

CHAPTER II

THEORETICAL CONSIDERATIONS

2.1 Suspension Polymerization of Vinyl Chloride Monomer (VCM)

Suspension polymerization process is carried out in a pressurized stainless steel autoclave with a jacket and/or a condenser for better heat removal. Liquid vinyl chloride is dispersed in water by vigorous stirring, this results in the formation of droplets which are stabilized against coalescence by suspending agents. The polymerization is initiated by monomer soluble free radical initiators such as organic peroxides. Progress of the polymerization reaction in a jacket autoclave can be followed by continuously monitoring the water temperature in the jacket. Most of the polymerizations are stopped at around 80-90% conversion.⁽⁶⁾ After venting off the unreacted monomer to the recovery plant, the wet cake is dried which resulted in afterwards free flowing PVC powder.

The outline of the VCM suspension polymerization process is shown in Fig. 2.1.

2.2 Molecular Weight Control for VCM Polymerization

Since a PVC molecule is growing via the free-radical addition process with normally used polymerization rates, the molecular weight is almost totally dependent on the polymerization temperature.⁽²⁾ This can be explained by considering the three processes that control the molecular weight of free radical

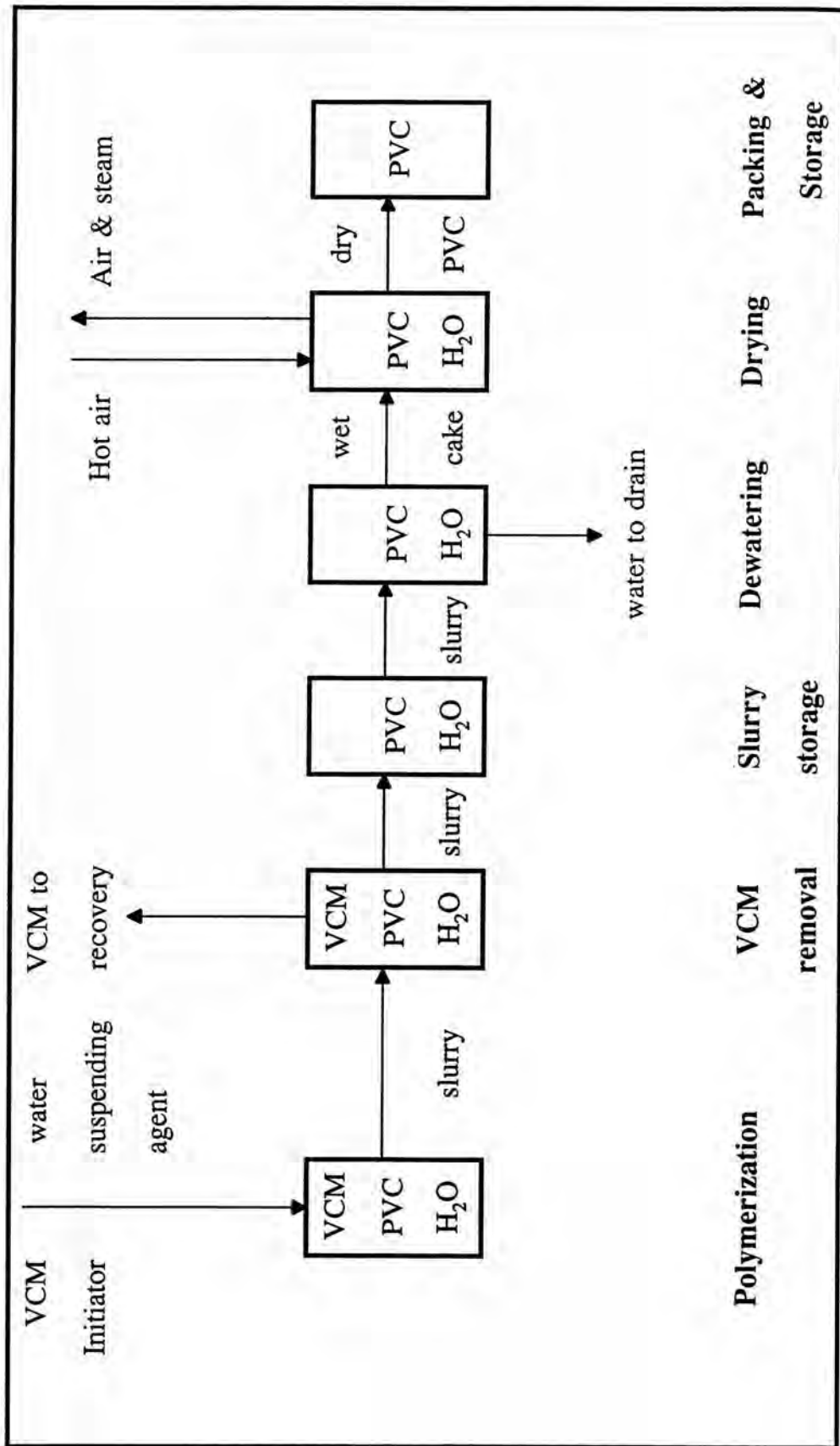
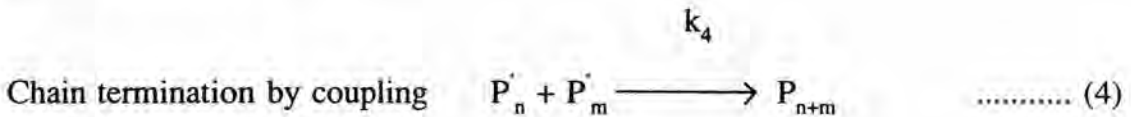
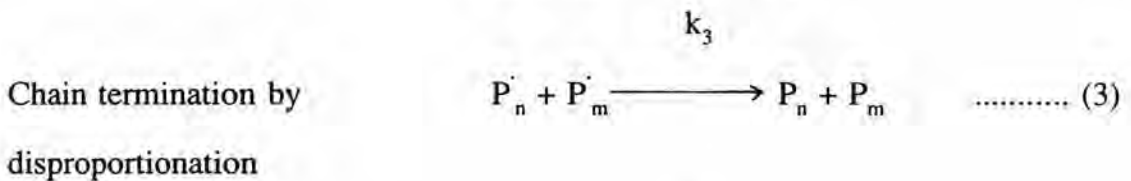
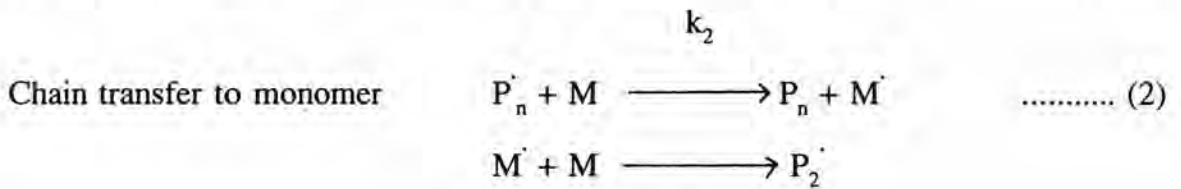
