

VINYLDENE CHLORIDE POLYMERS

Introduction

Vinylidene chloride (VDC) copolymers were among the first synthetic polymers to be commercialized. Their most valuable property is low permeability to a wide range of gases and vapors (see BARRIER POLYMERS). From the beginning in 1939, the word Saran has been used for copolymers with high VDC content, and it is still a trademark of The Dow Chemical Co. in some countries. Sometimes the names Saran and poly(vinylidene chloride) (PVDC) are used interchangeably. This can lead to confusion because, although Saran includes the homopolymer, only copolymers have commercial importance. The homopolymer, ie, PVDC, is not commercially used because it lacks the thermal stability required for processing.

The principal solution to fabrication difficulties is copolymerization. Three types of comonomers are commercially important: vinyl chloride; acrylates, including alkyl acrylates and alkyl methacrylates; and acrylonitrile. When extrusion is the method of fabrication, other solutions include formulation with plasticizers, stabilizers, and extrusion aids plus applying improved extrusion techniques. The literature on VDC copolymers through 1994 has been reviewed (1,2).

Monomer

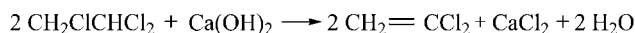
Properties. Pure vinylidene chloride [75-35-4] (1,1-dichloroethylene) is a colorless, mobile liquid with a characteristic sweet odor. Its properties are summarized in Table 1. Vinylidene chloride is soluble in most polar and nonpolar organic solvents. Its solubility in water (0.25 wt%) is nearly independent of temperature at 16–90°C (5).

Table 1. Properties of VDC Monomer^{a, b}

Property	Value
Molecular weight	96.944
Odor	Pleasant, sweet
Appearance	Clear, liquid
Color (APHA)	0–10
Solubility of monomer in water at 25°C, wt%	0.25
Solubility of water in monomer at 25°C, wt%	0.035
Normal boiling point, °C	31.56
Freezing point, °C	–122.56
Flash point, °C	
Tag closed cup	–28
Tag open cup	–16
Flammable limits in air (ambient conditions), vol%	6.5–15.5
Autoignition temperature, °C	513 ^b
Latent heat of vaporization, ΔH_v , kJ/mol ^c	
At 25°C	26.48 ± 0.08
At normal boiling point	26.14 ± 0.08
Latent heat of fusion at freezing point, ΔH_m , J/mol ^c	6514 ± 8
Heat of polymerization at 25°C, ΔH_p , kJ/mol ^c	–75.3 ± 3.8
Heat of combustion, liquid monomer at 25°C, ΔH_c , kJ/mol ^c	1095.9
Heat of formation	
Liquid monomer at 25°C, ΔH_f , kJ/mol ^c	–25.1 ± 1.3
Gaseous monomer at 25°C, ΔH_f , kJ/mol ^c	1.26 ± 1.26
Heat capacity	
Liquid monomer at 25°C, C_p , J/(mol·K) ^c	111.27
Gaseous monomer at 25°C, C_p , J/(mol·K) ^c	67.03
Critical temperature, T_c , °C	220.8
Critical pressure, P_c , MPa ^d	5.21
Critical volume, V_c , cm ³ /mol	218
Liquid density, g/cm ³	
–20°C	1.2852
0°C	1.2499
20°C	1.2137
Index of refraction, n_D	
10°C	1.43062
15°C	1.42777
20°C	1.42468
Absolute viscosity, mPa·s (=cP)	
–20°C	0.4478
0°C	0.3939
20°C	0.3302
Vapor pressure, ^e at $T^\circ\text{C}$	$\log P_{\text{kPa}} = 6.1070 - 1104.29/(T = 237.697)$

^aRefs. 3 and 4.^bInhibited with methyl ether of hydroquinone.^cTo convert J to cal, divide by 4.184.^dTo convert MPa to atm, divide by 0.101.^e P measured from 6.7 to 104.7 kPa. To convert kPa to mm Hg, multiply by 7.5 (add 0.875 to the constant to convert \log_{kPa} to \log_{mmHg}).

Manufacture. Vinylidene chloride monomer can be conveniently prepared in the laboratory by the reaction of 1,1,2-trichloroethane [79-00-5] with aqueous alkali:



Other methods are based on bromochloroethane [25620-54-6], trichloroethyl acetate [625-24-1], tetrachloroethane [79-34-5], and catalytic cracking of trichloroethane (6). Catalytic processes produce hydrogen chloride as by-product, rather than less valuable salts, but yields of VDC have been too low for commercial use of these processes. However, good results have been reported with metal-salt catalysts (7–9).

Vinylidene chloride is prepared commercially by the dehydrochlorination of 1,1,2-trichloroethane with lime or caustic in slight excess (2–10%) (5,10). A continuous liquid-phase reaction at 98–99°C yields ~90% VDC. Caustic gives better results than lime. Vinylidene chloride is purified by washing with water, drying, and fractional distillation. It forms an azeotrope with 6 wt% methanol (11). Purification can be achieved by distillation of the azeotrope, followed by extraction of the methanol with water. An inhibitor is usually added at this point. Commercial grades contain 200 ppm of the monomethyl ether of hydroquinone (MEHQ). Many other inhibitors for the polymerization of VDC have been described in patents, but MEHQ is the one most often used. The inhibitor can be removed by distillation or by washing with 25 wt% aqueous caustic under an inert atmosphere at low temperatures.

For many polymerizations, MEHQ need not be removed; instead, polymerization initiators are added. Vinylidene chloride from which the inhibitor has been removed should be refrigerated in the dark at –10°C, under a nitrogen atmosphere, and in a nickel-lined or baked phenolic-lined storage tank. If not used within 1 day, more inhibitor should be added.

Health and Safety Factors. Vinylidene chloride is highly volatile and, when free of decomposition products, has a mild, sweet odor. Its warning properties are ordinarily inadequate to prevent excessive exposure. Inhalation of vapor presents a hazard, which is readily controlled by observance of precautions commonly taken in the chemical industry (4). A single, brief exposure to a high concentration of VDC vapor, eg, 2000 ppm, rapidly causes intoxication, which may progress to unconsciousness on prolonged exposure. The $\text{LC}_{50}/4 \text{ h}$ in rats is 6350 ppm. However, prompt and complete recovery from the anesthetic effects occurs when the exposure is for short duration. A single, prolonged exposure and repeated short-term exposures can be dangerous, even when the concentration of the vapor is too low to cause an anesthetic effect. Such exposure may produce organic injury to the kidneys and liver. For repeated exposures, the vapor concentration of VDC should be much lower. The American Conference of Governmental Industrial Hygienists threshold limit value of 5 ppm has been established to provide an adequate margin of safety.

Vinylidene chloride is hepatotoxic, but does not appear to be a carcinogen (12–17). Pharmacokinetic studies indicate that the behavior of vinyl chloride and vinylidene chloride in rats and mice is substantially different (18). No unusual health problems have been observed in workers exposed to VDC monomer over

varying periods (19). Because VDC degrades rapidly in the atmosphere, air pollution is not likely to be a problem (20). Worker exposure is the main concern. As such, personal monitoring can be done using passive dosimeters. Refer to the dosimeter supplier for collection and analysis details.

The liquid is irritating to the skin after only a few minutes of contact. The inhibitor MEHQ may be partly responsible for this irritation. Inhibited VDC is moderately irritating to the eyes. Contact causes pain and conjunctival irritation, and possibly some transient corneal injury and iritis. Permanent damage, however, is not likely.

Peroxide Formation. In the presence of air or oxygen, uninhibited VDC forms a violently explosive complex peroxide at temperatures as low as 40°C. Decomposition products of VDC products are formaldehyde, phosgene, and hydrochloric acid. A sharp, acrid odor indicates oxygen exposure and probable presence of peroxides. This is confirmed by the liberation of iodine from a slightly acidified dilute potassium iodide solution. Formation of insoluble polymer may also indicate peroxide formation. The peroxide adsorbs on the precipitated polymer, and separation of the polymer may result in an explosive composition. Any dry composition containing more than ~15 wt% peroxide detonates from a slight mechanical shock or from heat. Vinylidene chloride that contains peroxides may be purified by being washed several times, either with 10 wt% aqueous sodium hydroxide solution at 25°C or with a fresh aqueous solution of 5 wt% sodium bisulfite. Residues in vessels containing VDC should be handled with great care, and the peroxides should be destroyed with water at room temperature.

Copper, aluminum, and their alloys should not be used in handling VDC. Copper can react with acetylenic impurities to form copper acetylides, whereas aluminum can react with VDC to form aluminum chloralkyls. Both compounds are extremely reactive and potentially hazardous.

Polymerization

Vinylidene chloride polymerizes by both ionic and free-radical reactions. Processes based on the latter are far more common (21). Vinylidene chloride is of average reactivity when compared with other unsaturated monomers. The chlorine substituents stabilize radicals in the intermediate state of an addition reaction. Because they are also strongly electron-withdrawing, they polarize the double bond, making it susceptible to anionic attack. For the same reason, a carbocation intermediate is not favored.

The 1,1-disubstitution of chlorine atoms causes steric interactions in the polymer, as is evident from the heat of polymerization (see Table 1) (22). When corrected for the heat of fusion, the heat of polymerization is significantly less than the theoretical value of -83.7 kJ/mol (-20 kcal/mol) for the process of converting a double bond to two single bonds. The steric strain apparently is neither important in the addition step because VDC polymerizes easily, nor is it sufficient to favor depolymerization. The estimated ceiling temperature for PVDC is about 400°C.

Homopolymerization. The free-radical polymerization of VDC has been carried out by solution, slurry, suspension, and emulsion methods. Solution polymerization in a medium that dissolves both monomer and polymer has been

investigated (23). The kinetic measurements lead to activation energies and frequency factors in the normal range for free-radical polymerizations of olefinic monomers. The kinetic behavior of VDC is abnormal when the polymerization is heterogeneous (24). Slurry polymerizations are usually used only in the laboratory. They can be carried out in bulk or in common solvents, eg, benzene. Poly(vinylidene chloride) is insoluble in these media and separates from the liquid phase as a crystalline powder. The heterogeneity of the reaction makes stirring and heat transfer difficult; consequently, these reactions cannot be easily controlled on a large scale. Aqueous emulsion or suspension reactions are preferred for large-scale operations. Slurry reactions are usually initiated by the thermal decomposition of organic peroxides or azo compounds. Purely thermal initiation can occur, but rates are very low (25).

Bulk Polymerization. The spontaneous polymerization of VDC, so often observed when the monomer is stored at room temperature, is caused by peroxides formed from the reaction of VDC with oxygen. Very pure monomer does not polymerize under these conditions. Irradiation by either uv or γ rays (24,26) also induces polymerization of VDC.

