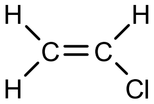
2

PVC MANUFACTURE TECHNOLOGY

2.1 MONOMER

Vinyl chloride is the sole monomer used in the production of PVC. Its structure and properties are given in Table 2.1.

Table 2.1. Typical properties of vinyl chloride

Property	Description
General	Vinyl chloride is a flammable, colorless gas with a sweet odor at room temperature. It is mainly used for production of PVC but also as a refrigerant and comonomer
Chemical structure	
Chemical formula	C_2H_3Cl
IUPAC name	1-chloroethene
Alternate names	chloroethylene, chloroethene, ethylene monochloride
~~Identifiers~~	~~CAS # 75-01-4; EINECS 200-831-0;~~ ~~UN # 1086; RTECS KU9625000~~
Molecular weight, g/mol	62.5
Odor	mild, sweet
Color	colorless
Melting point, °C	-153.8
Boiling point, °C	-13.37
Decomposition temperature, °C	450
~~Flash point, °C~~	~~-78~~
~~Autoignition temperature, °C~~	~~472~~
~~Explosive limits in air, vol%~~	~~3.6 and 33~~
~~Density, kg/m^3~~	~~2.56 (gas); 908.41 (liquid)~~
~~Vapor density (air=1)~~	~~2.15~~
~~Vapor pressure at 25°C, mm Hg~~	~~2600~~

~~**Table 2.1. Typical properties of vinyl chloride**~~

Property	Description
~~Solubility in water, wt%~~	~~0.95~~
~~Solubility of water in 100 g VC, ml~~	~~0.08 (~~20°C)
Solubility in solvents	alcohol, ether, carbon tetrachloride, benzene
~~Henry's law constant, atm m^3/mol~~	~~2.71E-02~~
~~Critical temperature, °K~~	~~432~~
~~Critical pressure, MPa~~	~~5.67~~
~~Enthalpy of vaporization, kJ/mol~~	~~21.998-23~~.3
~~Enthalpy of fusion, kJ/mol~~	~~4.92~~
~~Enthalpy of formation, kJ/mol~~	~~28.45~~
~~Specific heat capacity, J/kg/g~~	~~0.8592 (gas), 0.9504 (solid)~~
~~Heat capacity of liquid at 298.15K, J/molK~~	~~0.053625~~
~~Latent heat of vaporization, kJ/kg~~	~~333~~
~~Antoine equation parameters~~	~~A = 3.98598, B = 892.757, C = -35.051~~ ~~(165.2-259~~.3~~K)~~
~~Octanol/water partition, $\log K_{ow}$~~	~~1.36~~
~~Odor threshold, ppm~~	~~3000~~
~~Half-life in air, h~~	~~few~~

2.2 BASIC STEPS OF RADICAL POLYMERIZATION

2.2.1 INITIATION

Vinyl chloride has low reactivity but its radical is highly reactive. For this reason, PVC is manufactured by radical polymerization. Initiation is a two step process, as given by the following reactions:

$$I \longrightarrow 2\dot{I} \quad \text{(I - initiator)}$$

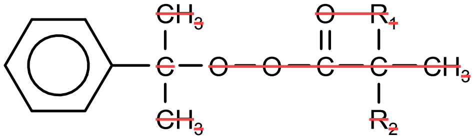
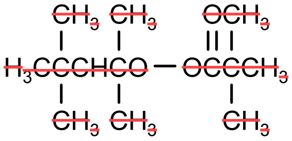
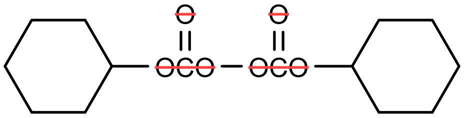
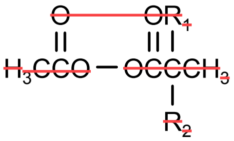
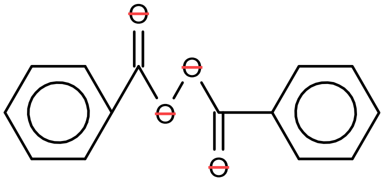
$$\dot{I} + M \longrightarrow R^{\bullet} \quad \text{(M - monomer; } \dot{R} \text{ - growing polymer radical)}$$

First, the initiator produces free radicals which then react with monomer, forming a radical ready for the next step – propagation.

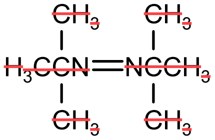
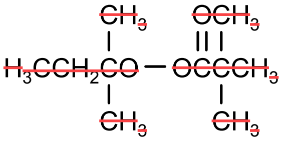
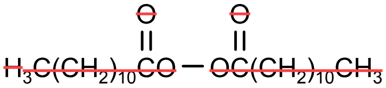
This method of initiation causes the chain end structure of PVC macromolecules to consist of initiator fragments.

