The Complete Book on Water Soluble Polymers
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Water soluble polymers cover a wide range of highly varied families of products of natural or synthetic origin, and have numerous uses. A water soluble polymer is a polymer that can be diluted in water, with or without the assistance of co solvents and neutralizing agents, to form transparent solutions. They may be classified into two types, totally synthetic polymers and natural products together with their chemically modified derivatives and further can be grouped into three main headings; naturally occurring, semi synthetic and completely synthetic polymers. The water based polymers are quick drying non inflammable, having mild odour and more environmentally acceptability than any other polymers. Most conventional coating polymers at present can be produced in a form that will allow them to be solubilized in water. These include alkydes, polyesters, acrylics epoxies. There are various types of polymerization methods of water soluble polymers such as bulk polymerization, solution polymerization, copolymerization, emulsion polymerization and suspension polymerization. Water soluble polymers are used widely as stabilizers or protective colloids in emulsion polymerization. Its most common use are gum acacia, starch either etherified or in its degraded form, dextrin, polyvinyl alchohol and hydroxyethyl cellulose. Polymers find many applications in oil recovery and production, including areas such as; drilling fluids, cementation of well bore, reservoir fracturing, controlling fluid flow in the reservoir and multistage processes of oil production and refining. The water soluble polymers market encompasses several categories, including starch, cellulose ethers, polyvinylacetate, polyvinyl alcohol and other synthetic water soluble polymers. The starch market is the largest.

This book basically deals with flow characteristics of water soluble polymer solutions, emulsion polymerization, water reducible resins, silicone modified alkyds and polyesters, cross linking of water soluble coatings, formulation of water soluble coatings, trouble shooting with water soluble polymers, acrylic solution resins, polyvinylpyrrolidone, commercial uses: compounding and formulating adhesives, methods of polymerization, methods for polymerization of acrylamide, fabrication of water soluble polymers, excluded volume interactions of neutral polymers etc.

The book covers classification of water soluble polymers, processes, properties, uses and applications of water soluble polymers with lot of other information. This book will be very resourceful for new entrepreneurs, existing units, technocrats, researchers and technical libraries.

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WATER SOLUBLE POLYMERS
The polymers discussed in this chapter are characterized as being commercially available in solid form and may be converted into aqueous solution without the aid of other chemicals. Those products that require reaction for example the neutralization of carboxylate polyacrylates to render them water soluble will not be considered.

CLASSIFICATION
The water soluble polymers may be broadly classified into two types totally synthetic polymers and natural products together with their chemically modified derivatives.

Synthetic Polymers
This category has three main types that are widely used commercially polyvinyl pyrrolidone polyvinyl acetate and polyethylene oxide. All are thermoplastic polymers which give pseudoplastic solutions and confer varying degrees of thixotropy to formulations. As they are fully synthetic a wide range of molecular weights is possible which controls the viscosity of each system. Their thickening power is variable depending upon the polymer type for example a polyvinyl alcohol of the same molecular weight as a polyethylene oxide normally produces a lower solution viscosity. Thus certain types find greater uses as thickeners and others are mainly used as stabilizers. In polyvinyl alcohol there is also considerable variation in polymer composition as it is made by hydrolysis of polyvinyl acetate and degree of hydrolysis controls the final ratio of hydroxyl to residual acetate groups on the polymer.

Natural Products and Their Derivatives
Natural Gums
This category embraces a range of naturally occurring gums and mucilages that are extracted from plants the most common of which are the seaweed extracts and gum acacia. These are essentially polysaccharides and they show marked variability in molecular weight and other properties depending on the conditions of plant growth for example climatic variability. As a group they also tend to be prone to bacteriological attack so they have limited use in the surface coatings industry.

Modified Polysaccharides
The reactions of certain natural gums with ethylene oxide or propylene oxide can yield useful products with substantially greater thickening power. Other properties such as resistance to attack by bacteria may also be improved. Products are now available from the action of specific enzymes on sugars under stringently controlled conditions. Certain of these xanthan gums yield water soluble polymers which show very high pseudoplasticity good resistance to bacteria and tolerance to wide variations in pH.

Starch and its Derivatives
Starch is a reserve polysaccharide in plants with corn potatoes tapioca rice and wheat being commercial sources. It is composed of about 25 per cent amylose and 75 per cent amylopectin a branched chain structure. In amylose the D anhydroglucose units are linked by) glucosidic linkages only
In amylopectin however there are also some glucosidic linkages
On continuous heating in water starch granules absorb water increase many times in size swell and gelatinize. Concurrently the initially thin opaque starch suspension becomes at a certain point viscous semi opaque and finally transparent. The temperature at which this drastic change occurs is termed the gelatinization or more correctly the pasting temperature of starch this temperature is a characteristic property of starch.
The thickening of some starch pastes and the gelling of others is caused by association of the linear molecules of amylose. Corn starch forms a rigid gel. Potato starch tapioca and sago have less tendency to gel probably because their amylose portion has a higher molecular weight and may be slightly branched.
Gel strength depends mainly on concentration and size of linear molecules and on crystalline areas within the swollen granules and between swollen granules and granule particles.

Even after complete dispersal in water and then dehydration the components of starch either separately or mixed may be soluble or insoluble when redispersed depending on the manner of drying. For example simple evaporation of water from naturally occurring mixtures of starch polymers permits re association when this is extensive it is called retrogradation. Amylose tends to retrograde more readily than amylopectin forming insoluble aggregates from dilute solutions and irreversible gels from concentrated solutions. The retrogradation rate of dilute dispersions of various starches in shown in figure 1.

The anhydroglucose units in starch contain on the average one primary and two secondary alcohol groups. Derivatives can be formed by treating the alcohol groups with acids or anhydrides to form esters and with reagents such as alkyl halides or alkylene oxides to form ethers. The degree of substitution (DS) is expressed as the average number of hydroxyl groups replaced per glucose unit. Many ethers in which the DS is one or less are water soluble and resemble the natural gums in colloidal properties. The introduction of a relatively small number of ether or ester groups of the order of one substituent per twenty five glucose units may profoundly alter the colloidal properties of the starch when it is dispersed in water. Of these improvements in the clarity of the aqueous sol diminished gelation effects and improved film forming properties are the most important industrially. Highly derivatized starch ethers and esters that is with a DS approaching the range of 2 to 3 substituent groups per glucose unit are relatively insoluble in water but are soluble in many organic solvents.

In both esterification and etherification of starch it is believed that the introduction of a relatively small number of substituent groups along the starch molecules exerts a strongly negative influence on the ability of these molecules to orientate and associate into aggregates. Association abnormally increases the viscosity of starch sols with age involves gelation effects or produces turbidity.

Cellulose and its Derivatives

Cellulose is the most abundant of all naturally occurring organic compounds. It consists of long chains of D anhydroglucose units linked by (14) glucosidic linkages (cf. starch with (glucosidic linkages) Its insolubility is accounted for by the strong hydrogen bonding between molecular chains within the fibrous structure. It is the reduction of this bonding amongst other things during etherification which results in a water soluble product.

These cellulose ethers are the most widely used water soluble polymers in the surface coatings industry. The most common types are

- Sodium carboxymethyl cellulose (SCMC)
- Sodium carboxymethyl 2 hydroxyethyl cellulose
- 2 hydroxyethyl cellulose (HEC)
- Methyl cellulose (MC)
- 2 hydroxypropyl methyl cellulose (HPMC)
- 2 hydroxyethyl methyl cellulose (HEMC)
- 2 hydroxybutyl methyl cellulose
- 2 hydroxyethyl ethyl cellulose (EHEC)
- 2 hydroxypropyl cellulose (HPC)

PROPERTIES OF CELLULOSE ETHERS

Three important characteristics of cellulose ethers are

- DP (degree of polymerization)
- DS (degree of substitution)
- MS (molar substitution)

Degree of Polymerization
The degree of polymerization (DP) is the number of units in the cellulose chain and it is this factor that largely controls solution viscosity. For commercial products the DP may range from 50 (molecular weight about 10000) for low viscosity grades up to about 1500 or 2000 (molecular weight 180000 to 250000) for high viscosity grades.

**Molar Substitution**

Molar substitution (MS) is the number of moles of substituent attached to each anhydroglucose unit. It can be seen from table 1 that there is a pronounced tendency for ethylene oxide molecules to add on to the side chains of the anhydroglucose unit by reaction with the OH group formed by the first addition. With HEC the OH in the 6 positions on the ring is preferentially reacted with ethylene oxide yielding a further OH group which is even more reactive than any of the anhydroglucose OH groups. Thus with HEC the MS is always higher than the DS commercial polymers having an MS range of 1.8 to 2.5 and a DS range of 0.9 to 1.6.

Apart from these relative reactivities the evenness of substitution is also dependent on the production process used. This distribution is an important factor in many properties of the polymers such as solution clarity resistance to bacteriological attack and degradative oxidation. An even distribution tends to give a higher solution clarity and greater resistance to depolymerization although it may be more prone to enzyme attack.

The main characteristics that distinguish between the cellulose ethers are summarized in table 2.

**APPLICATION**

Although certain polymers are used as film formers in their own right by far the greatest application of water soluble polymers is to thicken suspend stabilize gel solidify or in other ways modify the flow characteristics of aqueous systems. In order to understand these modifications a basic knowledge is required of rheology which is the science of the deformation and flow of matter when subjected to an applied force.

**Basic Concepts of Rheology**

For water itself for the common solvents and for non interacting liquid systems and solutions where the dissolved material is low in molecular weight non associating and with limited solute solvent interaction or solvation the characterization of flow is simple. Flow is directly proportional to the force applied the system is said to be Newtonian.

More complex solutions however will tend to respond in a non linear manner to the applied stress. Here the dissolved or solvated molecules are large the tendency to re associate is high and the solvent must exert some solvating force to maintain the polymer in solution. Such solutions are classified as non Newtonian.

**Flow Characteristics of Water Soluble Polymer Solutions**

One way of studying the flow behaviour is to determine shear stress at various shear rates as shown in figure 2. Here the shear stress (S) is plotted versus the shear rate (D). If these solutions had been Newtonian straight lines of unit slope would have resulted. However these solutions deviate from a straight line the deviation being greater at high shear stresses and rates. A more useful way of picturing the flow behaviour of water soluble polymers is shown in figure 3 where the apparent viscosity of hydroxyethyl cellulose is plotted against shear rate. (The shear rate is the response to an applied stress.) The data are taken from a plot similar to that shown in figure 2. Since a Newtonian system would give a straight line of zero slope it is seen that the low viscosity material is less pseudoplastic than the high. This is true of other cellulose derivatives as well. This figure also shows how the shear rate varies with usage. Normally the viscosity is measured at an intermediate shear rate range using for example a Brookfield viscometer. However as seen in figure 3 the differentiation obtained by Brookfield measurement may not hold under use conditions. Thus if high viscosity at high shear rate is wanted it might be desirable to use gum designated as low viscosity when measured in the intermediate shear range.

**Thixotropy**
Some fluids exhibit a flow pattern that is time dependent. The fluid tends to thicken or thin under fixed flow conditions. The term thixotropic is applied to systems that thin and the term rheopectic is applied to systems that thicken. Thixotropy arises when a reversible sol gel system is possible. Some sort of a three dimensional structure albeit weak is necessary. In thixotropic solutions this internal structure is temporarily broken down by shaking or stirring but reforms upon standing. The converse occurs with rheopectic systems.

Typical flow curves for a thixotropic system high viscosity SCMC are shown in figure 4. As the shear stress is increased the shear rate varies in typical pseudo plastic fashion. However when the shear stress is rapidly decreased the flow curve is less non Newtonian in character. The reason is that originally the SCMC was not molecularly dispersed that is it contained structure. As the shear stress is increased the aggregates or structural units become dispersed that is the gel structure is broken. The area of the loop between the two curves is a measure of the thixotropic breakdown. Upon standing structure will re form with time and the viscosity will increase. Depending on the material the temperature and the shear history the final viscosity may be the same as greater or less than the original viscosity. If the cellulosic polymer has a low DS and is not uniformly substituted gels may form. Thixotropic structure is also enhanced by the presence of multivalent cations.

