction and studies on swelling of formalated PVA films showed that CH_2O concentration was more important for cross-linking than formalation time or concentration of H_2SO_4 (80). Poly(vinyl acetal) based porous adsorbing materials have been reported(81).

Studies of water vapour sorption by water soluble polymers(Polyacrylic acid and its Na-Salts) showed that high concentration of polar or ionic groups caused anomalous concentration - dependent and complex diffusion(82).

Films of PVA of different degrees of polymerization were studied for solubility and swelling. If the mean degree of polymerization is the same, the heterogeneity of the molecular weight has no great influence on the swelling properties of the films(83). Linear relations between density and crystallinity and between swelling and crystallinity were observed(83).

Naito et al(84) studied the relation between swelling and solubility of PVA films and evaluated limited degree of swelling at zero concentration of dissolved films. Nakajima et al(85) studied swelling equilibria of PVA in binary mixtures. Matsumoto and Mizushima(86) found that the equilibrium concentrations of acetic (or caproic) acid distributed between aqueous (I) and swollen formalized PVA (II) phases can be related as $C_{II} = KC_I^n$ where K and n are constants. Swelling and solubility behaviour of copolymer (vinyl - allyl alcohol) was studied by Sakurada et al(87). Swelling of PVA film in water is markedly decreased by mixing a slight amount of formaldehyde with PVA (88).

I.5 PLAN OF PRESENT WORK

Considerable work has been carried out in our laboratories of different aspects of a wide variety of polymeric materials, Thus, work has been carried out on coordination polymers (89), semiconducting and pyrolyzed chelate polymers (90), chelating polymers (91), ion - exchange resins redox polymers, and ionomers (92), etc. Swelling of polymers was studied and interesting results were obtained (93). Review of literature showed that although various polymers had been widely studied for their solubility or swelling, few studies were reported on the swelling and solubility of poly(vinyl alcohol) esters. Such studies can help in evaluating the utility of these products in soils, lenses, lubricants, etc. The establishment of limits for both limited and unlimited swelling can be of theoretical as well as industrial importance. Hence it was planned

(1) to prepare poly (vinyl alcohol) esters from poly (vinyl alcohol) and various mono and polybasic acids.

(2) to determine their m.pt., water content, ester content, etc.,

(3) to get the products analysed for C, H and N and establish thus probable formula in correlation with their water content and ester content.

(4) to study the sorption of water and salts by these products from water and salt solutions, and .

(5) to evaluate swelling (by gravimetric and volumetric techniques) and solubility of these products and to correlate them to get an insight into limited and unlimited swelling of these products.

Experiments carried out and results obtained are presented and discussed in the following pages.