The heterogeneous nature of the bulk polymerization of VDC is apparent from the rapid development of turbidity in the reaction medium following initiation. The turbidity results from the presence of minute PVDC crystals. As the reaction progresses, the crystalline phase grows and the liquid phase diminishes. Eventually, a point is reached where the liquid slurry solidifies into a solid mass. A typical conversion–time curve is shown in Figure 1 for a mass polymerization

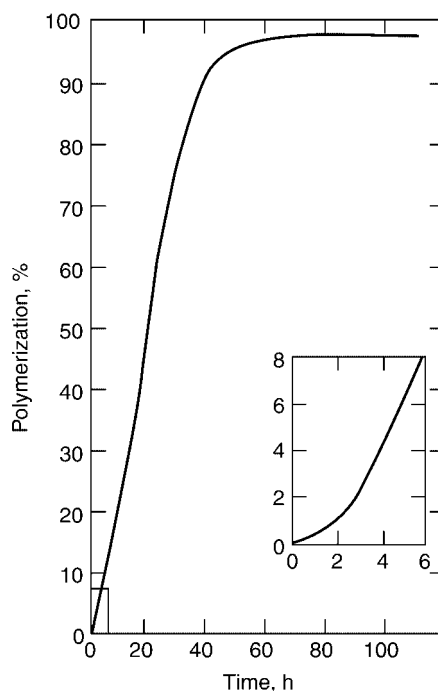


Fig. 1. Bulk polymerization of VDC at 45°C, with 0.5 wt% benzoyl peroxide as initiator (27).

catalyzed by benzoyl peroxide. The first stage of the reaction is characterized by rapidly increasing rate, which levels off in the second stage to a fairly constant value. This is often called the steady-state region. Throughout the first two stages, monomer concentration remains constant because the polymer separates into another phase. In the third stage, there is a gradual decrease in rate to zero as the monomer supply is depleted. Because the mass solidifies while monomer is still present (usually at conversions below 20%), further polymerization generates void space. The final solid, therefore, is opaque and quite porous. A similar pattern of behavior is observed when VDC is polymerized in solvents, eg, benzene, that do not dissolve or swell the polymer. In this case, however, the reaction mixture may not solidify if the monomer concentration is low.

Heterogeneous polymerization is characteristic of a number of monomers, including vinyl chloride and acrylonitrile. A completely satisfactory mechanism for these reactions has not been determined. This is true for VDC also. Earlier studies have not been broad enough to elucidate the mechanism (24,28,29). Morphologies of as-polymerized poly(vinyl chloride) (PVC) and polyacrylonitrile (PAN) are similar, suggesting a similar mechanism.

The morphology of as-polymerized PVDC is quite different (29). Nearly spherical aggregates form in the PVC and PAN systems, whereas anisotropic growth takes place in the PVDC case. The difference in morphology may be a consequence of the relative rates of polymerization and crystallization. Poly(vinylidene chloride) is unique because polymerization and crystallization probably occur nearly simultaneously. It has been reported that the average lifetime of a growing radical (τ_s) is between 0.1 and 10 s (30). The half-time ($t_{1/2}$) for crystallization of PVDC copolymers in monomer was measured to be about 1 s at 60°C and about 0.01 s at 90°C (31). This information is important for developing an understanding of a mechanism that includes a contribution from a surface reaction which has the potential for autoacceleration.

Emulsion Polymerization. Emulsion and suspension reactions are doubly heterogeneous; the polymer is insoluble in the monomer and both are insoluble in water. Suspension reactions are similar in behavior to slurry reactions. Oil-soluble initiators are used, and so the monomer-polymer droplet is like a small mass reaction. Emulsion polymerizations are more complex. Because the monomer is insoluble in the polymer particle, the simple Smith-Ewart theory does not apply (32).

A kinetic model for the particle growth stage for continuous-addition emulsion polymerization has been proposed (33). Below the monomer saturation point, the steady-state rate of polymerization, R_p , depends on the rate of monomer addition, R_a , according to the following reciprocal relationship:

$$\frac{1}{R_p} = \frac{1}{K} + \frac{1}{R_a}$$

where K depends on the number of particles and the propagation rate constant. A later study explored the kinetics of emulsion polymerization of nonswelling and swellable latex particles to define the locus of polymerization (34). There are no significant differences between the behavior of swelling and nonswelling emulsion particles and neither follows Smith-Ewart kinetics. The results indicate strongly that polymerization takes place at the particle-water interface or in a surface layer on the polymer particle.

Redox initiator systems are normally used in the emulsion polymerization of VDC to develop high rates at low temperatures. Reactions must be carried out below $\sim 80^{\circ}\text{C}$ to prevent degradation of the polymer. Poly(vinylidene chloride) in emulsion is also attacked by aqueous base. Therefore, reactions should be carried out at low pH.

Ionic Mechanisms. The instability of PVDC is one of the reasons why ionic initiation of VDC polymerization has not been used extensively. Many of the common initiators are sufficiently basic so as to promote E2 elimination of hydrogen chloride as the polymer is being formed. For example, butyllithium polymerizes VDC by an anionic mechanism, but the product is a low molecular weight, discolored polymer having a low chlorine content (35). Cationic polymerization of VDC seems unlikely in view of its structure (36). Some available data, however, suggest the possibility. In the low temperature, radiation-induced copolymerization of VDC with isobutylene, reactivity ratios vary markedly with temperature, indicating a change from a free-radical mechanism (37). Coordination complex catalysts may also polymerize VDC by a nonradical mechanism. Again, this speculation is based on copolymerization studies. Poly(vinylidene chloride) telomers can be prepared by using chlorine as the initiator and chain-transfer agent (38,39). Plasma polymerization of VDC in a radio-frequency glow discharge yields cross-linked polymer, which is partially degraded (40).

Copolymerization. The importance of VDC as a monomer results from its ability to copolymerize with other vinyl monomers. Its Q value equals 0.22 and its e value equals 0.36. It most easily copolymerizes with acrylates, but it also reacts, more slowly, with other monomers, eg, styrene, that form highly resonance-stabilized radicals. Reactivity ratios (r_1 and r_2) with various monomers are listed in Table 2. Many other copolymers have been prepared from monomers for which the reactivity ratios are not known. The commercially important copolymers include those with vinyl chloride (VC), acrylonitrile (AN), or various alkyl acrylates, but many commercial polymers contain three or more components, of which VDC is the principal one. Usually one component is introduced to improve the processibility or solubility of the polymer; the others are added to modify specific use properties. Most of these compositions have been described in the patent literature, and a list of various combinations has been compiled (41). A typical terpolymer might contain 90 wt% VDC, with the remainder made up of AN and an acrylate or methacrylate monomer.

Table 2. Reactivity of VDC (r_1) with Important Monomers (r_2)^a

Monomer	r_1	r_2
Styrene	0.14	2.0
Vinyl chloride	3.2	0.3
Acrylonitrile	0.37	0.91
Methyl acrylate	1.0	1.0
Methyl methacrylate	0.24	2.53
Vinyl acetate	6	0.1

^aRef. 42.

Bulk copolymerizations yielding high VDC-content copolymers are normally heterogeneous. Two of the most important pairs, VDC-VC and VDC-AN, are heterogeneous over most of the composition range. In both cases and at either composition extreme, the product separates initially in a powdery form; however, for intermediate compositions, the reaction mixture may only gel. Copolymers in this composition range are swollen but not completely dissolved by the monomer mixture at normal polymerization temperatures. Copolymers containing more than 15 mol% acrylate are normally soluble in the monomers. These reactions are therefore homogeneous and, if carried to completion, yield clear, solid castings of the copolymer. Most copolymerizations can be carried out in solution because of the greater solubility of the copolymers in common solvents.

During copolymerization, one monomer may add to the copolymer more rapidly than the other. Except for the unusual case of equal reactivity ratios, batch reactions carried to completion yield polymers of broad composition distribution. More often than not, this is an undesirable result.

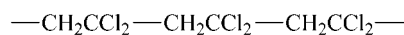
Vinylidene chloride copolymerizes randomly with methyl acrylate and nearly so with other acrylates. Very severe composition drift occurs, however, in copolymerizations with vinyl chloride or methacrylates. Several methods have been developed to produce homogeneous copolymers regardless of the reactivity ratio (42). These methods are applicable mainly to emulsion and suspension processes where adequate stirring can be maintained. Copolymerization rates of VDC with small amounts of a second monomer are normally lower than its rate of homopolymerization. The kinetics of the copolymerization of VDC and VC has been studied (43-46).

Studies of the copolymerization of VDC with methyl acrylate (MA) over a composition range of 0-16 wt% showed that near the intermediate composition (8 wt%), the polymerization rates nearly followed normal solution polymerization kinetics (47). However, at the two extremes (0 and 16 wt% MA), copolymerization showed significant autoacceleration. The observations are important because they show the significant complexities in these copolymerizations. The autoacceleration for the homopolymerization, ie, 0 wt% MA, is probably the result of a surface polymerization phenomenon. On the other hand, the autoacceleration for the 16 wt% MA copolymerization could be the result of Trommsdorff and Norrish-Smith effects.

Copolymers of VDC can also be prepared by methods other than conventional free-radical polymerization. Copolymers have been formed by irradiation and with various organometallic and coordination complex catalysts (26,41,48-51). Graft copolymers have also been described (52-56).

Polymer Structure and Properties

Chain Structure. The chemical composition of PVDC has been confirmed by various techniques, including elemental analysis, x-ray diffraction analysis, degradation studies, and infrared (ir), Raman, and nuclear magnetic resonance (nmr) spectroscopy. The polymer chain is made up of VDC units added head-to-tail:



Because the repeat unit is symmetrical, no possibility exists for stereoisomerism. Variations in structure can occur only by head-to-head addition, branching, or degradation reactions that do not cause chain scission, including such reactions as thermal dehydrochlorination, which creates double bonds in the structure to give, for example, $-\text{CH}_2\text{CCl}_2\text{CH}_2=\text{CClCH}_2\text{CCl}_2-$ and a variety of ill-defined oxidation and hydrolysis reactions that generate carbonyl groups.

The ir spectra of PVDC often show traces of unsaturation and carbonyl groups. The slightly yellow tinge of many of these polymers comes from the same source; the pure polymer is colorless. Elemental analyses for chlorine are normally slightly lower than the theoretical value of 73.2%.

The high crystallinity of PVDC indicates that no significant amounts of head-to-head addition or branching can be present. This has been confirmed by nmr spectra (57). Studies of well-characterized oligomers having degrees of polymerization (DP) of 2–10 offer further nmr evidence (38), ie, a single peak from the methylene hydrogens. Either branching or another mode of addition would produce nonequivalent hydrogens and a more complicated spectrum. However, nmr cannot detect small amounts of such structures. The ir and Raman spectra can also be interpreted in terms of the simple head-to-tail structure (58,59).