The presence of gel structure in a solution of SCMC is reflected in the appearance of a spur at the bottom of the ascending curve as shown in figure 6A or in very high viscosity at low shear rate as shown in figure 6B.

USES

Water soluble polymers have numerous applications. For the surface coatings industry the uses of most relevance are as thickeners and rheology modifiers in latex paints as stabilizers in emulsion polymerization and also as thickeners in paint removers. Other uses include but are not necessarily confined to adhesives cosmetics and pharmaceuticals detergents explosives depressants in mining non woven textiles paper and paper products refractories glazes ceramics textile printing and textile sizes.

Latex Paints

The thickener is an important component of latex paints. When properly selected it plays a vital part in the manufacture of the paint ensures can stability while in storage and controls rheological properties during application. And addition of part or all of the thickener during pigment grinding will increase the effectiveness of the shearing action and thus have a marked influence on the dispersibility of pigments. Although not mentioned in the classification of water soluble polymers at the beginning of this chapter casein was the first widely used thickener. While it contributed good leveling in some systems it had several drawbacks. It is soluble only at alkaline pH and hydrolyzes readily which results in gradual loss in viscosity. It is also sensitive to calcium ions and susceptible to putrefaction.

Each of the water soluble polymer types has been considered at some stage for thickening latex paints and has some particular advantages. However of those which are the subject of this chapter cellulose ethers are the most widely used as they offer the best compromise of properties. Table 3 summarizes the advantages and disadvantages of the water soluble polymers in question other than cellulose ethers. The following discussion of the effect of thickeners on the performance of latex paints refers particularly to cellulose ethers. However most of the comments would be relevant to the other types.

Stability

A latex paint is a heterogeneous dispersion of a latex polymer and pigment particles that requires protection against mechanical and chemical stability. The thickener contributes to this protection in two ways. Firstly it increases the viscosity of the paint and the mobility of the pigment and polymer particles is decreased. As a result the frequency and force of particle collisions are reduced which suppresses the resultant tendency to coagulate. Secondly the thickener contributes a protective colloid action by coating the particles. This
coating also reduces mobility which improves mechanical stability and at the same time provides protection against polyvalent cations with a consequent increase in chemical stability.

Since SCMC is ionic its interaction with pigment/latex is of a higher order and is less time dependent than is the case with non ionic thickeners. However SCMC is susceptible to heavy metal ions present either on the pigment surface or in the aqueous phase. The result of replacing sodium by say calcium will be redistribution of water resulting in a possible loss in viscosity but this can be offset by using material of suitable degree of substitution. In paints reactive ions present on pigment surfaces are more relevant in this regard than those in the aqueous phase.

Low molecular weight colloids such as polyvinyl alcohol and low viscosity cellulose ethers give good stability. It is not necessarily sound economics to use less of a high viscosity colloid to give satisfactory paint consistency since the amount of colloid present may be of greater importance. It may be an advantage to use a mixture of molecular weights (i.e. high and low viscosity grades) or even a mixture of types for example low viscosity SCMC and high viscosity HPMC or HEC to get optimum stability and consistency.

Satisfactory thixotropic emulsion paints can be made using all the main cellulose ethers. The pH conditions may be selected to give the desired results with combinations of colloids and complexing agents. Latex paint systems seem to require a certain minimum amount of colloid for satisfactory stability. When colloid free emulsions are used the amount of colloid added to the paint must be increased. The use of cellulose ethers as polymerization colloids can improve paint stability because of their low molecular weight (after degradation in the polymerization process) and their close association with the emulsion before mixing with other paint components.

WATER REDUCIBLE RESINS

A water soluble polymer is a polymer that can be diluted in water with or without the assistance of cosolvents and neutralizing agents to form transparent solutions. These solutions will remain clear on further dilution with water down to relatively low levels of polymer concentration.

This chapter deals with water soluble polymers that are capable of forming films that can meet a variety of requirements of the coatings industry. Current solvent borne film forming polymers are too hydrophobic to form solutions in water. Water soluble versions of these solvent borne polymer types can be produced by introducing specific functional groups along the polymer backbone. These functional groups are hydrophilic or can be modified to produce hydrophilic groups. A variety of water soluble polymers can also be used as thickening agents protective colloids dispersing agents etc. by the coatings industry. They include water soluble starches gums and other natural modified and synthetic materials. They will not be dealt with in this chapter as they are not considered to have major film forming properties.

HISTORY

Water soluble coatings have been with us for a very long time. The renaissance artists used binders such as egg whites reduced in water in their colorants. Water soluble casein starch and gum based coatings have had a long history and particularly the first were widely used in interior architectural finishes until the early 1950s. The use of maleinized drying oils neutralized with ammonia was reported in 1938. However it was not until the mid 1970s that the Australian paint industry showed any real interest in water soluble polymers as we know them now. During the period 1974 1981 the industry felt the impact of both an energy crisis and restrictive environmental legislation.

The energy crisis of the late seventies drove home the point that hydrocarbon solvents would not always be readily available and they would certainly never be as cheap as before. The paint industry started looking for cheaper more readily available solvents. Water is readily available and cheap.

Legislation related to environmental and safety issues have affected all areas of the industry. This can be
seen in the way companies handle and use their raw materials make their products and deal with the
disposal of waste. It has also affected the types of products made and their methods of application.
Environmental and safety legislation can be expected to become more restrictive. To gain some idea where
environmental legislation for Australia is heading we can look at what has happened in America since 1966.
In 1966 the County of Los Angeles adopted the Rule 66 regulations of the Los Angeles County Air Pollution
Control District. These regulations were the model for environmental legislation in many States as well as
the American E.P.A. In 1979 Rule 66 type regulations were in effect in twenty two states for controlling
baking oven emissions and eleven states had regulations controlling architectural coatings.
The pressure of both economic and environmental considerations has forced the industry to use water
soluble coatings in some areas.
**WATER SOLUBLE POLYMERS**

Most conventional coating polymers at present can be produced in a form that will allow them to be
solubilized in water. These include alkyds polyesters acrylics and epoxies. As a general rule free acidic or
basic functional groups are incorporated along the polymer backbone. These functional groups are capable
of being neutralized by acids or bases to produce water soluble soap as shown in figure 3.

**Maleinized drying oils**

It has been known for many years that maleinized drying oils produce water soluble coatings. Maleic
anhydride was with the unsaturation in drying oils able to produce maleic adducts with pendant carboxylic
acids. These acid groups were then neutralized with ammonia or amines to produce water soluble oils.
Maleinized oils or modified oils were the first vehicles used in electro deposition coatings.

**Alkyd Resins**

Alkyd resins are made by esterifying vegetable oils or fatty acids and various monofunctional and
difunctional acids or anhydrides with a variety of di tri and tetra functional polyols. Depending on the type of
oil or fatty acids used they may be classed as air drying that is cross linked by autoxidation of the fatty acid
residues or non air drying resins.

Water soluble alkyd resins are similar to their solvent borne counterparts. The major difference is that their
formulation is modified to introduce pendant carboxylic acid groups along the polymer backbone. These
pendant acid groups can be neutralized with basic compounds to produce water soluble soaps of the alkyd
polymer. Most water soluble alkyds in commercial use would have acid values of 40 to 65 (on resin solids).

These pendant acid groups can be incorporated into the polymer backbone in different ways

One method is to initially produce a maleinized oil. This is done by reacting maleic anhydride or fumaric
acid with an oil or fatty acid containing conjugated unsaturation. Usually this is carried out at temperatures
of 210° to 240°C. The maleinized oil is then reacted with a dibasic acid and a polyol. This is then processed
in a similar manner to conventional alkyds down to an acid value in the range of 40 to 60 at temperatures
between 175 and 200°C. The polymer is then cooled and thinned with water miscible cosolvents. The
second stage of this process involves the reaction of the unreacted anhydride groups and the polyols. The
reaction occurs at temperatures slightly above 150°C. The true acid polyol condensation reaction except for
fatty acids does not generally occur to any significant degree at temperatures below 200°C. Controlling the
temperature during this stage ensures that there will be sufficient free carboxylic acid groups available for
neutralization and solubilization in water.

Another method is to initially prepare a hydroxy rich prepolymer of low acid value usually below 10. The
prepolymer is in fact a partial alkyd. It is made by reacting suitable quantities of vegetable oils or their fatty
acids with dibasic acids or anhydrides and polyols. Normal alkyd processing techniques and temperatures
(220° to 240° C) can be used to make this prepolymer. When the desired acid value has been reached
more di or tri basic acid or anhydride is added. The reaction mixture is then usually processed at
temperatures in the vicinity of 170 to 200° C down to an acid value of 40 to 60. Materials such as phthalic
anhydride or trimellitic anhydride are typical of the acids or anhydrides used in this second stage. Generally water soluble alkyds are prepared from fatty acids rather than vegetable oils. This overcomes the need for an alcoholysis or acidolysis stage to produce a product that can readily react with the remaining acids and polyols.

Polyols containing primary hydroxyl groups such as trimethylol propane trimethylol ethane neopentyl glycol and 1,4 cyclohexanediethanol are preferred to polyols such as glycerine which contain secondary hydroxyl groups. Primary hydroxyl groups generally react with acids and anhydrides more readily than secondary hydroxyl groups. There is also some evidence to suggest that water soluble alkyds based on trimethylol propane trimethylol ethane neopentyl glycol or cyclohexanediethanol give better resistance to hydrolytic breakdown of the ester linkages than those based on glycerine when the polymers are dissolved in the water amine solution.

Owing to the slower drying properties of water soluble air dry alkyds it is common to use fatty acids with fairly high levels of conjugated unsaturation. This helps to compensate for the retardation of autoxidation of the fatty acid residues in the presence of water amines and alcohols.

Several attempts have been made to improve the early drying properties and early water resistance of water soluble alkyds. These have included

Processing a hard resin such as rosin or other resins with acidic functionality into the polymers
Cold blending of hard resins which have sufficiently high acid values to allow them to be soluble in the amine/water system
Reacting small amounts of multifunctional acrylates such as trimethylol propane triacrylate into the alkyd resin and
Copolymerizing conventional acrylic monomers such as styrene methyl methacrylate or vinyl toluene with the alkyd polymer.

Acrylic modified Water soluble Alkyds

Acrylic modified water soluble alkyds can differ from water soluble alkyds as follows. Their advantages are
Improved initial drying properties
Improved early water resistance
Improved resistance to yellowing
Improved hardness and
Improved gloss and gloss retention.
Their disadvantages are
Poor adhesion
Increased embitterment on exterior exposure
Reduced shelf life
Reduced pigment wetting and
Reduced flow and leveling.

Many of these disadvantages can be overcome by careful selection of the acrylic monomers used. Acrylic modification can be accomplished by techniques similar to those used for solvent borne acrylic modified alkyds.

One approach is to make a reactive acrylic polymer containing both hydroxyl and acidic functional groups. This reactive acrylic polymer can then be processed into the alkyd by condensation with the other alkyd constituents. Processing conditions are similar to those used to make unmodified water soluble alkyds.

If the alkyd portion is to be made from non conjugated fatty acids the following technique could be used. A hydroxy rich prepolymer is made from fatty acids dibasic acids and polyols. Ethylenic unsaturation is then introduced into the polymer. This can be done by condensing maleic anhydride with the hydroxy rich prepolymer. The acrylic monomers are then grafted onto the alkyd backbone via the ethylenic unsaturation
introduced by the maleic anhydride.

When the fatty acid component has a sufficiently high level of conjugated unsaturation the acrylic monomers can be directly copolymerized onto the fatty acids. This can be achieved by using Diels Alder type reactions or free radical polymerization. The acrylated fatty acids can then be used to make an acrylic modified alkyd using techniques similar to those employed in making unmodified water soluble alkyds.

Polyesters

Water soluble polyesters or oil free alkyds are based on components commonly used in alkyds. The processing techniques are also similar.