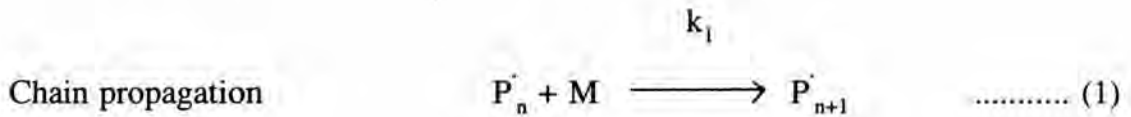


Fig. 2.1 : Outline of The VCM Suspension Polymerization Process.⁽⁶⁾

polymerization: chain propagation, chain transfer to monomer, and chain termination by disproportionation or by coupling. These processes may be schematically represented as ⁽²⁾:



where

P_n^\cdot = polymer radical of length n units

P_n = polymer of length n units

M = monomer

M^\cdot = monomer radical

If all the P_n^\cdot are assumed to be R^\cdot , the rate equations become

$$\text{Rate of propagation, } R_p \quad = \quad k_1[M][R^\cdot] \quad \dots\dots\dots (5)$$

$$\text{Rate of chain transfer, } R_{tr} \quad = \quad k_2[M][R^\cdot] \quad \dots\dots\dots (6)$$

$$\text{Rate of termination, } R_t \quad = \quad k_3[R^\cdot]^2 + k_4[R^\cdot]^2 \quad \dots\dots\dots (7)$$

$$= k_5[R^\cdot]^2 \quad \dots\dots\dots (8)$$

where

$[R\cdot]$ = concentration of radicals

$[M]$ = concentration of monomer

In the case of PVC, $k_5[R\cdot]^2$ is small and gets large enough to become important only if an unusually high level of initiator is used in order to increase $[R\cdot]$.⁽²⁾ For normal initiator levels and polymerization rates, only chain transfer and propagation need to be considered. The molecular weight is then dependent on the relative rates of these processes:

$$\overline{DP} = \frac{\text{rate of propagation}}{\text{rate of chain transfer}} = \frac{k_1[M][R\cdot]}{k_2[M][R\cdot]} = \frac{k_1}{k_2} \dots\dots\dots (9)$$

where \overline{DP} is the average degree of polymerization.