Molecular weights of PVDC can be determined directly by dilute solution measurements in good solvents (60). Viscosity studies indicate that polymers having DP from 100 to more than 10,000 are easily obtained. Dimers and polymers having DP < 100 can be prepared by special procedures (38). Copolymers can be more easily studied because of their solubility in common solvents. Gel-permeation chromatography studies indicate that molecular weight distributions are typical of vinyl copolymers.

Crystal Structure. The crystal structure of PVDC is fairly well established. Several unit cells have been proposed (61). The unit cell contains four monomer units with two monomer units per repeat distance. The calculated density, 1.96 g/cm^3 , is higher than the experimental values, which are $1.80\text{--}1.94 \text{ g/cm}^3$ at 25°C , depending on the sample. This is typically the case with crystalline polymers because samples of 100% crystallinity usually cannot be obtained. A direct calculation of the polymer density from volume changes during polymerization yields a value of 1.97 g/cm^3 (62). If this value is correct, the unit cell densities may be low.

The repeat distance along the chain axis (0.468 nm) is significantly less than that calculated for a planar zigzag structure. Therefore, the polymer must be in some other conformation (63–65). Based on ir and Raman studies of PVDC single crystals and normal vibration analysis, the best conformation appears to be $\theta_\phi\theta_{\phi'}$, where the skeletal angle θ is 120° , and the torsional angle $\phi(\phi'$ of opposite sign) is 32.5° . This conformation is in agreement with theoretical predictions (66).

The melting temperature T_m of PVDC is independent of molecular weight above DP = 100. However, as shown in Figure 2, it drops sharply at lower molecular weights. Below the hexamer, the products are noncrystalline liquids.

The properties of PVDC (Table 3) are usually modified by copolymerization. Copolymers of high VDC content have lower melting temperatures than PVDC. Copolymers containing more than $\sim 15 \text{ mol\%}$ acrylate or methacrylate are amorphous. Substantially more AN (25%) or VC (45%) is required to destroy crystallinity completely.

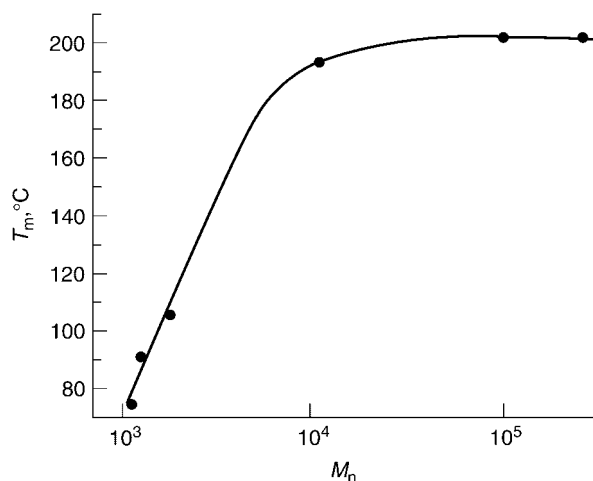


Fig. 2. Crystalline melting temperatures of PVDC (38).

The effect of different types of comonomers on T_m varies. VDC–MA copolymers more closely obey Flory's melting-point depression theory than do copolymers with VC or AN. Studies have shown that for the copolymers of VDC with MA, Flory's theory needs modification to include both lamellar thickness and surface free energy (67). The VDC–VC and VDC–AN copolymers typically have severe composition drift; therefore most of the comonomer units do not belong to crystallizing chains. Hence, they neither enter the crystal as defects nor cause lamellar thickness to decrease, and so the depression of the melting temperature is less than expected.

The glass-transition temperature T_g , of VDC copolymers has been studied extensively (68,69). The effect of various comonomers on the T_g is shown in Figure 3. In every case, T_g increases with the comonomer content at low comonomer levels, even in cases where the T_g of the other homopolymer is lower. The phenomenon has been observed in several other copolymer systems as well (71). In these cases, a maximum T_g is observed at intermediate compositions. In others, where the T_g of the other homopolymer is much higher than the T_g of

Table 3. Properties of PVDC

Property	Best value	Reported values
T_m , °C	202	198–205
T_g , °C	–17	–19 to –11
Transition between T_m and T_g , °C	80	
Density at 25°C, g/cm ³		
Amorphous	1.775	1.67–1.775
Unit cell	1.96	1.949–1.96
Crystalline		1.80–1.97
Refractive index (crystalline), n_D	1.63	
Heat of fusion, ΔH_m , J/mol ^a	6275	4600–7950

^aTo convert J to cal, divide by 4.184.

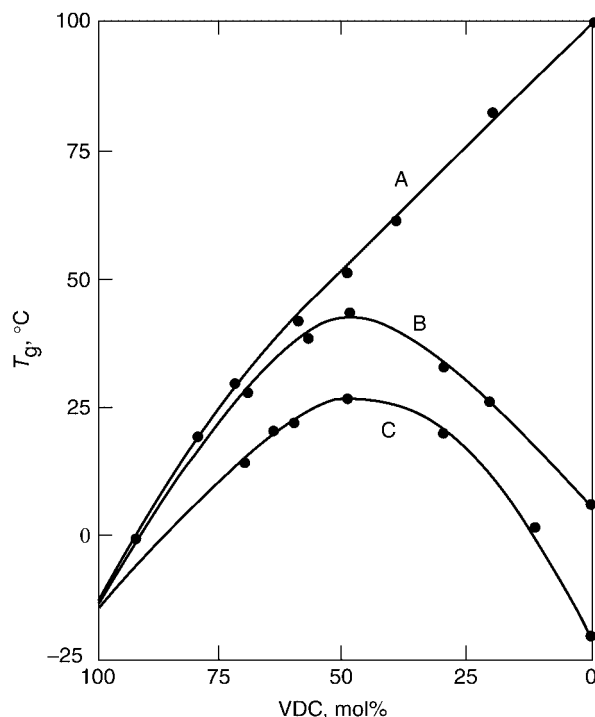


Fig. 3. Effect of comonomer structure on the glass-transition temperature of VDC copolymers (71), where A represents AN; B, MA; and C, EA.

PVDC, the glass-transition temperatures of the copolymers increase over the entire composition range. The T_g increases most rapidly at low AN levels but changes the slowest at low VC levels. This suggests that polar interactions affect the former, but the increase in T_g in the VDC-VC copolymers may simply result from loss of chain symmetry. Because of these effects, the temperature range in which copolymers can crystallize is drastically narrowed. Crystallization induction times are prolonged, and subsequent crystallization takes place at a low rate over a long period of time. Plasticization, which lowers T_g , decreases crystallization induction times significantly. Copolymers having lower glass-transition temperatures also tend to crystallize more rapidly (72).

Crystallization curves have been determined for 10 mol% acrylate copolymers of varying side-chain length. Among the acrylate copolymers, the butyl acrylate copolymer has a T_g of 8°C; the octyl acrylate, -3°C; and the octadecyl acrylate, -16°C. The rates of crystallization of these copolymers are inversely related to the glass-transition temperatures. Apparently, the long alkyl side chains act as internal plasticizers, lowering the melt viscosity of the copolymer even though the acrylate group acts to stiffen the backbone.

The maximum rates of crystallization of the more common crystalline copolymers occur at 80–120°C. In many cases, these copolymers have broad composition distributions containing both fractions of high VDC content that crystallize rapidly and other fractions that do not crystallize at all. Poly(vinylidene chloride)

probably crystallizes at a maximum rate at 140–150°C, but the process is difficult to follow because of severe polymer degradation. The copolymers may remain amorphous for a considerable period of time if quenched to room temperature. The induction time before the onset of crystallization depends on both the type and amount of comonomer; PVDC crystallizes within minutes at 25°C.

Recrystallization of a copolymer having 15 wt% VC has been found to be nucleated by material that survives the melting process plus new nuclei (72). The maximum crystallization rate occurred at 100°C; the maximum nucleation rate at 10°C. Attempts to melt all the polymer led to degradation that interfered with recrystallization.

Orientation or mechanical working accelerates crystallization has a pronounced effect on morphology. Crystals of uniaxially oriented filaments are oriented along the fiber axis (61). The long period (lamellar thickness), as determined by small-angle x-ray scattering, is 7.6 nm and decreases with comonomer content. The fiber is 43% crystalline and has a melting temperature of 195°C and an average crystal thickness of 4.5 nm. The crystal size is not greatly affected by comonomer content, but both crystallinity and melting temperature decrease with increasing comonomer.

Copolymerization also affects morphology under other crystallization conditions. Copolymers in the form of cast or molded sheets are much more transparent because of the small spherulite size. In extreme cases, crystallinity cannot be detected optically, but its effect on mechanical properties is pronounced. Before crystallization, films are soft and rubbery, with low modulus and high elongation. After crystallization, they are leathery and tough, with higher modulus and lower elongation.

Copolymers of VDC and MA have been studied by x-ray techniques (73). For example, the long period (lamellar thickness) for an 8.5 wt% MA copolymer was found to be 9.2 nm by small-angle x-ray scattering. The unit cell is monoclinic, with $a = 0.686$ and $c = 1.247$ nm by wide-angle x-ray scattering.

Significant amounts of comonomer also reduce the ability of the polymer to form lamellar crystals from solution. In some cases, the polymer merely gels the solution as it precipitates rather than forming distinct crystals. At somewhat higher VDC content, it may precipitate in the form of aggregated, ill-defined particles and clusters.

Morphology and Transitions. The highly crystalline particles of PVDC precipitated during polymerization are aggregates of thin lamellar crystals (74). The substructures are 5–10 nm thick and 100 or more times larger in other dimensions. In some respects, they resemble the lamellar crystals grown from dilute solution (75–77). The single crystals are better characterized than the as-polymerized particles. They are highly branched, with branching angles of 65–70°; the angle appears to be associated with a twin plane in the crystal (78).

Melting temperatures of as-polymerized powders are high, ie, 198–205°C as measured by differential thermal analysis (dta) or hot-stage microscopy (74). Two peaks are usually observed in dta curves: a small lower temperature peak and the main melting peak. The small peak seems to be related to polymer crystallized by precipitation rather than during polymerization.

As-polymerized PVDC does not have a well-defined T_g because of its high crystallinity. However, a sample can be melted at 210°C and quenched rapidly to

an amorphous state at $< -20^{\circ}\text{C}$. The amorphous polymer has a glass-transition temperature of -17°C as shown by dilatometry (68). Glass-transition temperature values of -19 to -11°C , depending on both method of measurement and sample preparation, have been determined.