The major difference is that polyesters do not contain any fatty acids. They rely on the use of long carbon chain dibasic acids (e.g. adipic acid) and suitable combinations of polyols to give them the required degree of flexibility. As water soluble polyesters do not contain conjugated fatty acids they will not air dry or cure by autoxidation. To achieve their intended levels of performance they generally need to be cross linked at elevated temperatures. The most common cross linking agents are monomeric or polymeric alkylated amino formaldehyde resins. Polyesters like alkyds can be made either by a two stage process using trimellitic anhydride or by a single stage process without trimellitic anhydride. In the latter case phthalic anhydride and adipic acid are commonly used.

Generally the differences between water soluble alkyds and water soluble polyesters in performance and end uses are analogous to those of their solvent borne counterparts. In some cases problems such as poor pigment dispersion poor substrate wetting and various flow and surface defects may be more pronounced. These can usually be overcome with careful formulation.

Silicone modified Alkyds and Polyesters

Water soluble silicone modified alkyds and polyesters are claimed to have the same advantages over unmodified water soluble resins as their solvent based counterparts. These improved properties include heat resistance and exterior durability.

One method of preparing water soluble silicone modified resins is to prepare a hydroxy rich alkyd or polyester prepolymer which is then reacted with a suitable silicone intermediate. This reaction may produce methanol as a by product. After the silicone intermediate is reacted trimellitic anhydride can be added and the resin processed to the desired viscosity and acid value.

Epoxy Resins

Water soluble modified epoxy resins are being used in commercial quantities in Australia as binders in electrodeposition primers which have significant usage in the automotive industry. Generally water soluble epoxy resins are modified epoxies which include products such as epoxy esters. The manufacture of water soluble epoxies generally involves reactions to increase the molecular weight and to introduce acidic or basic groups that can be neutralized to give water soluble polymers.

Anhydrides

One of the earliest methods of solubilizing an epoxy resin was to react commercially available epoxy resins with maleinized oils.

Another technique was to react the epoxy resin with a fatty acid via the epoxy groups and some of the pendant hydroxy groups. This is followed by the formation of a half ester of an anhydride or dibasic acid with the remaining hydroxyl groups. This gives a number of free carboxylic acid groups that are capable of neutralization and solubilization with a suitable base.

Defunctionalizing the Epoxide Ring

The potential for gelation of epoxy modified resins can be reduced by first defunctionalizing the epoxy resin by reactions that can cap the epoxide ring preventing excessive side reactions occurring at the epoxide group. This can be achieved by reacting the epoxy resin with materials such as Bisphenol A. The reaction with Bisphenol A may involve a controlled degree of polymerization of the epoxy resin. When the capping
reaction is complete mono di or tri functional acids or anhydrides can be reacted with the remaining secondary hydroxyl groups on the epoxy backbone. If maleinized oils or di or tri functional acids are used they will introduce enough pendant carboxylic acid groups to allow solubilization in water by neutralization.

Keeping the Epoxide Ring Available for Subsequent Cross-linking

The previous techniques involve destruction of the epoxide ring during manufacture of the water soluble resin. This approach retains the epoxide ring intact for use in cross linking the applied coating. Under specific conditions the secondary hydroxyl groups on the epoxy resin can be preferentially esterified with di or tri basic acids and anhydrides to form half esters carboxylic groups available for neutralization and solubilization.

**ACRYLIC SOLUTION RESINS**

Acrylic resins for protective coatings were first produced as commercial products in the 1930s and found initial acceptance with some low volume specialty applications. The use of acrylics remained limited until 1953 when the first acrylic emulsion polymer designed specifically for latex paints was introduced. Since then both acrylic emulsion and solution polymers have established a solid reputation for outstanding performance in exterior coatings.

The key property of acrylic polymers is a level of exterior durability that exceeds other common polymers of similar cost. This reputation and more recent advances in technology have contributed to the rapid expansion through the 1960s and 1970s to the present acrylic polymers are now used in a wide range of industrial and domestic applications.

The three principal forms of acrylic polymer used in surface coatings are
- Thermoplastic dispersion that is acrylic latex
- Thermoplastic solution (TPA) and
- Thermosetting solution (TSA).

Other less common acrylics are non aqueous dispersions and aqueous solutions base neutralized.

The technology of acrylic emulsion manufacture and applications are described in detail elsewhere. This chapter deals with the technology of acrylic thermoplastic and thermosetting solution resins and their applications in industrial surface coatings.

**TERMINOLOGY**

The term acrylic is commonly associated with such things as Plexiglas and Perspex acrylic sheet acrylic fibres for carpets or apparel or the acrylic water based paints for exterior and interior applications. The acrylic organic solution polymers although just as important to the consumer are less well known since they are used chiefly in industrial coatings and thus lose their identity by the time they reach the ultimate consumer. The term acrylic when applied to these products means a polymer based on acrylic or methacrylic monomers. The industry has however extended the terminology to cover a wide range of copolymer systems which in many cases consist of predominantly vinyl monomers (particularly styrene) as well as acrylic monomers. In practice the industry uses the term solution acrylic to cover virtually all thermosetting and thermoplastic compositions based on copolymers prepared from acrylic monomers or other monomers easily copolymerized with them.

The following monomers are commonly used in the synthesis of acrylic solution polymers. Vinyl chloride and vinyl acetate monomers are excluded from this group of monomers as they are used in the manufacture of PVC and PVA polymers.

Acrylic solution polymers can be further sub divided into two distinct groups thermosetting acrylics and thermoplastic acrylics. Thermosetting acrylics are polymers containing backbone monomers which make up the bulk of the polymer together with at least one monomer which contains a reactive group the latter will allow cross linking through heat or with catalyst. The term includes systems that comprise a mixture of
copolymers with a second compound or resin which will crosslink with it. Thermoplastic acrylics are prepared by the homopolymerization or copolymerization of a mixture of acrylic and methacrylic monomers and are usually considered relatively inert.

**BACKBONE MONOMERS**
The principal building blocks for thermoplastic acrylics are methacrylate and acrylate esters. Methacrylate esters differ in composition from the corresponding acrylate ester by the presence of a methyl group substituted at the alpha carbon. Ethyl methacrylate and ethyl acrylate monomers are shown in figure 1. Monomers used for coatings are usually based on methyl or ethyl esters but these are rarely higher than butyl as the polymer tends to become too soft when high esters are used.

**Synthesis**
Methylmethacrylate monomer can be made in a multi-step process from acetone hydrocyanic acid sulfuric acid and methanol. These steps may be shown in simplified form as follows:

Early production of acrylic ester monomers started with ethylene chlorohydrin and sodium cyanide. Following the Second World War one company developed a more economical continuous catalytic process in which carbon monoxide acetylene and alcohol are passed through a catalytic converter containing nickel carbonyl and hydrochloric acid. The acrylate monomer produced depends on the choice of alcohol; methanol for example produces methyl acrylate monomer while butyl alcohol produces butyl acrylate monomer. Chemically the process may be represented as follows:

**ADDITION POLYMERIZATION**
The most common method of manufacture of solution acrylic resins involves the addition polymerization of monomer in solvent using a free radical initiator at elevated temperature. The solvent is chosen on the basis of:

Correct polymerization conditions such as reflux temperature and viscosity and
The end use of the polymer solution solvent should suit the method of application and the drying requirements of a finished coating.

It is preferable for ease of control to carry out the reaction at reflux temperature but this is not essential. Several factors govern the choice of molecular weight range for a particular end use. Low molecular weight polymers have the advantage of good spraying properties and high solids at spray viscosity. On the other hand low molecular weight copolymers require more crosslinking to give the desired properties such as good durability; this may involve the use of more of the expensive reactive group monomers. For certain end uses it is possible to obtain a better balance of properties with higher molecular weight copolymers and less crosslinking. In the case of finishes applied by roller coating techniques higher molecular weight can be tolerated with good application properties.

In general conditions that encourage an increase in the rate of chain initiation lead to lower molecular weight. Thus high temperature relatively high initiator concentration and use of initiator with low decomposition temperature all lead to lower molecular weight. Chain transfer agents such as dodecyl mercaptan are often used to control molecular weight where a higher catalyst concentration or higher temperature is not practical.

Thus the chain transfer agent terminates a growing chain whilst creating a new free radical capable of initiating a further chain.

Solvents act as chain transfer agents to varying degrees. The monomer concentration in solvent will influence the molecular weight as the monomer concentration decreases the molecular weight becomes less. As a consequence lower molecular weight occurs when the monomer is added gradually to a solvent during polymerization rather than if all the monomer is charged before polymerization begins.

In a simple addition copolymerization where no crosslinking side reaction can occur the final viscosity is predetermined by the conditions of the reaction. The viscosity of the solution will increase only to the point
where full conversion is reached. The molecular weight of individual polymer chains will not increase after
termination. The molecular weight (viscosity) of the solid resin is actually higher at 50 per cent conversion
than at 100 per cent conversion. This is the opposite to condensation polymers in which the viscosity is low
in the early part of the cook and the reaction must be kept moving until the desired viscosity is obtained.

COPOLYMERIZATION
A number of studies have shown that improved properties are often obtained by a more uniform distribution
of plasticizing monomer and/or monomers containing reactive groups. Some improvement in distribution
can be obtained by adding the premixed monomers over a period of time to refluxing solvent. A more
precise approach involves consideration of reactivity ratios or in multi monomer mixtures copolymerization
constants known as Qe values. By the use of these methods an initial charge may be made that will result
in an initial copolymer with the required ratios. The remaining monomer is then fed in to give the desired
overall composition.

By using the techniques mentioned above to prepare to copolymer with distributed functional groups the
overall proportion of the more expensive monomer may be reduced whilst still maintaining minimum cross
linking requirements. At the same time individual polymer chains will not have a large number of cross
linking sites which could lead to poor stability and in some cases require the use of more expensive
solvents.

**The copolymer equation**

If both ratios are large (greater than 1.0) two homopolymers form rather than a uniform copolymer. If both
ratios are small a true alternating copolymer forms. If both ratios are close to 1 a copolymer forms which
has a random arrangement of monomer units along the chain. If the reactivity ratios differ greatly
copolymers do not form readily.

Figure 4 sets out examples of published reactivity ratios relevant to thermosetting acrylics. These figures
indicate that the following pairs will copolymerize satisfactorily methyl methacrylate/styrene methyl
methacrylate/methacrylamide methyl methacrylate/methacrylic acid. On the other hand styrene/vinyl
acetate will first form a virtual homopolymer of styrene because both radicals strongly prefer to add styrene
monomer. In the case of styrene/maleic anhydride where both r1 and r2 are nearly zero an alternating 1 1
copolymer will first form even if one monomer is in very high excess.

Hence the initial copolymer formed would have a mole ratio of 3 1 methyl methacrylate/ methacrylic acid
that is it will have a much higher functionality than the overall copolymer composition. No polymerization
proceeds the methacrylic acid content of the unreacted monomer will decrease because it is being used up
at a faster rate than methyl methacrylate. As a consequence the functionality of the copolymer being
formed will gradually decrease to a minimum below that of the average composition.

THERMOPLASTIC ACRYLICS

Selection of Monomer
The properties of acrylic and methacrylic ester polymers depend mainly on the alcohol used in the
preparation of the monomer. Methacrylate polymers with ten carbon atoms or less in the ester grouping are
harder and have higher tensile strength and less elongation than the corresponding acrylate polymers. This
increased rigidity is due to the presence of the methyl group on the alpha carbon of the main chain. For
example a film of polymeric methyl acrylate is tough moderately hard and rubbery with an elongation of
approximately 750 per cent. The polymer of approximately the same molecular weight made from methyl
methacrylate is considerably harder and more rigid with an elongation of only 4 per cent. Polymers of ethyl
and butyl methacrylate are softer and more flexible but free from appreciable tack. Table 1 shows some
general properties of acrylic and methacrylic monomers.