To relate the molecular weight and polymerization temperature, we need to use Arrhenius equation⁽²⁾ as follows:

$$\text{Arrhenius equation; } k = A \exp(-E/RT) \dots\dots\dots (10)$$

where

A is a constant

E is the activation energy

R is the universal gas constant

T is the absolute temperature

From Arrhenius equation (10), k_1 and k_2 are functions of temperature, thus the molecular weight depends only on polymerization temperature. The higher the temperature, the lower the molecular weight. The plot of the degree

of polymerization expressed as the number average molecular weight versus polymerization temperature in the normal PVC commercial range of 50° to 70°C is shown in Fig. 2.2.

2.3 Polymerization of Ultra-High Molecular Weight (UHMW) PVC

Commercial PVC resins range in DP from 410 to higher than 2000 as shown in Table 2.1.

Table 2.1 : Classification of PVC Molecular Weight

Molecular weight	\overline{DP}
Low MW	410-840
Medium MW	840-1300
High MW	1300-2000
Ultra-high MW	>2000

UHMW PVC can be manufactured via two routes,⁽³⁾ these are:

2.3.1 VCM polymerization at low temperatures

This route is to polymerize VCM monomer at low temperatures initiated by a fast peroxide. The temperature range is 32-42°C to manufacture \overline{DP} at 2000 and higher. This is the normal VCM polymerization method. Some disadvantages of this method are constraint of the cooling capacity of the PVC plant, difficult to control the low reaction temperature to be constant and