Once melted, PVDC does not regain its as-polymerized morphology when subsequently crystallized. The polymer recrystallizes in a spherulitic habit. Spherulites between crossed polarizing plates show the usual Maltese cross and are positively birefringent. The size and number of spherulites can be controlled. Quenching and low-temperature annealing generate many small nuclei that, on heating, grow rapidly into small spherulites. Slow crystallization at higher temperatures produces fewer but much larger spherulites. The melting temperature and degree of crystallinity of recrystallized PVDC also depend on crystallization conditions. The melting temperature increases with crystallization temperature, but the as-polymerized value cannot be achieved. There is no reason to believe that even these values indicate the true melting point of PVDC; it may be as high as 220°C . Slow, high temperature recrystallization and annealing experiments are not feasible because of the thermal instability of the polymer (79). Other transitions in PVDC have been observed by dynamic mechanical methods.

Solubility and Solution Properties. Poly(vinylidene chloride), like many high melting polymers, does not dissolve in most common solvents at ambient temperatures. Copolymers, particularly those of low crystallinity, are much more soluble. However, one of the outstanding characteristics of VDC polymers is resistance to a wide range of solvents and chemical reagents. The insolubility of PVDC results less from its polarity than from its high melting temperature. It dissolves readily in a wide variety of solvents above 130°C (79). However, it should be noted that significant degradation accompanies dissolution of the polymer in polar, aprotic solvents at these temperatures.

The polarity of the polymer is important only in mixtures having specific polar aprotic solvents. Many solvents of this general class solvate PVDC strongly enough to depress the melting temperature by more than 100°C . Solubility is normally correlated with cohesive energy densities or solubility parameters. For PVDC, a value of $20 \pm 0.6 (\text{J}/\text{cm}^3)^{1/2}$ [$10 \pm 0.3 (\text{cal}/\text{cm}^3)^{1/2}$] has been estimated from solubility studies in nonpolar solvents. The value calculated from Small's relationship is $20.96 (\text{J}/\text{cm}^3)^{1/2}$ [$10.25 (\text{cal}/\text{cm}^3)^{1/2}$]. The use of the solubility parameter scheme for polar crystalline polymers such as PVDC has limited value. A typical nonpolar solvent of matching solubility parameter is tetrahydronaphthalene. The lowest temperature at which PVDC dissolves in this solvent is 140°C . Specific solvents, however, dissolve PVDC at much lower temperatures. A list of good solvents is given in Table 4. The relative solvent activity is characterized by the temperature at which a 1 wt% mixture of polymer in solvent becomes homogeneous when heated rapidly.

Poly(vinylidene chloride) also dissolves readily in certain solvent mixtures (80). One component must be a sulfoxide or *N,N*-dialkylamide. Effective cosolvents are less polar and have cyclic structures. They include aliphatic and aromatic hydrocarbons, ethers, sulfides, and ketones. Acidic or hydrogen-bonding solvents have an opposite effect, rendering the polar aprotic component less effective. Both hydrocarbons and strong hydrogen-bonding solvents are nonsolvents for PVDC.

Table 4. Solvents for PVDC^a

Solvents	$T, ^\circ\text{C}$ ^b
<i>Nonpolar</i>	
1,3-Dibromopropane	126
Bromobenzene	129
1-Chloronaphthalene	134
2-Methylnaphthalene	134
<i>o</i> -Dichlorobenzene	135
<i>Polar aprotic</i>	
Hexamethylphosphoramide	-7.2
Tetramethylene sulfoxide	28
<i>N</i> -Acetylpiperidine	34
<i>N</i> -Methylpyrrolidinone	42
<i>N</i> -Formylhexamethyleneimine	44
Trimethylene sulfide	74
<i>N</i> - <i>n</i> -Butylpyrrolidinone	75
Diisopropyl sulfoxide	79
<i>N</i> -Formylpiperidine	80
<i>N</i> -Acetylpyrrolidinone	86
Tetrahydrothiophene	87
<i>N,N</i> -Dimethylacetamide	87
Cyclooctanone	90
Cycloheptanone	96
Di- <i>n</i> -butyl sulfoxide	98

^aRef. 79.^bTemperature at which a 1 wt% mixture of polymer in solvent becomes homogeneous.

As-polymerized PVDC is not in its most stable state; annealing and recrystallization can raise the temperature at which it dissolves (76). Low crystallinity polymers dissolve at a lower temperature, forming metastable solutions. However, on standing at the dissolving temperature, they gel or become turbid, indicating recrystallization into a more stable form.

Copolymers having enough VDC content to be quite crystalline behave much like PVDC. They are more soluble, however, because of their lower melting temperatures. The solubility of amorphous copolymers is much higher. The selection of solvents in either case varies somewhat with the type of comonomer. Some of the more common types are listed in Table 5. Solvents that dissolve PVDC also dissolve the copolymers at lower temperatures. The identification of solvents that dissolve PVDC at low temperatures makes possible the study of dilute solution properties. Both light-scattering and intrinsic-viscosity studies have been reported (60). Intrinsic viscosity-molecular weight relationships for the three solvents investigated ($[\eta]$ in dL/g) are

- (1) $[\eta] = 1.31 \times 10^{-4} M_w^{0.69}$ *N*-Methylpyrrolidinone (MP)
- (2) $[\eta] = 1.39 \times 10^{-4} M_w^{0.69}$ Tetramethylene sulfoxide (TMSO)
- (3) $[\eta] = 2.58 \times 10^{-4} M_w^{0.65}$ Hexamethylphosphoramide (HMPA).

Table 5. Common Solvents for VDC Copolymers

Solvents	Copolymer type	Temperature, °C
Tetrahydrofuran	All	<60
2-Butanone	Low crystallinity	<80
1,4-Dioxane	All	50–100
Cyclohexanone	All	50–100
Cyclopentanone	All	50–100
Ethyl acetate	Low crystallinity	<80
Chlorobenzene	All	100–130
Dichlorobenzene	All	100–140
Dimethylformamide	High acrylonitrile	<100

The relative solvent power (HMPA > TMSO > MP) agrees with solution-temperature measurements. The characteristic ratio C_∞ is about 8 ± 1 , which is slightly larger than that of a similar polymer, polyisobutylene.

The dilute solution properties of copolymers are similar to those of the homopolymer. The intrinsic viscosity–molecular weight relationship for a VDC–AN copolymer (9 wt% AN) is $[\eta] = 1.06 \times 10^{-4} M_w^{0.72}$ (81). The characteristic ratio is 8.8 for this copolymer.

An extensive investigation of the dilute solution properties of several acrylate copolymers has been reported (78). The behavior is typical of flexible-backbone vinyl polymers. The length of the acrylate ester side chain has little effect on properties.

Intrinsic viscosity–molecular weight relationships have been obtained for copolymers in methyl ethyl ketone. The value for a 15 wt% ethyl acrylate (EA) copolymer is $[\eta] = 2.88 \times 10^{-4} M_w^{0.6}$.

Earlier work characterized the molecular weights of PVDC and VDC copolymers by using the absolute viscosity of a 2 wt% solution in *o*-dichlorobenzene at 140°C. The exact correlation between this viscosity value and molecular weight is not known. Gel-permeation chromatography is the preferred method for characterizing molecular weight; studies of copolymers have been reported (82,83).

Mechanical Properties. Because PVDC is difficult to fabricate into suitable test specimens, very few direct measurements of its mechanical properties have been made. In many cases, however, the properties of copolymers have been studied as functions of composition, and the properties of PVDC can be estimated by extrapolation. Some characteristic properties of high VDC content, unplasticized copolymers are listed in Table 6. The performance of a given specimen is sensitive to morphology, including the amount and kind of crystallinity, as well as orientation. Tensile strength increases with crystallinity, whereas toughness and elongation decrease. Orientation, however, improves all three properties. The effect of stretch ratio applied during orientation on properties of VDC–VC monofilaments is shown in Table 7.

The dynamic mechanical properties of VDC–VC copolymers have been studied in detail. The incorporation of VC units in the polymer results in a drop in dynamic modulus because of the reduction in crystallinity. However, the glass-transition temperature is raised; therefore, the softening effect observed at room

Table 6. Mechanical Properties of High VDC Content Copolymers

Property	Range
Tensile strength, MPa ^a	
Unoriented	34.5–69.0
Oriented	207–414
Elongation, %	
Unoriented	10–20
Oriented	15–40
Softening range (heat distortion), °C	100–150
Flow temperature, °C	>185
Brittle temperature, °C	–10 to 10
Impact strength, J/m ^b	26.7–53.4

^aTo convert MPa to psi, multiply by 145.^bTo convert J/m to ft.lbf/in., divide by 53.38 (see ASTM D256).

temperature is accompanied by increased brittleness at lower temperatures. These copolymers are normally plasticized in order to avoid this. Small amounts of plasticizer (2–10 wt%) depress T_g significantly without loss of strength at room temperature. At higher levels of VC, the T_g of the copolymer is above room temperature and the modulus rises again. A minimum in modulus or maximum in softness is usually observed in copolymers in which T_g is above room temperature. A thermomechanical analysis of VDC–AN and VDC–MMA (methyl methacrylate) copolymer systems shows a minimum in softening point at 79.4 and 68.1 mol% VDC, respectively (84).

In cases where the copolymers have substantially lower glass-transition temperatures, the modulus decreases with increasing comonomer content. This results from a drop in crystallinity and glass-transition temperature. The loss in modulus in these systems is therefore accompanied by an improvement in low temperature performance. However, at low acrylate levels (<10 wt%), T_g increases with comonomer content. The brittle points in this range may therefore be higher than that of PVDC.

Table 7. Effect of Stretch Ratio on Tensile Strength and Elongation of a VDC–VC Copolymer^{a, b}

Stretch ratio	Tensile strength, MPa ^c	Elongation, %
2.50:1	235	23.2
2.75:1	234	21.7
3.00:1	303	26.3
3.25:1	268	33.1
3.50:1	316	19.2
3.75:1	330	21.8
4.00:1	320	19.7
4.19:1	314	16.2

^aRef. 84.^bAverage of five determinations, using the Instron test at 5 cm/min.^cTo convert MPa to psi, multiply by 145.

The long side chains of the acrylate ester group can apparently act as internal plasticizers. Substitution of a carboxyl group on the polymer chain increases brittleness. A more polar substituent, eg, an *N*-alkylamide group, is even less desirable. Copolymers of VDC with *N*-alkylacrylamides are more brittle than the corresponding acrylates even when the side chains are long (85). Side-chain crystallization may be a contributing factor.