In general the flexibility and hardness of acrylic and methacrylic ester copolymers can be predicted from the
molecular weight and the glass transition temperature of the monomers used in the preparation of the
copolymer. Acrylic polymers do not exhibit sharp melting points but have second order transition temperatures at which a glass like solid converts to a rubbery or semitacky state. The onset of polymer softening is usually identified as Tg (glass transition temperature) but the entire transition may occur over a wide temperature range. Another important property to be considered in the selection of monomer is the polarity and its effect on the solubility of the resin. Polymers from acrylic and methacrylic esters of lower alcohols are usually soluble in aromatic hydrocarbons esters ketones and various chlorinated solvents. Solubility in weak polar solvents such as mineral thinners and VM & P Naptha can be achieved by selecting methacrylate and acrylate esters of long chain alcohols. In general the more polar acrylics will have the best petrol resistance while the more hydrophobic acrylics will give the best water resistance.

Solution Polymerization

Solution polymerizations of acrylic esters are usually carried out in large agitated stainless steel nickel or glass lined cylindrical kettles. The kettle should be fitted with a jacket for heating or cooling reflux condenser inlets (for addition of the reaction mix initiator and inert gas if needed) sight glasses a thermometer and a rupture disc. There should be a bottom valve for discharging the finished solution to receiving tanks or drums. Monomers are pumped or gravity fed from weighing or measuring tanks situated close to the reactor.

Since the polymerization is accompanied by the liberation of considerable heat the danger of violent or runaway reaction must be considered. This is most easily controlled by gradual addition of the reactants to the kettle. The amount of initial charge and the rate of addition depend on the composition of the reaction mixture the size of the kettle and the efficiency of the condenser and cooling jacket. Too high a concentration of unreacted monomer must be avoided.

The usual reaction mixture is a 40 to 60 per cent solution of the monomers in solvent. Acrylic polymers are soluble in aromatic hydrocarbons and chlorohydrocarbons. Polyacrylates and polymethacrylates of the lower alcohols are also soluble in esters and ketones but only slightly soluble in aliphatic hydrocarbons ethers and alcohols. The higher alkyl polymers are readily soluble in aliphatic hydrocarbons but insoluble in oxygenated solvents. Liquids that are good solvents for acrylic polymers must of course be used in this reaction system.

Most of the solvent is placed in the kettle and heated to the desired temperature or to reflux. Separate streams of the monomers and the initiator dissolved in the reaction solvent are then added slowly. Part of the solvent is often withheld until the end of the reaction to permit the attainment of higher molecular weight. The initiators are either oil soluble organic peroxides or azo derivatives which are used in amounts from 0.22 to 2 per cent of the mass of monomer. The duration of the polymerization is usually 8 to 24 hours. Conversion can be determined during and after the reaction by evaporation of a sample to constant mass under reduced pressure at 100º to 120º C.

Although solvents themselves act as chain transfer agents thereby affecting the molecular weight of the product more effective agents such as mercaptans may be added when it is desired to produce polymers of particularly low molecular weight.

Methods of Polymerization

Water soluble polymers may be grouped under three main headings

Naturally occurring

Semi synthetic in which inherently insoluble polymers are modified by suitable chemical treatment in order to disturb their normal structures and enhance their interaction with water

Completely synthetic polymers which are produced by condensation addition or ring opening polymerization.

The most commercially important examples of this group are the polymers of acrylamide and its C and N
substituted derivatives acrylic and methacrylic acids N vinyl amines cyclic and vinyl ethers. The present chapter will deal with completely synthetic polymers and in view of their commercial importance and the considerable amount of work published will concentrate mainly on the free radical polymerization of the acrylamides and acrylic and methacrylic acids with the aim of describing the present state of the art discussing where possible the chemical principles involved.

The actual relationships observed in practice are of course strongly influenced by the various complicating factors which occur. Typical examples of such effects are radical caging radical and monomer complexing conformational effects in the growing chains degradative transfer the nature of the initiation step etc. Complicating effects are frequently encountered in copolymerization as well as in homopolymerization and have been the subject of much study and speculation.

A considerable effect is also exerted by the polymerization temperature. This is further complicated if the polymerization is carried cut under approximately adiabatic conditions as is often the case.

ACRYLAMIDE

Acrylamide and its C and N substituted homologues readily polymerize by free radical mechanisms in the absence of oxygen. Several detailed literature reviews of the subject have appeared.

At high pH anionic initiation yields poly alanine (nylon 3) by a hydrogen transfer mechanism. At low pH and high temperature imidization occurs.

If intermolecular imidization occurs the product is insoluble but this is not necessarily the case if the reaction is intramolecular.

Initiation Methods

The major methods of free radical initiation are:

- Thermal or photolytic decomposition of an initiator (sometimes in the presence of a promoter)
- Redox initiation
- Physical excitation of monomer in bulk or solution.

Photolytic decomposition often presents practical problems thermal decomposition of a heat sensitive compound is usually preferred. Unfortunately however common initiators require the use of temperatures rather higher than are convenient for easy dissipation of heat resulting from the relatively high exothermicity of an acrylamide polymerization. One method of overcoming this problem is by the addition of a promoter which lowers the energy of activation of the decomposition process thus giving higher rates and lessened temperature dependence. An equivalent approach is to use a redox initiation system. The individual components of the latter system are quite stable but react rapidly when mixed at relatively low temperatures. The major difficulty with such systems is the rapid disappearance of the redox system components and the possible effect of chain transfer etc. on the degree of polymerization of the product.

Rapid consumption of redox initiator components may lead to a cessation of polymerization before complete conversion of monomer to polymer. Continuous addition of the redox components is not usually possible because of the high viscosity of the polymerizing system.

An alternative approach has been to combine a redox system with a heat sensitive initiator. In this case the approximately adiabatic polymerization is initiated during the first stage of the process by the redox system as the temperature rises the heat sensitive compound becomes the radical source as the redox system becomes exhausted.

The above are the major commercial methods of initiation employed in the polymerization and copolymerization of acrylamide and its analogues. Initiation methods involving physical excitation of monomer in bulk or solution are however becoming of increasing technical importance. They include electron beam irradiation electrolytic initiation plasma polymerization high pressure shear and mechano chemical methods ultrasonic photosensitized and high energy radiation methods. Polymerization can also occur in the solid state.
SINGLE COMPONENT INITIATORS
A large number of heat and light sensitive compounds suitable for use as initiators is available. An excellent review by Sheppard and Kamath has recently appeared. Amongst the many compounds suggested are the following

**Inorganic peroxides** Various persulphates (sometimes promoted by metal ions such as Cu Ag) peroxy diphosphate nitrogen peroxide.

**Organic peroxides** A wide range of diacyl dialkyl peroxides hydroperoxides and peroxy esters is available. A major disadvantage of the use of peroxides is the likelihood of trace impurities and chain transfer agents etc. acting as reductants so forming redox couple systems inadvertently.

**Organic azo compounds** Bis (cyanoalkyls) bis (cyanocarboxylic acids) bis(alkylamidines) amino acetic acid derivatives are widely used. These have the advantage of usually being less susceptible to the effects of solvent and impurities and are therefore less likely to cause initiation problems. The introduction of polar substituents increases water solubility and in recent years various workers have reported data for many such initiators.

**Metal complexes** Ce(IV) Co(III) Mn(III) Fe(III) Ni(II) and Cu(II) have been reported in the literature.

REDOX INITIATORS
Many long established systems are still used including for example persulphate coupled with metabisulphite sulphite thiosulphate and Fe (II). Hydrogen peroxide is coupled with hydroxylamine Fe (II) etc. More recent work has concentrated on the attack on particularly susceptible groups. Persulphate has been used to oxidize the S H group of water soluble mercaptyls such as cysteine hydrochloride thioglycollic thiomalic and thiolacetic acids 2 mercaptoethylamine 2 mercaptoethanol etc.

Attack on a number of amino substituted oxidants has been studied. Examples are the attack of persulphate on dimethylamino propionitrile morpholinopropionamide urea and silver aminoacetate.

MECHANISM OF INITIATION
Many accounts of the elucidation of the initiation mechanisms of a wide range of initiators have been published. Fission of the relatively labile O-O bond is the usual route to radical production in the case of the peroxides. C-N bond rupture is the typical route in the case of the azo compounds. Decomposition may be affected by the solvent. As an example low pH favours the non radical decomposition of persulphate whilst azo bis(isobutyronitrile) is comparatively insensitive to pH difference.

Addition of promoters to increase the rate of decomposition of the initiator is commonly practised. In general such addition leads to decreased energy of activation. The amine promoted decomposition has been exploited to a limited extent in acrylamide polymerization. A redox mechanism has been reliably confirmed and the increased rate of decomposition has been ascribed to distortion of the peroxidic bond due to the formation of charged intermediates. It is also found that the presence of electron donor groups on the amine and electron acceptor groups on the peroxide enhance the rate of decomposition.

Both systems are affected by pH the former displaying a rate maximum around pH 4 due possibly to ionic strength effects coupled with the increasing importance of a non radical decomposition route at low pH the mercaptyl containing systems display a reduction in rate with increase in pH. This has been ascribed to the consequent increase in the degree of ionization and the reduction in concentration of RSH. Systems which employ combinations of oxidizing agents coupled with amino substituted oxidants resemble in general the amine promoted initiators previously mentioned. In such systems decomposition of an intermediate complex leads to production of radicals.

Oxidation of carboxylic acids by acidified permanganate is very complex and mechanisms are highly specific to each acid. Highly reactive Mn(III) is generally claimed to be involved and is thought to result from the disproportionation of Mn(II) and Mn(IV). The initiating radicals are usually fragmented species originating from the relevant carboxylic acid. It is usually essential to maintain a sufficiently low pH to
ensure that the MnO2 remains in solution.

DEPENDENCE OF POLYMERIZATION ON TEMPERATURE

The effect of temperature variation in an adiabatic polymerization has already been mentioned. It was pointed out that this is controlled mainly by the energy of activation of the initiation process which is of great importance in determining the overall energy of activation of the entire process. Table 1 lists such data for a few common initiators only since there are extensive compilations in the literature. These values are seen to lie within fairly narrow limits but decomposition rate is very sensitive to the value of the energy of activation for the decomposition (Ed).

A more practically useful quantity for comparing initiators is the 10 hour half life temperature. This is the temperature at which 50% of the initiator is consumed in 10 hours. Clearly CAT 78 (2 2 azobis(2 amidinopropane) hydrochloride) is the most rapidly decomposing of the initiators quoted. In general a useful rule of thumb is that the temperature chosen should be that at which the half life is equal to the time of reaction.

Redox and promoted polymerizations usually but not always display lower energies of activation than do single component initiators. This is apparent from the data of Table 2. Rationalization of such data is not easy however. The most surprising feature is of course the negative values displayed by a few of the initiators. Decrease in rate with increase in temperature is not commonly encountered in free radical polymerization. The phenomenon in these cases has been ascribed to entropy effects on termination between primary and polymer radicals.

PROPAGATION AND TERMINATION

The propagation process is significantly affected by the nature of the polymerization medium by pH solvent presence of salts complexing agents surfactants etc. all of which exert a strong influence on the rate of polymerization and on the nature of the produce. Results of such studies are sometimes contradictory and reproducibility is not always good.

EFFECT OF pH

Table 3 shows that the velocity coefficients for propagation and termination in aqueous solution both increase with fall in pH. The variation is such however that the ratio kp/kt½ remains substantially constant. As a result the rate of polymerization is virtually constant provided that the initiation process itself is independent of pH. Dainton et al. suggested that the variation in kp and kt is the result of change in reactivity due to alkaline hydrolysis of the amide group repulsion between reactant species and change in conformation and mobility of the growing radicals.

Abkin (Table 3) reported a decrease in Ep as the pH changes from 13 to 7. These workers explained this mainly in terms of the increasing extent of protonation of the amide group with decrease in pH. The consequent localization of the unpaired electron by the positive charge on the nitrogen atom would be expected to lead to an increase in the reactivity of the growing radical and thus a decrease in Ep with decrease in pH. It may be presumed that this effect more than compensates for charge repulsion effects which would also be expected to increase with fall in pH and would therefore give an increase in Ep. Despite the expected increase in kt being in fact observed the value of Et surprisingly increases as the pH falls. This has been ascribed to increased repulsive forces between the terminating radicals. The larger value of kt is thus a consequence of the marked increase in At at lower pH values. Changes in shape size and nature of the growing radicals will undoubtedly affect entropy of activation with significant effects. Copolymerization studies which are discussed below have led to the suggestion that pH controlled keto enol tautomerism may be responsible for the effect.