Initiators are important components of industrial polymerization formulations. ~~Table 2.2 shows chemical structures of the most common representatives with their half life temperatures, HLT.~~

~~Table 2.2. Examples of common initiators~~[1,2]

~~Name~~	~~Abr.~~	~~HLT, °C~~	~~Chemical formula~~
~~Cumyl peroxyneodecanoate~~	~~CUPND~~	~~55~~	
~~tert-Octyl peroxyneodecanoate~~	~~TOPND~~	~~56~~	
~~Dicyclohexyl peroxydicarbonate~~	~~CHPC~~	~~57~~	
~~tert-Butyl peroxyneodecanoate~~	~~TBPND~~	~~64~~	
~~Benzoyl peroxide~~	~~BPO~~	~~65~~	

~~**Table 2.2. Examples of common initiators**~~[1,2]

~~**Name**~~	~~**Abr.**~~	~~**HLT, °C**~~	~~**Chemical formula**~~
~~2,2' azobisbutylnitrile~~	~~AIBN~~	~~73~~	 ~~$H_3C\overset{CH_3}{\underset{CH_3}{C}}N{=}N\overset{CH_3}{\underset{CH_3}{C}}CH_3$~~
~~tert-Amyl peroxypivalate~~	~~TAPPI~~	~~74~~	 ~~$H_3CCH_2\overset{CH_3}{\underset{CH_3}{C}}O-O\overset{O}{\overset{\Vert}{C}}\overset{CH_3}{\underset{CH_3}{C}}CH_3$~~
~~Dilauroyl peroxide~~	~~LP~~	~~80~~	 ~~$H_3C(CH_2)_{10}\overset{O}{\overset{\Vert}{C}}O-O\overset{O}{\overset{\Vert}{C}}(CH_2)_{10}CH_3$~~

~~Selection of initiator influences the molecular weight of polymer and the polymerization rate. The molecular weight is controlled by chain transfer to monomer and propagation rate. If the temperature of polymerization increases, the rate of chain transfer to monomer will be higher than the propagation rate. The higher the temperature, the lower the molecular weight. For PVC resins having K=70 and above, the polymerization temperature should be below 52°C. Initiators having HLT about 57°C are used as primary initiators. To boost the slow initial rate, initiators having HLT lower than 57°C are used. Less active initiators (TAPPI to LP) are used as secondary initiators in production of PVC grades below K=60.~~

2.2.2 PROPAGATION

The propagation reaction can be schematically written as

$$R^{\bullet} + M \longrightarrow R^{\bullet}$$

Addition of monomer increases molecular weight of the growing radical, which continues to react according to the same scheme. Vinyl chloride may add onto the polymer chain in two ways: head-to-head and head-to-tail. The head-to-tail addition prevails. ~~But in some cases head-to-head structures are formed which contribute to the defect formation similar to any other anomaly of polymerization reaction, which result in other typical chain defects as discussed in Chapter 1.~~

~~From the point of view of polymerization conditions, defects are formed with increased incidence at high monomer conversions (above 60%).~~

~~Polymerization rate is almost independent of initiator concentration because the presence of polymer in the reaction mixture exerts a catalytic effect, promoting further polymerization. The catalytic effect of polymer is proportional to its actual surface area. The propagation rate constant, k_p, is given by the following equation:[1]~~

~~$k_p = 3.3 \times 10^6 \exp\left(\frac{3700}{RT}\right)$ [2.1]~~

~~where:~~

~~R gas constant~~
~~T absolute temperature.~~

~~This equation confirms the previous statement that initiator concentration does not enter the relationship, which is only controlled by temperature.~~

~~The rate of polymerization is not uniform throughout the mixture because it is higher inside a swollen particle of polymer. This is most likely due to the catalytic effect of polymer and reduction of radical termination rate because of reduced mobility of the growing radical. The rate of polymerization is thus auto accelerating, which, in combination with its high exothermic effect (106 kJ/mol), puts emphasis on effective cooling which controls the process rate and quality of the product.~~

2.2.3 TERMINATION

Termination occurs by disproportionation and combination, as shown by the following reactions:

$$R_1CH_2\dot{C}HCl + R_2CH_2\dot{C}HCl \longrightarrow R_1CH{=}CHCl + R_2CH_2CH_2Cl$$

$$R_1CH_2\dot{C}HCl + R_2CH_2\dot{C}HCl \longrightarrow R_1CH_2CHClCHClCH_2R_2$$

~~The rate constant of termination, k_t, is expressed by the following relationship:~~

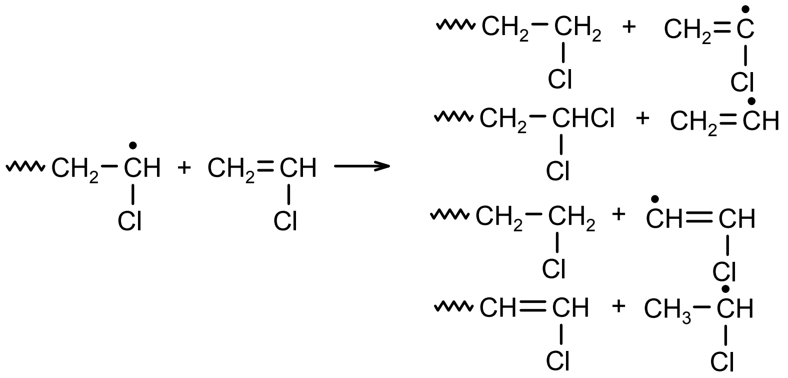
~~$k_t = 1.3 \times 10^{12} \exp\left(\frac{4200}{RT}\right)$~~