Barrier Properties. Vinylidene chloride copolymers are unique in that they have low permeability to a wider range of gases and liquids than other polymers. VDC copolymers are “barrier polymers” in a broad sense. Historically, the operating definition of a barrier polymer meant having an oxygen permeability less than 1.0 (cm³(STP)·mil)/(100 in.²·day·atm) [2.0 nmol/(m·s·GPa)]. A more useful descriptor for a barrier polymer is related to the application. A barrier polymer would have a set of permeabilities for important molecules sufficiently low to satisfy the containment needs. Some polymers have low permeability to gases. Others have low permeability to water. Still other polymers have low permeability to flavor/aroma/solvent (F/A/S) molecules. However, only rarely does a single polymer have low permeability in more than one category. VDC copolymers have low permeability in all three categories (see BARRIER POLYMERS).

The good barrier properties of VDC copolymers are a consequence of crystallinity and low free volume in the amorphous phase. The symmetric nature of the VDC unit in the polymer leads to nested packing that is adequate for crystallization and that leaves very little “dead” volume in the amorphous phase. Both polyisobutylene and PVDC have unusually low permeability to water compared to their monosubstituted counterparts, polypropylene and PVC (86). The values listed in Table 8 include estimates for the completely amorphous polymers. The estimated value for highly crystalline PVDC was obtained by extrapolating data for copolymers.

The effect of copolymer composition on gas permeability is shown in Table 9. The inherent barrier in VDC copolymers can best be exploited by using films containing little or no plasticizers and as much VDC as possible. However, the permeabilities of even completely amorphous copolymers, eg, 60 wt% VDC–40 wt% AN or 50 wt% VDC–50 wt% VC, are low compared to that of other polymers. The primary reason is that the diffusion coefficients for molecules in VDC copolymers

Table 8. Comparison of the Permeabilities of Various Polymers to Water Vapor^a

Polymer	Density, g/mL		Permeability ^b	
	Amorphous	Crystalline	Amorphous	Crystalline
Ethylene	0.85	1.00	200–220	10–40
Propylene	0.85	0.94	420	
Isobutylene	0.915	0.94	90	
Vinyl chloride	1.41	1.52	300	90–115
Vinylidene chloride	1.77	1.96	30	4–6

^aRefs. 42,86 and 87.

^bIn g/(h·100 m²) at 7.1 kPa (53 mm Hg) pressure differential and 39.5°C for a film 25.4 μm (1 mil) thick.

Table 9. Effect of Composition on the Permeability of Various Gases through VDC Copolymers^a

Polymer	Gas	<i>T</i> , °C	<i>P</i> , nmol/(m·s·GPa) ^b
PVDC	O ₂	25	<0.04
	N ₂	25	<0.02
	CO ₂	25	<0.10
90/10 VC	He	25	2.23
	H ₂	25	2.54
	O ₂	25	0.14
	N ₂	25	0.03
	CO ₂	25	0.98
	H ₂ S	30	0.10
	He	34	10
85/15 VC	O ₂	25	0.40
	CO ₂	20	2.0
70/30 VC	O ₂	25	0.36
50/50 VC	O ₂	25	1.2
80/20 AN	O ₂	25	0.14
	N ₂	25	0.02
	CO ₂	25	0.35
60/40 AN	O ₂	25	0.71
	N ₂	25	0.09
	CO ₂	25	1.6

^aRef. 88.^bTo convert nmol/(m·s·GPa) to (cm³·cm)/(cm²·s·kPa), divide by 4.46×10^{12} .

are very low. This factor, together with the high crystallinity and the low solubility coefficients for many gases in VDC copolymers, results in very low permeabilities. A change from PVDC to a copolymer containing 40 wt% AN or 50 wt% VC increases the permeability 10-fold but has little effect on the solubility coefficient.

The addition of a more polar comonomer, eg, AN, increases the water vapor transmission rate more than the addition of a less polar comonomer, eg, VC, when other factors are constant. For the same reason, AN copolymers are more resistant to penetrants of low cohesive energy density. All VDC copolymers, however, are very impermeable to aliphatic hydrocarbons. Comonomers that lower T_g and increase the free volume in the amorphous phase increase permeabilities more than other comonomers. Higher acrylates are examples of this phenomenon. Plasticizers increase permeabilities for similar reasons.

The effects of plasticizers and temperature on the permeabilities of small molecules in a typical VDC copolymer have been studied thoroughly. Data for oxygen permeability are contained in Figure 4. The oxygen permeability doubles with the addition of about 1.7 phr (parts per hundred of resin) of common plasticizers or a temperature increase of about 8°C (89). The moisture (water) vapor transmission rate (MVTR or WVTR) doubles with the addition of about 3.5 phr of common plasticizers (90). The dependence of the WVTR on temperature is a little more complicated. Water vapor transmission rate is commonly reported at a constant difference in relative humidity and not at a constant partial pressure

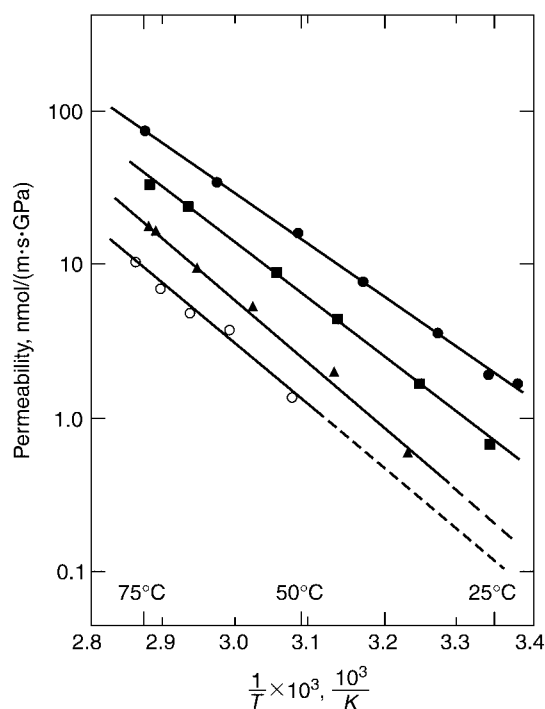


Fig. 4. Oxygen permeability in a VDC copolymer film at selected levels of plasticizer (Citroflex A-4). Plasticizer level in parts per hundred of resin (phr); ●, 7.2 phr; ■, 4.9 phr; ▲, 2.7 phr; and ○, 0.5 phr. To convert $\text{nmol}/(\text{m}\cdot\text{s}\cdot\text{GPa})$ to $(\text{cm}^3\cdot\text{mil})/(\text{100 in.}^2\cdot\text{d}\cdot\text{atm})$, divide by 2.

difference. Hence, WVTR is a mixed term that increases with increasing temperature because both the permeability and the partial pressure at constant relative humidity increase. Carbon dioxide permeability doubles with the addition of about 1.8 phr of common plasticizers, or a temperature increase of 7°C (91).

Table 10 contains a comparison of the permeabilities of small molecules for several common polymers. The oxygen permeability is an important property for food packaging. In some cases the relative humidity is an important environmental variable. The oxygen permeability is not affected by humidity for VDC copolymers, nitrile barrier resins, poly(vinyl chloride), polystyrene, and polyolefins. The oxygen permeabilities of most nylons are increased modestly by increasing humidity, and the oxygen permeability of poly(ethylene terephthalate) is decreased modestly by increasing humidity. In contrast, the ethylene-vinyl alcohol copolymers (EVOH) are very sensitive to humidity. At low humidity, the oxygen permeabilities of EVOH are quite low. However, at the high humidity encountered in food packaging, the oxygen permeabilities of EVOH are much higher. Small changes in humidity can cause large changes in the oxygen permeabilities. Hence the data in tables need to be used carefully.

The data in Tables 11, 12, 13 describe VDC copolymers as good barriers for both gases and water. They are also good barriers to F/A/S molecules. This property for polymers has become more important since more sophisticated foods

Table 10. Barrier Properties of Polymers^a

Polymer	Gas permeability at 23°C, nmol/(m·s·GPa) ^b			WVTR ^c , nmol/(m·s) ^d
	O ₂	N ₂	CO ₂	
High barrier vinylidene chloride copolymers	0.04–0.3	0.01–0.1	0.1–0.5	0.02–0.1
Nitrile barrier resin	1.6	—	6	1.0–1.2
Nylon-6,6; nylon-6	2–5	—	3–9	1.5–5.5
Polypropylene	300	60	1200	0.06–0.2
Poly(ethylene terephthalate)	10–18	2–4	30–50	0.4–0.7
Polylactide	90	—	375	5.1
Rigid poly(vinyl chloride)	10–40	—	40–100	0.2–1.3
High density polyethylene	300	—	1200	0.1
Low density polyethylene	500–700	200–400	2000–4000	0.2–0.4
Polystyrene	500–800	80–120	1400–3000	0.5–3.0
Ethylene vinyl alcohol				
32 mol% ethylene				
0% RH	0.02	0.002	0.09	0.9 ^e
100% RH	2.3	—	—	—
44 mol% ethylene				
0% RH	0.18	0.015	0.8	0.3 ^e
100% RH	1.3	—	—	—

^aRefs. 92–94.^bTo convert nmol/(m·s·GPa) to (cm³·mil)/(100 in.²·d·atm), divide by 2.^cWVTR = water vapor transmission rate at 90% RH and 38°C.^dTo convert nmol/(m·s) to (g·mil)/(100 in.²·d), multiply by 4.^e40°C.

are being packaged in plastics. The permeation of F/A/S molecules differs from the permeation of small molecules in some important ways. The diffusion coefficient D for F/A/S molecules is typically 10^2 – 10^5 times smaller. These molecules move slower because they need to find larger openings in the polymer. The solubility coefficient S is typically 10^2 – 10^6 times larger. This is related to higher boiling

Table 11. Diffusion Coefficients and Solubility Coefficients of Selected Penetrants in Polymers at 75°C^a

Penetrant	Polymer	D , m ² /s	S , kg/(m ³ ·Pa)
Oxygen	Poly(ethylene terephthalate)	3×10^{-13}	9.8×10^{-7}
Oxygen	High density polyethylene	1.7×10^{-11}	6.6×10^{-7}
Oxygen	VDC copolymer	1.5×10^{-14}	3.5×10^{-7}
Carbon dioxide	Acrylonitrile copolymer	1.0×10^{-13}	1.6×10^{-6}
Carbon dioxide	Poly(vinyl chloride)	8.9×10^{-13}	3.4×10^{-6}
Carbon dioxide	VDC copolymer	1.4×10^{-14}	1.1×10^{-6}
<i>d</i> -Limonene	High density polyethylene	7.0×10^{-14}	0.3
<i>d</i> -Limonene	VDC copolymer	3.0×10^{-18}	0.6
Methyl salicylate	Nylon-6	2.1×10^{-17}	0.9
Methyl salicylate	VDC copolymer	5.8×10^{-16}	0.3

^aRef. 95.