Unfortunately copolymerization studies in general have not clarified the situation. Many of the studies of the effect of pH carried out using aqueous phase copolymerization techniques have involved ionogenic comonomers whose behaviour is also pH dependent. Values obtained for the ratio kp/kt½ are very much
greater than for most monomers (for example 0.01 0.04 and 0.12 for styrene methyl methacrylate and vinyl acetate polymerization respectively at 25°C.). The high value of this ratio is responsible for the rapid rate of polymerization and high molar mass polymers obtained from acrylamide.

Effect OF MONOMER CONCENTRATION
Studies using different initiators solvents and monomer concentration ranges have indicated values of 1 to 1.5 for the dependence of rate of polymerization on monomer concentration. Explanations for such values are usually in terms of radical caging monomer complexation diffusion control solvent transfer etc. although these suggestions have been criticised. In this context too the proposals of Chapiro involving matrix and oriented polymerizations which are discussed later cannot be ignored.

EFFECT OF POLYMERIZATION MEDIUM
Homogeneous polymerization of acrylamide is usually carried out in the aqueous phase. The presence of additives can exert a profound effect and can yield information about the component processes involved. Organic reagents such as alcohols acetone dimethylsulphoxide (DMSO) and tetrahydrofuran (THF) generally depress kp kt Rp and Pn and at some stage may cause polymer precipitation according to many workers. Abkin have been very active in the field and have shown that the rate of polymerization varies with this nature of the solvent in the following order
Rate in the presence of water  formamide dimethylsulphoxide Table 4. shows some of their results. Dioxan (DO) and THF also exert a significant effect but unfortunately cause precipitation of the polymer is they are present in amounts greater than 10%. For reasons of brevity discussion will be restricted to the DMSO water systems. These workers also studied the importance of the various monomer solvent and radical interactions by cryoscopy heat of solution NMR reactant and product solution measurements.

Fabrication of Water Soluble Polymers
The conversion of both plasticized and rigid PVC into finished products can be carried out by the usual processing techniques such as extrusion injection molding compression molding blow molding and calendaring. Plasticized compounds can be processed more easily than rigid products because the reduced softening point makes it possible to use lower temperatures 140 160°C compared with 185 190°C. The high processing temperature for unplasticized compounds requires that equipment be designed so that the material flows through without holdup otherwise stagnation results in thermal decomposition which will be evident by partial discoloration of the product and in more severe cases by an explosive generation of hydrogen chloride.

Extrusion
Both flexible and rigid vinyl formulations can be extruded into a variety of shapes including profiles tubes and sheet as well as wire sheathing by use of a crosshead die. The compound can be processed from either a powder blend or granulated material. Generally the granulated material can be handled on extruders of shorter screw length in the case of plasticized PVC an extruder with a screw of 16 1 length to diameter (L/D) ratio is satisfactory whereas if powder blends are being extruded equipment with a screw of 20 1 L/D ratio is required for pellets and 25 1 for powder. Single screw machines are normally used for plasticized compounds the compression ratio being 1.5 1 to 2.5 1 for granules and 2.5 1 to 4 1 for powder blends. Rigid compounds can also be processed on single screw extruders but with increasing use of powder blends higher outputs of better quality extrudates are obtained with multiscrew machines. The twinscrew extruder has been developed extensively for the extrusion of rigid compounds and is widely used in Europe where it is generally considered to be the best type of machine for this type of material the single screw machine however is still favored in the United States. The temperatures at which extrusion is carried out depend on the type of compound being processed and can be determined only by careful experimentation to obtain the best physical properties in the finished product the temperature of the
compound as it leaves the die must be maintained at its correct value. The temperature gradient on the extruder must be adjusted so that the head temperature approximates the temperature at which the compound emerges from the breaker plate. The quality of surface finish is determined by the correct adjustment of head temperature which should correlate as closely as possible with the temperature of the compound as it passes through to the die. Typical extruder temperatures for processing vinyl compounds are given in Table 1.

The temperatures used for powder blends are at the upper end of the scale and those for granulated compounds at the lower end. Since higher compression ratio screws are used for powder blends there is an increase in backpressure which will increase the shear forces this in turn will lead to faster fusion and greater development of heat. The control of temperature along the barrel may become a problem and it is not unusual for the frictional heat developed along the screw to be sufficient for maintaining the temperatures listed. The screw speed determines the temperatures that develop along the screw and if it is maintained at too high a value it may prove impossible to hold the temperatures within the limits given. Cooling the screw by water circulation increases the shearing effect this may be necessary to ensure adequate fusion and mixing of the compound in the extrusion of rigid products from powder blends.

Dies for extruding any vinyl compound must be highly streamlined to minimize burning during long production runs a hard polished chrome plating on the interior gives additional protection against decomposition improves the surface appearance of the extrudate and extends the useful life of the die. Unplasticized PVC has a very high melt viscosity at processing temperatures and therefore it is important that the machinery be sufficiently robust to contain the considerable pressures induced by the high carrying efficiency of the screw. The screw speeds employed for rigid PVC are generally between 5 and 40 rpm but the larger machines operate only between 5 and 15 rpm. Such low speeds require particularly strong bearings and low gearing of the motor drive. Completely variable screw speed is considered a necessity for the extrusion of rigid PVC. An extensive study of the effect of the various components of a plasticized PVC compound on its extrusion performance has been carried out (2) from which it is evident that for a compound of given softness i.e. fixed polymer plasticizer ratio the type and concentration of lubricant play a very important role.

**Wire Coating.** A significant part of extruded plasticized PVC is used for wire and cable insulation in which high rates of output are of paramount importance. The wire to be coated passes straight through a crosshead die at right angles to the length of the extruder. The polymer melt enters the crosshead from the extruder and is directed through 90° before it surrounds the wire and emerges through the die (Fig. 1) which controls the final thickness of material around the wire. The temperature of the die must be carefully controlled and the centering of the wire is critical. Since the insulation covering of the electric wire must be kept free from foreign particles that may produce a breakdown of the insulation a fine meshed screen is used in front of the breaker plate to remove any contaminants.

The wire which is pulled through the die by action of a capstan may be preheated electrically or flamed to remove lubricants and to improve adhesion. It is essential to maintain the wire speed within very close limits to ensure that a uniform thickness of the PVC coating is maintained. Both granules and powder blends can be used as feed to the extruder but the latter are prone to produce porosity in the wire covering unless a vented extruder is used. The rate at which the wire can be coated satisfactorily depends on the composition of the PVC compound the surface finish being the controlling factor. See also WIRE AND CABLE COVERINGS.

**Rigid Pipe and Tubing.** The extrusion of rigid PVC pipe and tubing has contributed in a very large degree to the expansion of the use of PVC. Heavy walled pipes can be extruded up to a diameter of 1 m and are used for water and gas distribution for drainage and for industrial applications. Thin walled pipes and tubes are used for gutters and downspouts ventilation ducting waste disposal and electrical conduit. The
extrusion of hollow profiles can be carried out using either granular or powder compounds. Single screw extruders are used mainly with granular material but the economic advantages obtained with powder blends have resulted in a considerable extension of the use of multiscrew extruders. In plant compounding of powder blends with the use of a multiscrew extruder can produce savings in the cost of raw material of 1 3/lb over buying the granulated compound.

The extrusion of hollow profiles requires a special die with an internal mandrel design as shown in Figure 2. The quality of the extruded product depends on correct die design one of the main requirements is for a smooth finish with an adequate land length ordinarily about twenty times the wall thickness of the pipe. Land length cannot be used alone and another factor to be taken into consideration is that the volumetric capacity of the head should be at least thirty times that of the die land. Crosshead dies may also be used but careful design of the radius of entry into the die is required to prevent stagnation on the radius which should be as great as possible. For small pipe and profiles the use of polytetrafluoroethylene coated dies and mandrels helps to produce high quality extrusions.

Various cooling and sizing devices are used to adjust the internal and external diameters after the tube emerges from the die. Either pressure or vacuum sizing may be employed in the former the most satisfactory means of maintaining pressure in a pipe is by use of a floating bung. This allows lengths of pipe to be removed without losing pressure and prevents unnecessary scrap. Vacuum sizing is achieved by applying a vacuum through separate sections in the cooled sizing die to the hollow section during extrusion. This draws the section against the wall of the sizing die ensuring that the external dimension is maintained. Two separate vacuum zones are required in the sizing die to maintain the exact dimensions of heavier sections.

Another method of maintaining shape is by using an extended mandrel that is water cooled. After leaving the sizing equipment the pipe passes through a cooling bath refrigerated water is often necessary for rapid cooling to prevent distortion. The best results in sizing and cooling devices are obtained with minimum friction or drag. The haul off equipment which must provide a steady pull may be comprised of an electrically driven double belt with fully adjustable speed and height.

There is a growing trend to manufacture pipes of larger diameters with greater thicknesses. Machines that can produce pipe of up to 40 in. diameter are capable of a production rate of about 1000 lb/hr the thickness of the pipe may be up to 2 in.

**Blown Film.** Blown PVC film both rigid and plasticized is obtained by extrusion through a special tubular die in a manner similar to that which is used for polyethylene. Plasticized film must be extruded vertically upward using a right angle die on a normal horizontal extruder. This die must avoid the occurrence of points of stagnation or regions of decompression. Best results are obtained from dies of gooseneck design in which the compound is extruded through a cylindrical section with a gradual change in direction from the horizontal to the vertical. Air pressure is introduced through the die increasing the diameter of the bubble up to about three times the diameter at the die. Temperature control is required to maintain a constant film thickness and bubble diameter. The blown tube passes through pinch rolls ensuring the maintenance of the air pressure within the bubble. A perforated ring for cooling is located above the die and its position affects the film thickness which is also determined by the rate of haul off of the film. Orientation can be introduced into the film by stretching to produce a product suitable for shrink film applications this orientation is controlled by adjustment of the blow ratio and the speed of windup.

Rigid film can be produced using a similar technique except that the greater stiffness of the extrudate allows the process to be operated in a completely horizontal setup. This makes die construction simpler in that the polymer melt does not have to travel through 90° a very important feature in design when processing unplasticized compounds. Rigid PVC films are normally unplasticized although in Europe there is a large production of film usually described as rigid PVC and containing about 17% plasticizer. Film...
thicknesses can be as great as 0.02 in. but the usual value is about 0.001 in. For greater thicknesses a flat sheet die is used this technique has now been developed for thin film as well.

**Sheet Extrusion.** There has been a rapid increase in the market for unplasticized PVC sheet owing to its use for building applications. A large portion of the product is produced as transparent corrugated sheet with a thickness of 1/16 1/8 in. by extrusion from a flat sheet or circular die the tube in the latter case being cut at the die exit and opened out into a flat sheet. After the sheet has been extruded it is corrugated by passage through forming rollers. Both single and twin screw machines can be used satisfactorily for the extrusion with flat sheet dies whereas circular dies are normally employed only with a twin screw extruder. Best results are obtained from compounds using PVC resins with a K value of 55 60 it is now usual to extrude directly from dry blends using high bulk density polymers with relatively non porous particles. The design of the flat sheet die is complicated because the extrudate enters the manifold as a cylindrical slug which must be formed into a flat sheet in such a way that the rate of flow must be the same at all points from the outside edges of the die to the center. The length of the flow path to the extreme edges of the die is much longer than to the center and uniformity of flow of the polymer melt is obtained by the combined use of a profiled restrictor bar and a temperature gradient across the die lips. The shape of the manifold is largely determined by the melt flow characteristics of the PVC compound so that the formulation is critical (and the die will probably be unsuitable for other plastics). This complication is much less evident with circular dies but on the other hand slitting and opening of the extrudate may give rise to distortion in the final product.

When the sheet leaves the equipment it is usually passed through polishing rolls operating at 90 100°C to improve the surface finish. If it is to be corrugated the sheet is reheated on leaving the polishing rolls using infrared heaters before going through the corrugating equipment. Corrugation is normally done longitudinally with a marked reduction in the overall width of the sheet.