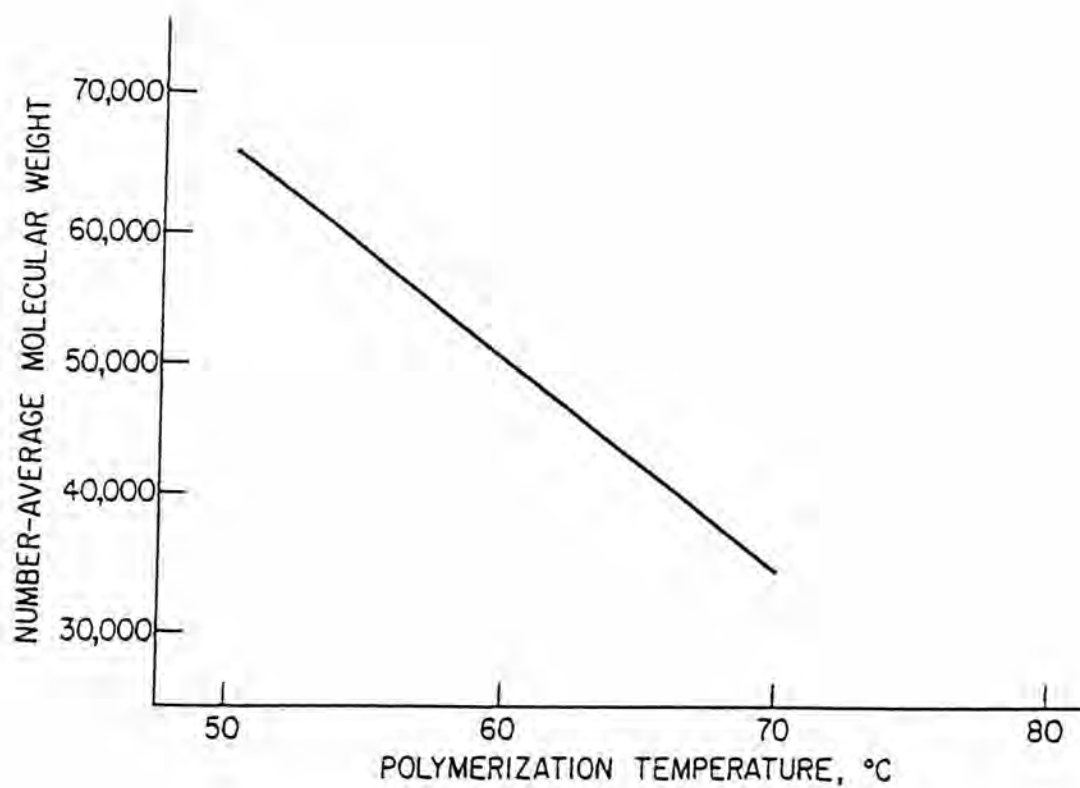


Fig. 2.2 : Effect of Polymerization Temperature on the Molecular Weight of PVC in the Normal Commercial Temperature Range⁽²⁾

the uses of highly reactive initiators which are dangerous in both using and handling. The dosage of the lower reactive initiators should be, in addition, higher than that of the higher reactive ones in order to obtain same reaction rate. This will be the cause of a higher level of decomposition products in the final PVC.

2.3.2 VCM polymerization at More Elevated Temperatures in The Presence of Multiunsaturated Comonomer.

High MW PVC can also be manufactured at higher temperatures by an addition of multiunsaturated comonomer. If comonomers are applied at high temperatures it is possible to manufacture UHMW PVC. In principle, the quality of the PVC manufactured with a comonomer will be different from that of PVC produced at low temperatures, because the polymer is more branched by incorporation of the comonomer.

The popular multiunsaturated comonomers for UHMW PVC production are polyfunctional allyl esters such as diallyl phthalate, triallyl cyanurate, and triallyl isocyanurate.⁽³⁾ The minor proportions of these comonomers in VCM polymerization act as a cross-linking agent. These cross-linking agents or comonomers will link each short PVC chain to form many long chains, branching or cross-link structure which result in higher molecular weight. Polyfunctional allylic compounds of high boiling point can stabilize the polymer against oxidative degradation and heat discoloration.⁽⁷⁾

The reaction of PVC radicals with allyl groups is faster than the recombination reaction to give higher-molecular weight PVC due to the bigger molecules with more branches in its structure. Fig. 2.3 is a schematic

illustration of a polymerized and crosslinked state of vinyl chloride and diallyl esters.

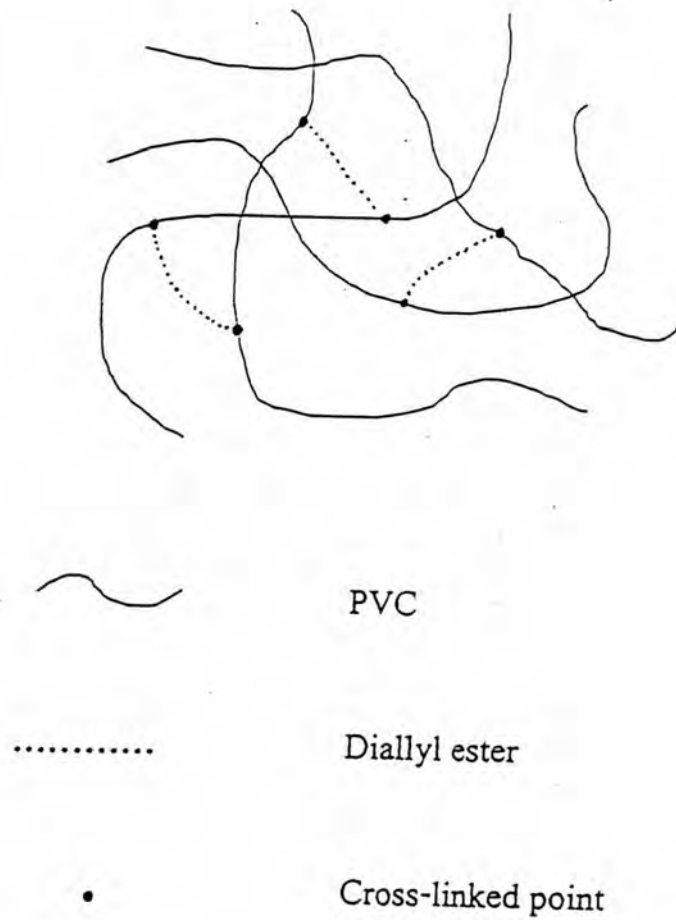


Fig. 2.3 : A Polymerized and Cross-linked State of Vinyl Chloride and Diallyl Ester.