Table 12. Transport of *trans*-2-Hexenal in Barrier Films at 75°C

Film	Condition	Permeability P , MZU ^a	Diffusivity D , m ² /s
VDC copolymer ^b	Dry	4500	4.4×10^{-15}
VDC copolymer	90/0 ^c	4100	3.9×10^{-15}
EVOH ^d	dry	2300	1.6×10^{-14}
EVOH	90/0 ^c	98,000	7.2×10^{-13}

^aTo convert MZU (10^{-20} kg·m)/(m²·s·Pa) to nmol/(m·s·GPa), divide by 9.8.

^bDow experimental resin XU32024.13.

^c90% RH on the upstream side, 0% RH on the downstream side.

^d44 mol% ethylene.

temperatures. Table 11 compares the D and S of large and small molecules in several polymers. A low D and a high S may mean that the principal mechanism for flavor loss is its being lost into the package wall (also known as scalping).

Humidity does not affect the permeability, diffusion coefficient, or solubility coefficient of F/A/S molecules in VDC copolymers. Studies using *trans*-2-hexenal and *d*-limonene are compared in Table 12. The transport in an EVOH copolymer is strongly plasticized by humidity.

Table 13. Examples of Permeation of Flavor and Aroma Compounds in Selected Polymers^a at 25°C^b, Dry^c

Flavor/aroma compound	Permeability P , MZU ^d	Diffusivity D , m ² /s	Solubility S , kg/(m ³ ·Pa)
<i>Vinylidene chloride copolymer</i>			
Ethyl hexanoate [123-66-0] (C ₈ H ₁₆ O ₂)	570	8.0×10^{-18}	0.71
Ethyl 2-methylbutyrate [7452-79-1] (C ₇ H ₁₄ O ₂)	3.2	1.9×10^{-17}	1.7×10^{-3}
<i>d</i> -Limonene [5989-27-5] (C ₁₀ H ₁₆)	32	3.3×10^{-17}	9.7×10^{-2}
<i>Ethylene-vinyl alcohol copolymer</i>			
Ethyl hexanoate	0.41	3.2×10^{-18}	1.3×10^{-3}
Ethyl 2-methylbutyrate	0.30	6.7×10^{-18}	4.7×10^{-4}
<i>d</i> -Limonene	0.5	1.1×10^{-17}	4.5×10^{-4}
<i>Low density polyethylene</i>			
Ethyl hexanoate	4.1×10^6	5.2×10^{-13}	7.8×10^{-2}
Ethyl 2-methylbutyrate	4.9×10^5	2.4×10^{-13}	2.3×10^{-2}
<i>d</i> -Limonene	4.3×10^6	—	—
<i>High density polyethylene</i>			
<i>d</i> -Limonene	3.5×10^6	1.7×10^{-13}	2.5×10^{-1}
<i>Polypropylene</i>			
Ethyl hexanoate	8.7×10^4	3.1×10^{-15}	2.8×10^{-1}
<i>d</i> -Limonene	1.6×10^4	7.4×10^{-16}	2.1×10^{-1}

^aRefs. 96–100.

^bValues for VDC copolymer and EVOH copolymer are extrapolated from higher temperatures.

^cPermeation in the VDC copolymer and the polyolefins is not affected by humidity; the permeability and diffusion coefficient in the EVOH copolymer can be as much as 1000 times greater with high humidity.

^dTo convert MZU (10^{-20} kg·m)/(m²·s·Pa) to nmol/(m·s·GPa), divide by molecular weight of permeant/10.

Table 13 contains some representative data for the permeation of F/A/S molecules. VDC copolymers are good barriers to the migration of F/A/S molecules. Dry EVOH copolymers are also good barriers to the migration of F/A/S molecules. However, polyolefins are not good barriers to F/A/S molecules. The fact that most glassy polymers are good barriers to the migration of F/A/S molecules is not shown in this table.

Degradation Chemistry. Vinylidene chloride polymers are highly resistant to oxidation, permeation of small molecules, and biodegradation, which makes them extremely durable under most use conditions. However, these materials are thermally unstable and, when heated above about 120°C, undergo degradative dehydrochlorination. Furthermore, the homopolymer degrades with rapid evolution of hydrogen chloride within a few degrees of its melting temperature (200°C). For this reason, the superior characteristics of the homopolymer cannot be exploited. As a consequence, the copolymers of VDC with vinyl chloride, alkyl acrylates or methacrylates, acrylonitrile or methacrylonitrile, rather than the homopolymer, have come to commercial prominence. Such copolymers have often served as substrates for a study of the degradation reaction (101–104).

The thermal degradation of VDC copolymers occurs in two distinct steps. The first involves degradative dehydrochlorination via a chain process to generate poly(chloroacetylene) sequences (103,105). Subsequent Diels–Alder-type condensation between conjugated sequences affords a highly cross-linked network, which, upon further dehydrochlorination, leads to the formation of a large-surface-area, highly absorptive carbon (1,106). The initial dehydrochlorination occurs at moderate temperatures and is a typical chain process involving distinct initiation, propagation, and termination phases (107,108). Initiation is thought to occur via carbon–chlorine bond scission promoted by a defect structure within the polymer. An effective defect site in these polymers is unsaturation (105). Introduction of a random double bond produces an allylic dichloromethylene unit activated for carbon–chlorine bond scission. Initiation by the thermally induced cleavage of this bond, followed by propagation by successive dehydrochlorination along the chain, ie, the so-called unzipping reaction, can then proceed readily (Fig. 5).

The thermal stability of these polymers is decreased by pretreatment with uv irradiation (109), electron-beam irradiation (110), and basic solvents or reagents (111,112); by an atmosphere of oxygen (109,113–116) or nitric oxide (109); and by the presence of peroxide linkages within the polymer (113,117), residues of emulsifying agents (113), organometallic initiator residues (113), ash from a previous decomposition (113), peroxide initiator residues (109–113,117–120), or metal ions (121). All the foregoing are sufficient to introduce random double bonds into the polymer structure. This can be demonstrated by examination of the treated sample by uv and ir spectroscopic methods (110). Prolonged treatment of the polymer with basic reagents leads to more extensive dehydrohalogenation (121–126). In fact, electrolysis of a solution of tetra(*n*-butyl)ammonium perchlorate in *N,N*-dimethylformamide generates a basic medium, presumably containing the formamide radical anion, capable of degrading the polymer (127). High energy radiation from a variety of sources may induce damage of several kinds, including carbon–carbon bond cleavage (109). A prominent radiation-induced process is carbon–chlorine bond scission followed by elimination of hydrogen chloride

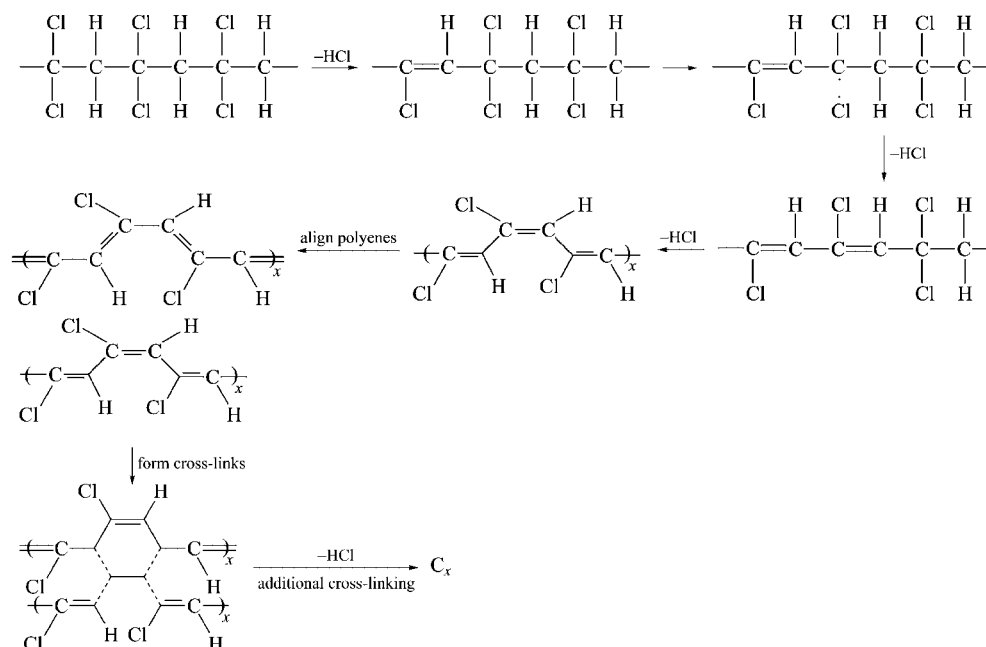
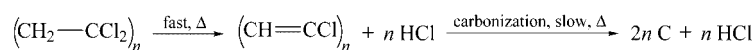


Fig. 5. Schematic of the degradation of PVDC to carbon.

(128,129). Property changes other than a decrease in thermal stability may arise as a consequence of high energy irradiation (130,131).

The principal steps in the thermal degradation of VDC polymers are formation of a conjugated polyene sequence followed by carbonization.



On being heated, the polymer gradually changes color from yellow to brown and finally to black. Early in the reaction, the polymer becomes insoluble, which indicates that cross-linking has occurred. The temperature of melting decreases, and the presence of unsaturation may be detected by spectroscopic (uv, ir, nmr) methods. The polymer eventually becomes infusible, and the crystal structure as detected by x-ray diffraction disappears even though the gross morphology is retained (132). The presence of carbon radicals can be detected by electron spin resonance (esr) measurements. If the temperature is raised substantially above 200°C , aromatic structures are formed. Finally, at very high temperatures ($>700^\circ\text{C}$), complete carbonization occurs.