Thinner rigid sheet than the above for packaging applications can be produced using the flat sheet die and reducing the thickness by stretching the sheet as it leaves the die lips. This produces orientation in the direction of the machine operation. This technique is particularly suitable for producing heavier gage sheet (0.02 in.). The sheet is water cooled and passed through polished steel rolls this method produces flat sheet of maximum clarity and free from distortion.

**Molding**

**Injection Molding.** The molding of PVC has developed rapidly with the availability of the screw type injection molding machines prior to this when the ram type injection machine was standard only plasticized PVC could be molded and it required special attention to prevent holdup of material with consequent degradation. Unplasticized PVC can be handled only on screw type machines which have the advantage of being able to deliver a low viscosity homogeneous melt into the mold cavity with the minimum possibility of stagnation and with the maximum possible pressure on the melt. The working life of rigid PVC at the temperatures required for injection molding necessitates the introduction of the polymer melt into the mold in the shortest possible time once the optimum temperature has been reached at most this should take only two cycles. This was almost impossible to achieve with ram machines but the reciprocating screw injection molding machine is similar to a single screw extruder in that a homogeneous melt is obtained by shear forces set up by the rotation of the screw. As the material accumulates at the front of the screw the latter retracts until a preset position is reached at which the volume of accumulated molten material is sufficient to fill the mold the screw then stops rotating and moves forward to inject the melt into the mold. The screw then starts to rotate again and prepares the melt for the next shot. The screw is ordinarily of constant pitch with a compression ratio of about 2 1 has a long tapering cone with a very sharp tip and rotates at a speed of 20 50 rpm. The molding cycle can be varied over a wide range by adjustment of the speed of rotation of the screw and the times for the various stages of the process. The molten compound has a high melt...
viscosity compared with the majority of moldable thermoplastics and there is no need to use a non return flow valve at the outlet of the injection molding machine. In fact the use of such a valve must be avoided otherwise holdup with subsequent degradation occurs.

The pressures during injection of rigid compounds are approximately 12 000 15 000 lb/in.2 for plasticized compounds it is considerably less. (These pressures pertain to rigid compounds based on low molecular weight PVC with a K value of about 55.) High molecular weight resins such as used for extrusion are not suitable for the injection molding of rigid PVC compounds because their melt viscosity creates pressures too high for most machines. Some variations in molding performance can be obtained by varying the composition of the compound particularly the concentration of the lubricant. The feedstock may be in the form of either granules or powder blend the latter as in other processing techniques offers economic advantages but generally poses some problems.

**Blow Molding.** The blow molding of rigid PVC is generally limited to the manufacture of bottles. These are produced by extrusion of a tubular parison which is fed directly to a blow molding device and blown while it is still hot. Some of the first production of PVC bottles used a two stage process in which the parison was extruded as a continuous tube which was then cut into the required lengths these were then reheated prior to feeding to the blow molding operation. This process had some advantages eg more efficient extruder operation but the uniform reheating of the parisons required close control which could be attained only with expensive equipment specially designed for the operation. The main advantage that better quality control could be achieved in the extrusion of the parisons has now largely disappeared with the general improvements in blow molding machinery and the process has been largely superseded.

There is now a wide range of equipment suitable for blowing PVC bottles the design takes account of the need to avoid holdup or exposure of the compound to a high temperature for too long a time. Thus most of the equipment involves either continuous extrusion of a parison or the use of a reciprocating screw system to form the parison. Reciprocating screw systems are not yet widely used but appear to have some advantages such as production of less scrap the molding of special shapes giving better control of wall thickness and more uniform parison temperature. The equipment has the disadvantage that it gives lower production rates than the extrusion process. Normally continuous extrusion equipment is operated in conjunction with a multiple mold indexing system in which the previously blown bottles are cooled as additional parisons are formed clamped and blown from a continuously extruded tube.

The production of PVC bottles is usually limited to about 2500/hr. A recent development claims that it is now possible to design a machine with an output of at least 10 000/hr in sizes from 8 to 32 oz. The size of blown PVC containers is significantly less than the dimensions that can be obtained with polyolefins. This is due mainly to the fact that the thermal instability of PVC prevents the use of the accumulator type of equipment that is essential for blow molded items of large capacity. Two liter PVC containers are in general production and it has proved technically possible to manufacture containers of up to two gallon capacity.

Machines can operate both with powder blends and with granular compounds although the latter have now been superseded because of their high production costs. The compounds are normally based on PVC with a K value of 55 if glass clear bottles are required organotin stabilizers must be used for the best results. Copolymers of vinyl chloride and propylene have been developed primarily for the manufacture of PVC bottle compounds and are used for this application to some extent in the United States. They can be processed at lower temperatures than would be needed for homopolymers so that reduced amounts of stabilizer are required. With the increasing use of PVC for food packaging there is need for non toxic stabilizer calcium zinc stabilizers are now widely used although the clarity of the final product is not as good as with the tin stabilizers. Changes in the Food and Drug Administration regulations now permit the use of certain organotin stabilizers for packing some foods as long as extractability into the food does not exceed
Although strength of a bottle depends largely upon its design impact resistance can be improved by the incorporation of impact improvers which can be used without substantially reducing the clarity of the bottle.

**Compression Molding.** Compression molding has only limited use with PVC but it is used for processing rigid material into phonograph records with good surface properties. In the manufacture of phonograph records a rigid compound based on a copolymer containing about 15% vinyl acetate is used in order to have a low viscosity melt that gives an accurate reproduction of the details of the grooves of the record. The compound is mixed and fused and passed to a two roll mill from which it is stripped off and cut into biscuits of the requisite weight. These are then compression molded in a record press under a pressure of about 2000 psi. Some cooling is required at the end of the cycle to ensure that the record can be removed from the mold without distortion. The initial compound can also be prepared in pellet form using a continuous compounding. This is then fed to the press as preheated agglomerate by heating a preweighed amount of pellets to a temperature slightly above their softening point usually in a container through which a heated air stream can pass. This technique has been superseded largely by a method in which a powder blend is fed directly to a small extruder mounted in a vertical position over each record press. This is known as the boomer method. The equipment can be operated to deliver the requisite amount of material for each pressing cycle in the form of a molten extrudate directly into the mold. Other techniques such as injection molding are now replacing compression molding as this has occurred because of the improvements in molding machinery that allow higher pressures to be used.

Compression molding is the only way of making thick high quality rigid sheet. A number of sheets of calendared material are pressed together to form a heavy sheet up to 1 in. thick. The compound used for this process is usually based on a vinyl chloride copolymer containing a small amount of vinylide chloride. The product has excellent clarity and good impact properties.

**CALENDARING**

Calendar is used extensively for the production of both plasticized and rigid PVC sheet it is capable of producing high quality material at very high rates of output. Calendars first used for poly (vinyl chloride) were designed for processing rubber the latest equipment incorporates improvements resulting in increased efficiency high production rates wider sheets with improved thickness control and better equipment performance.

Although the cost of a calendar together with the auxiliary equipment is very high this is the most economical method for the production of PVC film and sheeting particularly for materials of relatively great thicknesses. A calendar can operate on thin plasticized PVC sheeting in widths up to 84 in. and thicknesses of 0.003 0.004 in. with a tolerance of 0.0001 in. at speeds in excess of 100 yd/min. At this speed the quantity of PVC compound being processed is about 3500 lb/hr with heavier sheets the output will probably be on the order of 5000 lb/hr. It is important if good quality sheeting is to be produced that the compound fed to the calendar be homogeneous and at the correct temperature this temperature must be closely controlled and is different for different types of compound. It is essential that the compound be subjected to the minimum heating cycle during the process because of the high temperatures encountered at the final calendar nip in the manufacture of thin sheet these temperatures may exceed 200°C. The normal method for feeding the compound to the calendar is by mixing the polymer with all the other ingredients in a ribbon type blender from which the powder blend is fed to a Banbury mixer which discharges the mixed compound onto a two roll mill. This compounding step ensures that batch to batch variation is minimized. From the mill the compound is fed to the calendar either as rolls of sheet or continuously by strips feeding. Continuous compounders such as the Buss Ko Kneader or the Werner and Pfleiderer Plastificator are used to feed the calendar directly.

Because of the high temperatures encountered in the nip of the calendar rolls where the compound is
subjected to high shear it is possible to use high molecular weight polymers (K value about 70) as the basis of the formulation. The various types of sheeting produced at present require the development of a special compound for each particular end use special stabilizers are required to avoid sulfur staining and plate out and to give good weatherability whereas special plasticizers are used for low temperature performance fire retardancy and resistance to extraction. Acrylic polymers and other polymeric processing aids are used to improve calendaring performance particularly in rigid formulations (see the section on Compound Ingredients above). The composition affects the surface properties of the sheet such as the ease with which it can be printed. All these variations in formulation require specific operating conditions on the calendar which must be established by almost empirical means on production equipment since laboratory equipment is capable of giving only a broad guide to start up conditions.

Properties of Water Soluble Polymers

Structure

The determination of the average chemical structure of individual PVC chains has been beset with great difficulties. The extent and type of stereo regularity and branching and the factors which control these properties are of paramount importance since they reflect the polymerization mechanism and can often dominate certain polymer properties eg thermal and photochemical stability crystallinity and rheology of polymer melts and solutions. It is convenient and appropriate to consider both branching and stereo regularity together since attempts to define and estimate the variation of stereo regularity have frequently been compromised by the concomitant variation in chain branching.

Reduction with zinc dust leads to the conclusion that in PVC prepared at normal temperatures the monomer units are incorporated predominantly in a head to tail sequence.

Branching. Branching in PVC has generally been determined by reduction of the polymer in tetrahydrofuran solution by lithium aluminum hydride to a polyethylene structure followed by estimation of the CH3 CH2 ratio in the molten product by infrared measurements usually through the absorbances at 1378 cm⁻¹ and 1368 cm⁻¹. Although a calibration curve for CH3 CH2 against ratio of optical densities can be relatively accurate at high CH3 CH2 ratios using a range of n paraffins the biggest source of error arises in extrapolating this curve into the range of ratios encountered in the reduction products of PVC. It has not yet been resolved whether the branching in PVC is predominantly short or long chain in nature and this factor will also influence the estimates.

Although most investigators agree that the branching decreases significantly as the temperature of polymerization decreases and becomes trivial below about -40 to -60°C there are wide discrepancies among absolute values. The results published in two detailed studies on branching may be quoted to illustrate the extent of the variation. The numerical values for branching incidence are expressed as the number of methyl groups per 100 methylene groups in the polyethylene structures obtained by reduction of the PVC. For example polymers prepared at 90 50 -15 and -75°C to undisclosed conversions yielded branching indexes of 0.27 0.20 0.05 and 0 respectively. A commercial polymer presumably a high conversion sample made at 55 60°C gave a value of 0.20. In another study polymers prepared at low conversion (~5%) with alkylboron and oxygen as initiator at 25 -20 and 60°C had indexes. of 1.78 1.30 and 0.65 respectively. A commercial polymer made at 50°C to 95% conversion gave a value of 1.80. Some of the discrepancies may be associated with varying interference by initiator end groups.

If the mechanism of bulk polymerization of vinyl chloride put forward is correct no significant variation of branching with conversion would be anticipated at least up to 70 80% conversion irrespective of whether the branching arose intramolecularly (short branches) or intermolecularly (long branches). One author claimed that branching was constant up to 95% conversion. The same author failed to find evidence for sufficient terminal CH2=CH-groups in the reduced polymers to account for the general claim that monomer
transfer controls the molecular weight in PVC.

Based on the measured transfer constant to 2,4,6 trichloroheptane an analog of PVC, one can calculate a branching incidence of one branch per molecule at 50°C. In establishing solution viscosity molecular weight relationships for PVC it has frequently been observed that the double logarithmic plot of intrinsic viscosity versus molecular weight for polymer fractions was linear for molecular weights up to about 150 000 170 000 but that significant deviations from linearity occurred in the direction of low viscosity for the fractions with molecular weights in excess of this value. The departure is consistent with a higher incidence of long chain branches per molecule in the higher molecular weight fractions. The Zimm and Kilb function has been applied to one set of data to derive a branching index of approximately 0.15 for certain polymers made at 50°C. Another estimate of branching is based on the assumption that the branch points will be initiated predominantly at the carbonhydrogen bonds of the CHCl groups leading to tertiary carbon chlorine bonds in the branched polymer.