The ratio of disproportionation to combination is difficult to determine but the combination is known to be a prevalent mechanism of termination.[1,5]

One peculiarity of PVC polymerization is that polymer is not soluble in its monomer and it precipitates when formed. ~~Monomer is capable of swelling polymer, which results in a porous structure of polymer grains formed, as well as the possibility that reaction of polymerization continues in a portion of monomer used for swelling the already formed grains. This gives PVC peculiar morphological structures which can be manipulated by process.~~

2.2.4 CHAIN TRANSFER TO MONOMER

A growing radical may react with monomer, forming polymer and a monomer radical, which further grows, due to reaction with monomer. These reactions, called chain transfer reactions, may occur according to one of the schemes below:[1]



~~The third reaction scheme is considered to be the main reaction of a new radical generation based on activation energies of reactions.[1]~~

~~Chain transfer constant for PVC is given by the following equation:~~

$$\cancel{C_m = 125 \exp\left\{\frac{7300}{RT}\right\}} \qquad \cancel{[2.2]}$$

~~The values of C_m are large due to the high reactivity of vinyl chloride. This reaction controls the molecular weight of polymer. With temperature of reaction increasing, the value of constant increases, which results in an increased number of chain transfers and lower molecular weight of the resultant polymer.~~

~~Chain transfer to polymer results in formation of long branches as discussed in Chapter 1.[3]~~

~~Various chain transfer agents, such as dodecylmercaptan, 2-mercaptoethanol, α thioglycerol, or thioglycolic acid, may be used to decrease molecular weight of the resultant polymer.[4]~~

2.3 POLYMERIZATION TECHNOLOGY

PVC production has grown by about 4% per year since 1990. The largest growth is experienced in Asia (especially in China), followed by North America and Europe.[6] There are four major methods of production of PVC, including bulk, emulsion, solution, and suspension polymerizations. Suspension polymerization is the most common since it accounts for 80% of world production of PVC (75% in USA and 93% in Japan).[6] It is followed by production of paste-type resins by emulsion (12% in the world) and microsuspension polymerization (3% USA and 5% Japan). Bulk polymerization contributes 8% of world production of PVC. Solution polymerization is not a commercial scale method.

2.3.1 SUSPENSION

Suspension polymerization is a batch process which includes four unitary operations:

- polymerization
- stripping residual vinyl chloride
- centrifugation of water suspension to remove water
- drying.

The typical formulation of reactor charge is given in Table 2.3.

Table 2.3. Typical formulation for suspension polymerization.[6]

Component	Concentration, parts
Vinyl chloride	100
Demineralized water	120
Suspending agent	0.05-0.1
Initiator	0.03-0.16

~~Types of initiators used are presented in Table 2.2 and their role is discussed in the previous section. A suspending agent (frequently called a protective colloid) prevents agglomeration of vinyl chloride droplets changing later into sticky particles of formed polymer. Without a suspending agent, uniformity of suspension will suffer and particle size will have a very broad range, with large lumps which will diminish the quality of PVC. Water soluble natural and synthetic polymers are known to prevent coalescence of droplets and agglomeration of particles. Partially hydrolyzed polyvinyl acetate (polyvinyl alcohol) and hydroxypropyl methylcellulose are the most popular suspension agents. Two types of commercial products are used: primaries and secondaries.[6] Primaries, which have a degree of hydrolysis in the range of 71 to 82%, are used to control particle size of PVC. Secondaries, which have a degree of hydrolysis in the range from 45 to 57%, are known to increase porosity. Depending on application and, thus, required morphology, different combinations of both suspending agents are used. It is quite obvious from formulation that suspension PVC contains limited amounts of additives which may complicate its further processing and its thermal and UV stability.~~

~~Polymerization is performed in large reactors (usually having a volume of up to 200 m^3). Considering that vinyl chloride is carcinogenic, most reactors are operated without opening. Several hundred batches can now be run without opening the reactor. This is due to excellent coating which prevents deposition of reacting mass on the reactor walls. It is also very important to control the temperature of reaction which is exothermic. The rate of heat removal is usually the rate controlling factor.~~

~~After reaction is complete, walls of the reactor are rinsed with water to remove any particles. If such particles are left in the reactor for the next batch, a monomer will be absorbed by them and polymerized within particles, resulting in non porous particles which will cause formation of so called "fish eyes". In addition, these particles will hold more vinyl chloride and increase its residual concentration in the final product. The reactor is coated with adhesion preventive compound before a new batch begins. The reactor is charged again and reaction mixture is brought to a desired temperature to begin a new~~