The first of these reactions, ie, the loss of the first mole of hydrogen chloride, has had the greatest impact on the end use of VDC polymers and has been the most studied and well characterized. The propensity of these polymers to undergo degradation is influenced by a wide variety of factors, including physical changes in the solid (annealing effects) and the method of preparation and purity of the polymer. The most stable polymers are those produced by bulk polymerization at low temperature with the use of a nonoxygen initiator. In general, the stability of

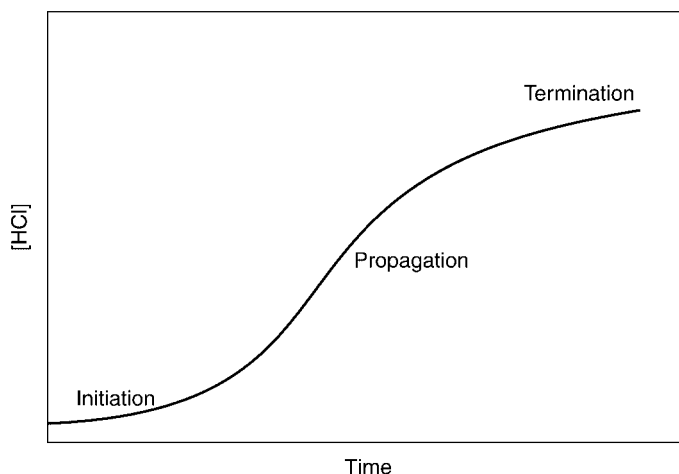


Fig. 6. Hydrogen chloride evolution for the thermal degradation of a typical VDC polymer.

the polymer reflects the method of preparation, with bulk > solution > suspension \gg emulsion (133). In the absence of elevated temperatures, suspending agents, polar solvents, redox initiators, etc, a more perfect polymer structure is formed, ie, one containing a minimum level of unsaturation.

The impact of a less defective structure may be seen in Figure 6, which depicts hydrogen chloride evolution for the thermal degradation of a typical VDC polymer. Initiation of degradation occurs at activated allylic sites within the polymer, but initiation does not occur simultaneously at all sites. Therefore, early in the reaction, hydrogen chloride evolution increases as a function of time as initiation occurs at more and more sites. In other words, unzipping is started in an increasing number of chain segments. This gives rise to the acceleratory induction period characteristic of VDC copolymer degradation. When a greater number of initiation sites are present within the polymer, ie, at higher levels of unsaturation, the rate of hydrogen chloride evolution during the initiation phase of the degradation is greater. After unzipping has begun in all chains containing defect structures, hydrogen chloride production is essentially first order until termination by completion or other means becomes a prominent reaction. Undoubtedly, some random double-bond initiation continues to occur during propagation. However, during this period termination is roughly in balance with initiation. As the rate of termination significantly exceeds that of initiation, deceleration of degradation is observed (105,108,109). An accurate representation of the dehydrochlorination reaction over the entire range of degradation may be achieved using a kinetic expression containing two constants (107,134).

Since the low temperature degradation, ie, that which occurs at process temperatures, involves only dehydrochlorination of VDC sequences, mass loss reflecting evolution of hydrogen chloride provides a convenient means of monitoring polymer decomposition. Thus, thermogravimetry analysis (tga) is an appropriate method for assessing the degradation characteristics of VDC polymers (135,136). Rate constants may be obtained as the slopes of the appropriate linear portions of a plot of $\ln[w_\infty - w_0]/(w_\infty - w_t)$ versus time. The variable w_∞ is the weight of

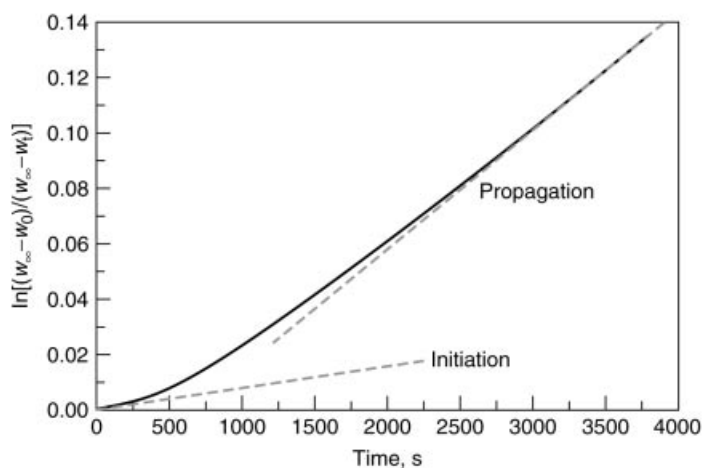


Fig. 7. Thermal degradation of a typical VDC polymer.

the sample at infinite time (t_∞) taken as that weight which would remain after 37.62% of the initial VDC component weight (corresponding to the complete loss of 1 mole of hydrogen chloride per VDC unit in the copolymer). The variable w_0 is the weight at time zero (t_0), ie, the time at which the first point was recorded, and w_t is the weight at any time t during the run. This is illustrated for a typical VDC polymer in Figure 7.

Initiation rate constants (k_i) for the degradation may be obtained by least-squares analysis of the linear segment of the early portion of this plot. Propagation rate constants (k_p) may be obtained in a similar manner from data obtained later in the run when propagation has become the dominant reaction. This is illustrated in Figures 8 and 9. Table 14 shows the rate constants obtained in this manner for the degradation of VDC/butyl acrylate copolymers.

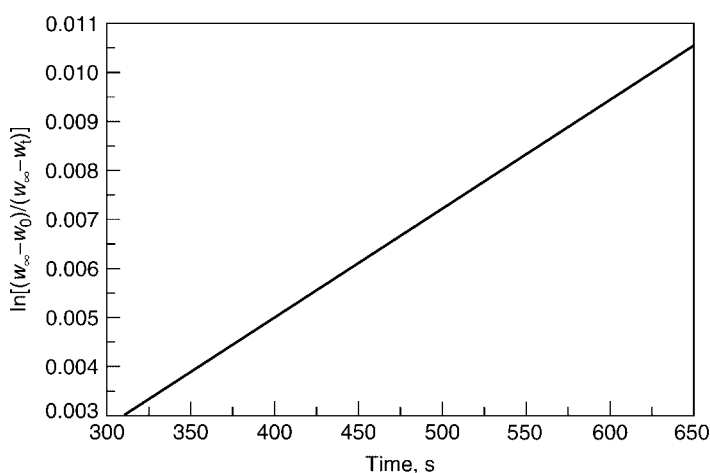


Fig. 8. Initiation rate constant (k_i) for the thermal degradation of a typical VDC polymer.

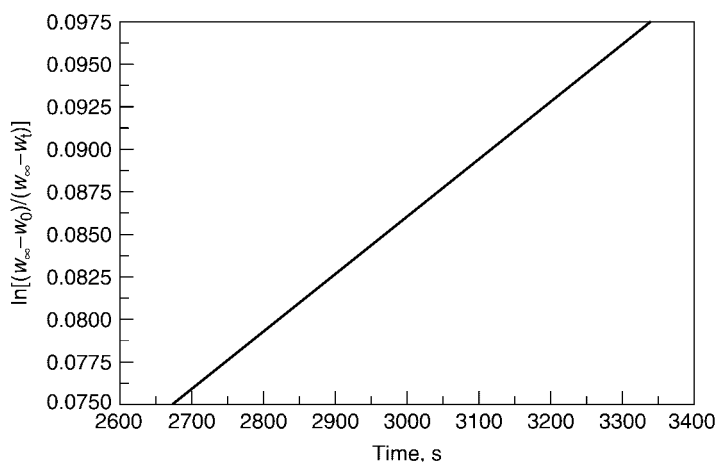


Fig. 9. Propagation rate constant (k_p) for the thermal degradation of a typical VDC polymer.

Much evidence has been accumulated to establish the radical nature of the degradation reaction (1). Prominent components of this include slight inhibition of the reaction by certain radical scavengers and changes in the esr spectrum of a sample undergoing degradation (137,138). Both suggest that radical intermediates are generated during the degradation. The exact nature of the chain-carrying species is made more apparent from the results of degradation in bibenzyl solution (103,105). Bibenzyl is an efficient radical scavenger that is converted to stilbene on interaction with a radical. Stilbene can be readily quantitated by gas-liquid partition chromatography. For the degradation of typical VDC polymers, the ratio of hydrogen chloride evolved to stilbene produced is approximately 35:1 (103,105). This is in sharp contrast to the 2:1 ratio expected for trapping of chlorine atoms with perfect efficiency and suggests that the propagating species is a radical pair that does not dissociate appreciably. Thus propagation most probably occurs by a radical chain process in which the chain-carrying species is a radical pair that decomposes to alkene and hydrogen chloride without dissociation.

Table 14. Rate Constants for the Thermal Degradation of Vinylidene Chloride/Butyl Acrylate Copolymers at 180°C

Butyl acrylate, wt% ^a	k_i , 10^{-5} s^{-1b}	k_p , 10^{-5} s^{-1b}
0	3.02 ± 0.09	8.75 ± 0.14
4	4.48 ± 0.004	8.34 ± 0.28
8	2.83 ± 0.25	6.73 ± 0.01
12	2.76 ± 0.03	5.35 ± 0.18
18	2.45 ± 0.25	4.08 ± 0.05
20	2.21 ± 0.005	3.74 ± 0.33

^aWeight percent of monomer loaded.

^bAverages of at least two determinations.

To some extent, the stability of VDC polymers is dependent on the nature of the comonomer present. Copolymers with acrylates degrade slowly (139,140). Apparent degradation propagation rates decrease somewhat as the acrylate content of the copolymer increases (139). The polyene sequences generated by dehydrochlorination are limited in size by the level of acrylate incorporation; that is, the acrylate molecules act as stopper units for the unzipping reaction. The impact of this chain-stopping is that the termination rate for higher acrylate content polymers is greater than for those containing smaller amounts of acrylate. Therefore, initiation and termination rates are in balance for a shorter portion of the overall reaction period. Despite the suggestion that the presence of a hydrogen-rich pendant might serve as a source of hydrogen atoms to disrupt degradation propagation (113), there is no apparent relationship between the degradation rate and the size of the alkyl portion of the acrylate comonomer (140,141).

Copolymers with AN or MA undergo degradation more readily. In addition, the degradation is more complex than that observed for acrylate copolymers. Acrylonitrile copolymers release hydrogen cyanide as well as hydrogen chloride; products of thermal degradation of MA copolymers contain methyl chloride in addition to hydrogen chloride (102,104,142,143). In both cases, degradation apparently begins in VDC units adjacent to comonomer units (142,143).

The degradation of VDC polymers in nonpolar solvents is comparable to degradation in the solid state (103,138,144,145). However, these polymers are unstable in many polar solvents (146). The rate of dehydrochlorination increases markedly with solvent polarity. In strongly polar aprotic solvents, eg, hexamethylphosphoramide, dehydrochlorination proceeds readily (144,147). This reaction is clearly unlike thermal degradation and may well involve the generation of ionic species as intermediates.

Polymers of high VDC content are reactive toward strong bases to yield elimination products and toward nucleophiles to yield substitution products. Agents capable of functioning as both a base and a nucleophile react with these polymers to generate a mixture of products (124,148–151). Weakly basic agents such as ammonia, amines, or polar aprotic solvents accelerate the decomposition of VDC copolymers. Amines function as bases to remove hydrogen chloride and introduce unsaturation along the polymer mainchain which may serve as initiation sites for thermal degradation. The overall effectiveness of a particular amine for dehydrohalogenation may be dependent on several factors, including inherent basicity, degree of steric hindrance at nitrogen, and compatibility with the polymer (152–154). Phosphines are more nucleophilic but less basic than amines. However, phosphines also promote dehydrohalogenation rather than displacement of allylic chlorine (155).