A recent publication discloses branching indexes varying from 0.33 to 0.82 for PVC samples prepared over the temperature range -50°C to +60°C.

**Stereoregularity and Crystallinity.** Commercial poly(vinyl chloride) is a largely amorphous polymer but with a small proportion (about 5%) of small and imperfect crystallites. The rather diffuse X-ray diffraction pattern has a repeat distance of about 5 Å and agrees with a syndiotactic planar zigzag structure. A reduction of the polymerization temperature gives sharper but still diffuse X-ray patterns and the polymer becomes less soluble in solvents. Estimated melting points range from 155°C for polymers made at 125°C to 310°C for those made at 75°C. There is a corresponding increase in glass transition temperature from 68 to 105°C. Commercial poly(vinyl chlorides) have Tg values of about 80–85°C.

Significant changes also occur in the infrared spectra. There are a number of absorbances in the region 700–600 cm⁻¹ and the relative intensities of several of these vary with polymerization temperature. Using frequencies at 635 and 692 cm⁻¹ the ratio of intensities was found to change from 1.3 at 70°C to 2.5 at -70°C. The assignments for these bands were considered from the spectra of model compounds to correspond to the stable conformations of syndiotactic and isotactic configurations of adjacent monomer units and it was concluded that there was an increase in syndiotacticity with decreasing polymerization temperature. Other investigators using different bands calculated that the syndiotacticity changed from 0.52 at 50°C to 0.86 at 60°C. These figures were based however on an assumption made to fit the observed temperature dependence of the infrared absorption ratio that kcal/mole and they cannot be regarded as absolute values and are the differences in enthalpy and entropy of isotactic and syndiotactic placement respectively.

Conducting the polymerization in aliphatic aldehydes as solvents led to an even more marked increase in crystallinity accompanied by an increase in the 635 cm⁻¹ 692 cm⁻¹ intensity ratio to a value in the region of 3.5–4 independent of the polymerization temperature. The explanation was thought to be the solvation of the growing chain end by the aldehyde favoring approach of the monomer for syndiotactic addition. Alternative and more reasonable explanations for the effect of the aldehyde are given. The effect of aldehydes in increasing polymer crystallinity has been consistently confirmed.

The conclusion that PVC produced at low temperatures or in aldehyde solution is highly syndiotactic has been challenged. NMR studies indicated that the polymer structure was of almost constant composition with about two syndiotactic units to each isotactic unit irrespective of the temperature of polymerization. The value of was estimated to be 0.2 kcal/mole at most and the increased crystallinity was attributed to reduced branching. Two other infrared frequencies were used for assessing the chain stereochromy the results quoted have been in fair agreement with NMR data but unlike the results of later workers a moderate dependence of syndiotacticity on temperature was found.

Significant contributions have been made to the assignment of the infrared bands previously subject to
some doubt by examining stereoisomers of 2 4 dichloropentane (DL and meso forms) and 2 4 G trichloroheptane (DLD DLL and DDD isomers). Dipole moment measurements have been used to supplement the data and resolve dubious assignments. Frequencies at 608 and 641 cm\(^{-1}\) were found to correspond to the planar zigzag (tttt) syndiotactic isomer the heterotactic form absorbs at 610 627 and 687 cm\(^{-1}\) (probably from the ttg with one tttg conformation) and the isotactic structure probably tgn or gtn at 619 an 688 cm\(^{-1}\). From this it would appear that the steric assignments ascribed to the spectra of poly(vinyl chloride) are correct although the quantitative estimates may be subject to some error. Recent NMR estimates agree with the conclusions that the stereochemistry is almost independent of polymerization temperature. On the basis of the two kinds of accessible rotational isomers assumed by heterotactic 2 4 6 trichloroheptane (tttg ttgt) it has been suggested that the flexible joints in the PVC chain are located in the atactic regions.

Earlier published data on poly(vinyl chloride) are given in Table 1. From these values a definite conclusion about the effect of polymerization temperature on configuration cannot be reached. The infrared data which are thought to be less reliable give considerably higher values than NMR and in one study a distinct temperature dependence is observed. The last value in Table 1 showing the absence of any influence of n butyraldehyde on the stereochemistry of poly(vinyl chloride) is in agreement with the previously expressed views and in contrast with the infrared data. The generally high estimates obtained from infrared spectra force the conclusion that the band intensities may be affected by factors other than chain configuration for example by changes in crystallinity. It has also been shown that the infrared spectra in the solid state of a given sample of PVC can be very dependent on the pretreatment given to the sample.

It is suggested that significant but variable concentrations of high energy chain conformations can be generated by the constraints existing in the solid state.

Ambiguities in the interpretation of the NMR spectra now seem to have been resolved. The meso methylene groups in PVC or the model compounds are heterosteric and the protons of such groups are generally magnetically non equivalent. Substantial non equivalence was confirmed for meso methylene protons in the 2 4 dichloropentanc model compounds. However the differences between the methylene protons of the isotactic or meso meso form of the higher homolog 2 4 6 trichloroheptane are very small. As the isotactic chain is lengthened this difference would presumably become insignificant leading to the conclusion that the protons of meso methylene groups in PVC are fortuitously equivalent. Differences in the methylene protons in PVC should be detected more easily in the dideutero polymers which possess neither vicinal nor geminal proton proton spin couplings. Poly (cis d2 vinyl chloride) has been examined and although eight of the ten expected methylene proton resonances were displayed it was concluded that not only are the average shieldings of all the meso methylene protons nearly the same but also the shieldings of all the racemic or syndio protons are nearly the same. More highly resolved spectra of the poly (d2 vinyl chloride) obtained recently have supported these findings and also indicated Bernouillian distributions of tactic placements in PVC. The final conclusion is that PVC prepared at 100°C is virtually atactic and that decreasing the polymerization temperature even to 78°C does not promote the syndiotactic placement content very significantly. In numerical terms if \( n \) is the probability that a polymer chain will add a monomer unit to give the same configuration as that of the last unit at the growing end in other words generation of an isotactic diad then the deduced values of \( n \) are 0.46 at 100°C falling to 0.37 at 78°C.

The increase in size and perfection of crystallites along with the increase in melting point and glass transition temperature with reduced polymerization temperature seems to be much more pronounced than can be accounted for by the increase in syndiotacticity. A reduction in other forms of structural irregularity such as head to head addition or branching with lower polymerization temperatures could help to relieve the dilemma. Complexing with an aldehyde solvent may be equivalent to a lowering of the temperature in
this context. An alternative explanation for the effect of aldehyde solvents would be reduction of molecular weight which would facilitate crystallization. A reasonable correlation was observed between crystallinity and degree of polymerization. Poly (vinyl chlorides) with low molecular weights (DP 32) has been prepared using various solvents (including butyraldehyde) and it was observed that the degree of crystallinity increased with decrease in molecular weight. Even for the highest branching indexes reported a significant proportion of molecules will be branch free when Mn falls to around 1800.

There could also be differences in the distribution of steric sequences in polymers of the same average tacticity. It has been suggested that the crystallites in PVC are formed from short syndiotactic blocks of about four or five units which would not occur frequently in a nearly random polymer of 50-60% syndiotacticity.

Mention should be made of a novel free radical polymerization of vinyl chloride carried out in urea canal complexes or clathrates. By analogy with the geometrical proposals for the related polymerization of substituted butadienes in thiourea canal complexes it is assumed that the vinyl chloride molecules are stacked in the channel in the appropriate spatial disposition for propagation but protected from termination or branching with adjacent sequences by the walls of the canal (Fig. 1). Initiation was by radiation and the urea was removed with aqueous acetone. Infrared evidence was advanced indicating that the product was highly syndiotactic however a more detailed examination by the recent sophisticated NMR techniques should be extremely revealing.

Property Values

Poly (vinyl chloride) is available commercially in a wide range of particle sizes the particular range depending on the method of polymerization. Emulsion polymers which include those used for making plastisols have a particle size of 0.2-2 µ the polymers that are not paste forming fall in the lower end of the range and have a more regular size than the paste forming resins which have a particle size distribution across this whole range. Some paste forming polymers have a bimodal size distribution with about 75% of the particles around 0.8 µ and 25% around 0.2 µ. Suspension resins have a particle size range of 5-300 µ. The shape of the particles can vary from almost perfect spheres to irregular structures that have a surface area at least eight times that of a spherical particle of the same weight. The increased surface area improves the rate of interaction with plasticizers so that dry powder blends can be produced by simple mixing in a stirred vessel. The powder mixing properties depend on the particle size distribution and are best for those resins with a uniform particle size. This is to be expected since particles of approximately the same diameter and shape absorb plasticizers at much the same rate. The inner structure of the polymer particles is also a determining factor in the rate at which interaction takes place.

Typical property ranges for vinyl chloride homopolymers and copolymers are given in Table 2.

**Molecular Weight.** The number average molecular weight (Mn) for most commercial PVC resins lies in the range 50 000-120 000. Processing characteristics can be varied by producing polymers of different molecular weights. The higher molecular weight polymers give finished products both plasticized and rigid with better physical properties than would be obtained with the lower molecular weight polymers. These latter however produce compounds with a lower melt viscosity so that they are essential for some fabrication techniques eg the injection molding of thin walled articles of rigid PVC. The softening point of the resins is reduced in the low molecular weight products which also have improved solubility in organic solvents.

The use of dilute solution viscosity measurements is an effective means of determining the molecular weight although the value obtained will correspond to or only if the polymer is homogeneous and monodisperse. The results shown in Table 3 were obtained with cyclohexanone as solvent.

More recently both number and weight average molecular weights were determined for PVC fuctions of a commercial emulsion resin precipitated from tetrahydrofuran. Special precautions were taken to avoid
diffusion of low molecular weight fractions a complication that may account for some of the variations found in the data of Table 3. Determinations were made in cyclohexanone at 25°C and the following values were obtained.

Another possible cause for the variations obtained by different workers may be due to the use of different types of polymer the conditions prevailing in an emulsion system would favor the formation of more branched polymer than in suspension polymerized PVC and this would tend to give lower values for a.

**Solubility.** The compatibility of polymers with solvents and plasticizers can be predicted by using solubility parameters. Values of the solubility parameter of PVC have been calculated and determined experimentally and fall in the range 9.48–9.7.

Solubility of polymers containing functional groups such as the acetate groups in vinyl chloride vinyl acetate copolymers is also determined by hydrogen bonding and to some extent by dipole interactions. In the case of PVC it is considered that the C–H is sufficiently negative to form weak hydrogen bonds. To predict the solubility in solvent it is necessary to take account of both the solubility parameter and the proton attracting power of the media.

The best solvents for PVC are tetrahydrofuran and cyclohexanone but a wide range of other organic solvents can also be used. These include ketones halogenated hydrocarbons and aromatic compounds such as nitrobenzene. Alcohol solvents and aliphatic hydrocarbons have very little solvent action and can be used as precipitants for retrieving the polymer from solutions. This treatment can be extended to predict the effectiveness of plasticizers since the process of plasticization is simply a matter of the polymer becoming completely compatible with a solvent. The dielectric constant of the plasticizer can also be used to predict compatibility and is particularly useful when used with the solubility parameter.

The molecular weight distribution can be established by subjecting PVC to fractionation by progressive precipitation of the polymer from a dilute solution. The polymer is dissolved in cyclohexanone or tetrahydrofuran to a concentration of up to about 1% successive precipitation is obtained by addition of a non-solvent such as butyl or amyl alcohol or in the case of tetrahydrofuran water can be used. It is essential to maintain effective agitation of the solution during the addition of precipitant to obtain the polymer in a finely divided form which can be easily filtered. The polymer fractions produced with each successive addition of prescribed volumes of precipitant are isolated and after weighing are used to measure the intrinsic viscosity. The higher molecular weight polymer precipitates in the first fraction and progressively lower molecular weight material is obtained with successive additions of precipitant. The precipitation can be followed continuously by turbidimetric titration so long as the particle size of the polymer precipitated does not vary. The increase in absorbance is measured with the progressive addition of the non-solvent. Some anomalies have been reported in the use of this method for fractionating PVC because the fractions are not pure and tend to carry down polymer of other molecular weights. This has occurred in systems using cyclohexanone or tetrahydrofuran as solvent and aliphatic monohydric alcohols as precipitants the effect was independent of the initial polymer concentration. This overlap results in a molecular weight distribution curve that is too narrow as has been reported using the system cyclohexanone butyl alcohol. It is apparently due to association of the polymer molecules into independent clusters so that only part of the tangled molecules can interact with the solvent precipitant mixtures.

Fractionation and Characterization

The molecular structure of polymers is very complex and characterization is never an easy task. Characterization is important scientifically as it relates to mechanisms of polymer formation and degradation and technically as it relates to industrially significant properties of polymers. Thus the effectiveness of polyacrylic acid in the inhibition of boiler scale depends on molar mass and the rate at which polymer solution can be pumped through rock in oil reservoirs is critically dependent upon the
number and size of the largest solution species present. There are so many sources of molecular heterogeneity that a complete description of a polymer sample would be quite impractical. Even for a homopolymer of a monosubstituted alkene one needs to consider degree of polymerization branching (short and long chain) tacticity and mode of monomer addition (head to head tail to tail). Copolymers introduce the further complications of comonomer sequence. In principle a polymer sample can be described in terms of the distribution of each of those structural variables. In practice we must be content with a partial characterization of one or two of these variables.

Nearly all producers or users of water soluble polymers wish to know more about the structure of the materials. In this chapter an overview is presented of the most important methods of polymer characterization as they apply to water soluble polymers. Most of the methods available were developed in application to polymers of relatively simple molecular structure that is soluble in non polar solvents. Water soluble polymers present more difficulties for a number of reasons solutions often contain persistent molecular aggregates particularly when the molar mass is high polymer adsorption on filters membranes column materials and glassware frequently intrudes electrostatic effects with polyelectrolytes complicate many measurements and few reference samples are available to facilitate comparison of results and refinement of techniques.

Molecular characterization of polymers employs techniques of two general kinds. Short chain branching mode of monomer addition and some features of comonomer distribution are best investigated by techniques such as infra red spectroscopy and nuclear magnetic resonance spectroscopy which are sensitive to local chemical structure. Molecules that differ in degree of polymerization and long chain branching on the other hand are often indistinguishable chemically and spectroscopically characterization of these features depends on polymer solution properties. This Chapter deals mainly with the latter type of characterization.

MOLAR MASS AND ITS DISTRIBUTION
The most fundamental structural variable in synthetic polymers is the degree of polymerization the number of monomer units linked together. The degree of polymerization is inferred from measurements of polymer molar mass. Synthetic polymers are invariably heterogeneous in molar mass and are characterized by molar mass distributions (MMD). For a sample containing molecules of molar mass \( M_i \) and mass \( m_i = n_i M_i/ N_0 \) molar mass distribution can be described in two equivalent ways by relating respectively \( n_i \) and \( m_i \) to \( M_i \). The former relation is called the number distribution and the latter the mass distribution of molar mass. Classical means of molar mass measurement yield average values when applied to polymers. The number average molar mass is the mean of the number distribution. The mass average molar mass is the mean of the mass distribution. The ratio the polydispersity is a convenient index of heterogeneity in molar mass.

An ideal homogeneous sample has a polydispersity of unity. Polymers made by living anion polymerization have polydispersities around 1.1 and are loosely termed monodisperse. Water soluble polymers of this kind can be made directly from ethylene oxide and indirectly by the controlled sulphonation of polystyrene made by anionic polymerization. Commercial water soluble polymers have polydispersities in the range 3-8.

PREPARATIVE FRACTIONATION
The more homogeneous the polymer the more simple its characterization. The production from a whole polymer of subsamples which are more homogeneous that the starting polymer is termed fractionation. Fractions are used in relating properties to structure and in testing polymer theory which usually refers to ideally homogeneous polymer fractions often offer the closest practical approach to this objective. Characterized polymer fractions serve also as polymer reference samples which have an important role in transferring scales of molar mass measurement between laboratories.

There are two general methods for producing fractions of water soluble polymers. The first depends upon
the controlled phase separation which occurs when increasing amounts of a miscible non solvent or salts are added to a dilute polymer solution. Homopolymer of high molar mass partitions preferentially into the concentrated polymer rich phase. The efficiency of fractionation is low and complete separation of a whole polymer into fractions of similar low polydispersity requires tedious refractionation procedures. For the production of small fractions of high molar mass however this classical procedure remains the method of choice. Theoretical models are available which give some insight into the fractionation process since they begin with a polymer of known MMD however their predictive value is small. For copolymers the partitioning in phase separations is dominated by chemical differences and little fractionation by molar mass occurs. Polymers such as polyethylene oxide and polyvinylpyrrolidone which are soluble in both water and organic solvents can be fractionated in the latter often with greater success. Crystalline polymers such as polyethylene oxide and isotactic polyvinyl alcohol are fractionated in terms of their molar mass only above their crystalline melting point.

The principal alternative to fractionation by phase separation is preparative size exclusion chromatography (SEC) which is also and less aptly known as gel filtration and gel permeation chromatography (GPC). A sample of the dissolved polymer is added to a stream of solvent flowing through a column packed with a porous solid. If the pores are of sizes similar to those of polymer molecules in solution the larger molecules may be excluded from the smaller pores and so pass through the column more rapidly. The sample emerges dilutes and sorted in inverse order of molecular size. Dissolved molecules so large that they are totally excluded from the porous substrate emerge at a retention volume $V$ which is a measure of the interstitial fluid volume of the column. Dissolved molecules so small that they penetrate all the pores of the substrate emerge at a retention volume $V_0 + V_i$ where $V_i$ represents the total pore volume. Dissolved molecules of intermediate size emerge at retention volumes which vary approximately linearly with the logarithm of molecular size.

Column materials for aqueous size exclusion chromatography (Table 1.) have improved significantly since the introduction of cross linked dextran gels (Sephadex) in 1959. The porosity of these gels depends on controlled swelling in aqueous media they lack dimensional stability particularly when the pores are large so that the chromatographic behaviour is poorly reproducible. Cross linked polyacrylamide and agarose poly(acryloymorpholines) and poly(2 hydroxyethylmethacrylate) offer some improvement in dimensional stability but all suffer from inconsistency of commercial supply. Rigid inorganic materials controlled pore glass and silica gels are dimensionally stable but their high energy surfaces often retain polymer by adsorption so that size separation is degraded. Coating the inorganic solids with silanes or polyethylene glycol reduces adsorption but there is growing scepticism concerning published reports of the stability of the coatings and indeed of the organic solid itself during aqueous chromatography. The latest addition to the list of packing materials for preparative SEC is Toyopearl a proprietary gel made by polymerization of hydrophilic monomers and containing ether and hyroxyl groups impressive claims are made for its stability and resolution. All of the column materials are available in ranges of pore size so that it is possible to tailor a column to particular fractionation. It should be noted that the claimed ranges of molar mass separated often refer to globular proteins and therefore greatly overestimate the range for synthetic polymers.

The efficiency of fractionation in SEC increases with dilution so that sharp fractions are best produced cumulatively from repeated separations dimensional stability of the substrate is particularly important therefore. If the concentration of whole polymer is increased (and the viscosity therefore raised) fractionation is degraded first at large dilution volumes. It is prudent to use electrolyte of moderate ionic strength (say 0.1 M. salt) to suppress electrostatic interactions between polymer and substrate which will degrade fractionation by size.

Fractionation by SEC reflects the degree of polymerization long chain branching tacticity (marginally) and chemical heterogeneity all of which determine molecular size in solution.
The metrology of polymer molar mass features in every text on polymer science and needs no detailed elaboration here. Instead the relation between the methods of measurement will be described indicating the special features of their application to water soluble polymers. Polymer molar mass can be measured by a variety of methods which have a hierarchical relationship (Fig. 1.). The triangular shape emphasizes the fundamental role of the reference methods membrane osmometry light scattering photometry and ultracentrifugation.

All three reference methods are based securely in thermodynamics and yield absolute determinations in the sense that molar mass is derived from measurements of the fundamental physical quantities of mass length and time. Each method depends on relating equilibrium differences of concentration in dilute solution to the osmotic work needed to produce them and thereby to solvent activity. At infinite dilution solvent activity can be equated with mole fraction so that solute (polymer) mole fraction and hence molar mass follow. Extrapolation to infinite dilution employs virial polynomials. When applied to a polydisperse polymer sample each reference method yields a characteristic average molar mass. These points are summarized in Table 2.

Reference Methods

The reference methods are demanding of time and expertise and are in established use in few laboratories. Their application to water soluble polymers introduces some features not always clear from texts that emphasize characterization of non polar molecules. First and most generally it is essential to suppress polyelectrolyte effects by working with solutions containing an excess of simple electrolyte unless electrostatic interactions are suppressed in this way the relation of osmotic work to molar mass via a virial expansion is invalid.

Turning now to details of the specific methods modern membrane osmometers measure the pressure needed to prevent net transport of solvent through a membrane and are capable of rapid measurements (~10 minutes) in non polar solvents. Equilibrium is reached with aqueous solutions much more slowly (1–2 hr.) Instruments employing pressure transducers are more effective with aqueous solutions than those which follow solvent transport by the movement of an air bubble in a capillary. In general membrane osmometry yields reliable results only with fractionated polymer.

Interest in light scattering photometry has been stimulated by the recent introduction of instruments which measure the scattered intensity at low angles of scatter (Figure 2.). This avoids the necessity of extrapolating to zero angle of scatter data collected over a wide angular range by conventional photometers but at the price of a loss of information concerning molecular size radius of gyration can be inferred from the angular dependence. Exclusive reliance upon measurements at low & angles is open to error for two reasons firstly molecular aggregates are not uncommon and dominate scattering at low angle and secondly it is more difficult to eliminate scattering from extraneous dust in aqueous solutions that in non polar solvents. Most of the dust is organic in origin and the refractive index contrast is higher in aqueous solutions. The angular dependence of scattering gives valuable information concerning both interferences.

Ultracentrifugation is traditionally the tool of the biochemists and has not been applied widely to synthetic polymers. Analysis of polydisperse non ideal solutions requires considerable effort. The difficulties of other means of characterization of the molar mass distribution of water soluble polymers are reviving interest in ultracentrifugation. The radial distribution of a polydisperse solute at equilibrium in a centrifugal field can be calculated from the molar mass distribution. The reverse derivation is an ill posed mathematical problem unavoidable experimental errors give rise to catastrophic oscillations in the calculated. Techniques have been developed to circumvent this difficulty and been applied to polysaccharides. In the more straightforward measurement of mass average molar mass ultracentrifugation is much less sensitive than light scattering photometry to extraneous dust.
It should be noted that the exponent is unchanged but the K value will differ in the ratio it is difficult in practice to establish that the ratio is constant for a series of fractions. Evidence of similar polydispersities or similar breadths of size exclusion chromatograms is to be preferred but is rarely available in published work. If the series of fractions is such that the ratio changes monotonically with M a relation of the form of Eqtn. 2 may fit the experimental results closely but the parameters K and will have no wider validity. It is also desirable to consider two factors which may give rise to low values of the measured [n] especially at high molar mass firstly the polymer size in solution a molecule with long chain branching is more compact than its linear isomer and so has a smaller viscosity. Secondly the non Newtonian viscosity which is common for polymers of high molar mass should be noted since a shear rate (200s⁻¹) in conventionally capillary viscometry is large enough to lower the viscosity significantly below the zero shear value needed for Mark Houwink correlations. A further source of disagreement lies in the insensitivity of the logarithmic least squares fitting procedure used to derive K. For the same reason it is unwise to extrapolate beyond the calibrated region. Finally theoretical predictions suggest that over a wide range of M the logarithmic form of Eqtn. 1. is non linear.