Amines can also swell the polymer, leading to very rapid reactions. Pyridine, for example, would be a fairly good solvent for a VDC copolymer if it did not attack the polymer chemically. However, when pyridine is part of a solvent mixture that does not dissolve the polymer, pyridine does not penetrate into the polymer phase (111). Studies of single crystals indicate that pyridine removes hydrogen chloride only from the surface. Kinetic studies and product characterizations suggest that the reaction of two units in each chain-fold can easily take place; further reaction is greatly retarded either by the inability of pyridine to diffuse into the crystal or by steric factors.

Aqueous bases or nucleophiles have little impact on VDC polymers, primarily because the polymer is not wetted or swollen by water. However, these polymers do slowly degrade in hot concentrated aqueous sodium hydroxide solution (121).

Lewis acids, particularly transition-metal salts, strongly promote the thermal degradation of VDC polymers (121,138,156–166,166,167). The rate of initiation of degradation is greatly enhanced in the presence of metal ions (159). The metal ion (or other Lewis acid) coordinates chlorine atoms, making them much better leaving groups. This facilitates the introduction of initial double bonds, which act as defect sites from which degradative dehydrohalogenation may propagate. Care must be taken to avoid metal ions, particularly precursors of iron chloride, during the preparation and processing of VDC polymers.

Copolymers of VDC that are free of impurities do not degrade at an appreciable rate in the absence of light below 100°C. However, when exposed to uv light, these polymers discolor (168). Again, the primary reaction seems to be dehydrochlorination. Hydrogen chloride is evolved and cross-linking occurs (109). Polyene sequences of narrow sequence length distribution are often formed (169–171). These function as initiation sites for subsequent thermal degradation (109). Laser-induced photochemistry may be used for the generation of polyene structures uncomplicated by cross-linking and graphitization (172,173). Laser-promoted dehydrohalogenation has some characteristics in common with the corresponding thermal process. Long-lived carbon radicals are formed, and the propagation of the dehydrochlorination reaction apparently proceeds via an allylic carbon radical, chlorine atom pair (173). Similar structures may be generated by chemical means (150,151,174). Other photodegradation processes, eg, hydroperoxide formation at the methylene groups, probably also occur but are less important for these polymers than is polyene formation (158).

Stabilization. The stabilization of VDC polymers toward degradation is a highly developed art and is responsible for the widespread commercial use of these materials. Although the mode of action is often not understood, some general principles of effective stabilization have been established (175). The ideal stabilizer system should

- (1) absorb or combine with evolved hydrogen chloride irreversibly under conditions of use, but not strip hydrogen chloride from the polymer chain;
- (2) act as a selective uv absorber;
- (3) contain a reactive dienophilic moiety capable of preventing discoloration by reacting with and disrupting the color-producing conjugated polymer sequences;
- (4) possess nucleophilicity sufficient for reaction with allylic dichloromethylene units;
- (5) possess antioxidant activity so as to prevent the formation of carbonyl groups and other chlorine-labilizing structures;
- (6) be able to scavenge chlorine atoms and other free radicals efficiently;
- (7) chelate metals, eg, iron, to prevent chlorine coordination and the formation of metal chlorides.

Acid acceptors are of two general types: alkaline-earth oxides and hydroxides (176) or salts of weak acids, such as barium or calcium fatty acid salts; and

epoxy compounds, such as epoxidized soybean oil or glycidyl ethers and esters. Epoxidized oils are less effective for the stabilization of VDC polymers than for other halogenated polymers (160). The function of these materials as plasticizers and processing lubricants is probably responsible for modest improvements in processing stability. Effective light stabilizers have a chemical structure which imparts exceptional conjugative stability and very good uv absorption properties. The principal compounds of commercial interest are derivatives of salicylic acid, resorcylic acid, benzophenone, and benzotriazole. The typical hindered amine light stabilizers cannot be used in this application since they are sufficiently basic so as to promote dehydrohalogenation. This introduces allylic dichloromethylene units into the polymer mainchain, which act as initiation sites for thermal degradation. Consequently, satisfactory processing of the polymer in the presence of these additives is not possible. Examples of dienophiles that have been used are maleic anhydride and N-substituted maleimides (177).

Antioxidants are generally of two types: those that react with a free radical to stop a radical chain, that is, to scavenge chlorine atoms or peroxy radicals; and those that reduce hydroperoxides to alcohols. Phenolic antioxidants, eg, 2,6-di-*tert*-butyl-4-methylphenol and substituted bisphenols, are of the first type. Because the chain-carrying species for the degradative dehydrochlorination is a tight chlorine atom, carbon radical pair that does not dissociate appreciably during the reaction, the effectiveness of these agents is limited (161). The second type is exemplified by organic sulfur compounds and organic phosphites. The phosphites, ethylenediaminetetraacetic acid [60-00-4] (EDTA), citric acid [77-92-9], and citrates, can chelate metals. The ability of organic phosphites to function as antioxidants and as chelating agents illustrates the dual role of many stabilizer compounds. It is common practice to use a combination of stabilizing compounds to achieve optimum results (168). In addition, stabilization packages usually contain lubricants and other processing aids that enhance the effectiveness of the stabilizing compounds. The presence of these agents is particularly important to minimize the shearing component of degradation during extrusion and other processing steps (163).

Metal carboxylates have been considered as nucleophilic agents capable of removing allylic chlorine and thereby affording stabilization (162). Typical PVC stabilizers, eg, tin, lead, cadmium, or zinc esters, actually promote the degradation of VDC polymers. The metal cations in these compounds are much too acidic to be used with VDC polymers. An effective carboxylate stabilizer must contain a metal cation sufficiently acidic to interact with allylic chlorine and to facilitate its displacement by the carboxylate anion, but at the same time not acidic enough to strip chlorine from the polymer mainchain (163,167). Copper(II) carboxylates may have the balance of cation acidity and anion reactivity required to function as effective stabilizers for VDC polymers. This is reflected in Figure 10, which illustrates increasing stability of a typical VDC copolymer as it is aged at 150°C in the presence of copper(II) formate.

Vinylidene chloride polymers containing stabilizing features have been prepared. More generally, these have been polymers containing comonomer units with functionality that can consume evolved hydrogen chloride such that good radical scavenging sites are exposed (164,165,178,179).

For example, copolymers containing 4-isopropylphenyl acrylate display greater thermal stability than do the corresponding polymers containing simple

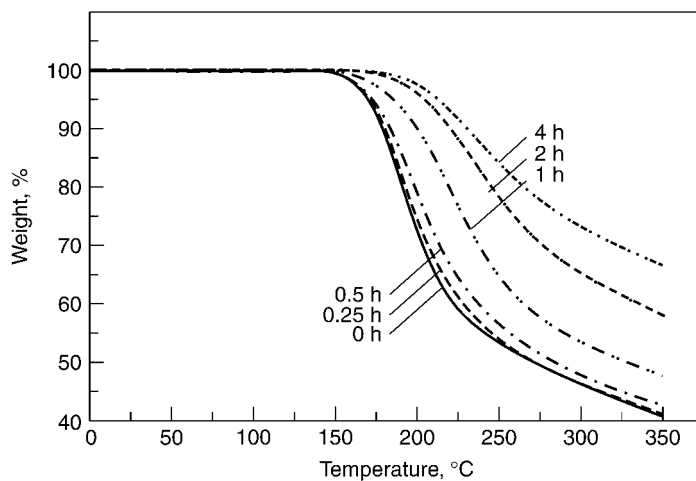


Fig. 10. Thermal degradation of a VDC/MPA (5 mol%) copolymer aged at 150°C in the presence of 5 wt% copper(II) formate for 0.25, 0.50, 1.0, 2.0, and 4.0 h.

alkyl acrylates as comonomer (164). This is illustrated in Figure 11. Stability of the copolymer increases as the level of the comonomer containing the *t*-cumyl group, capable of scavenging chlorine atoms, increases. A more quantitative reflection of this effect is provided by the rate constants displayed in Table 15. It may be noted that the magnitude of the initiation rate constant k_i decreases by a factor of 2 as the isopropylphenyl acrylate content of the polymer is increased from 0 to 5 mol%.

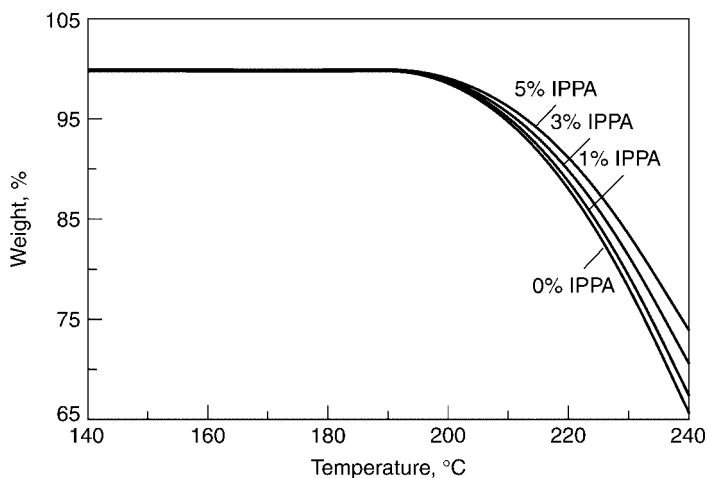


Fig. 11. Thermal degradation of vinylidene chloride/4-isopropylphenyl acrylate copolymers.

Table 15. Rate Constants for the Degradation of Vinylidene Chloride/4-Isopropylphenyl Acrylate Copolymers at 140°C

IPPA, mol%	$k_i, 10^{-7} \text{ s}^{-1a}$	$k_p, 10^{-7} \text{ s}^{-1a}$
0.0	3.02 ± 0.09	8.75 ± 0.14
1.0	4.48 ± 0.004	8.34 ± 0.28
3.0	2.83 ± 0.25	6.73 ± 0.01
5.0	2.76 ± 0.03	5.35 ± 0.18

^aAverages of at least two determinations; average deviation $\leq \pm 0.10$.

Commercial Methods of Polymerization and Processing

Processes that are essentially modifications of laboratory methods and that allow operation on a larger scale are used for commercial preparation of VDC polymers. The intended use dictates the polymer characteristics and, to some extent, the method of manufacture. Emulsion polymerization and suspension polymerization are the preferred industrial processes. Either process is carried out in a closed, stirred reactor, which should be glass-lined and jacketed for heating and cooling. The reactor must be purged of oxygen, and the water and monomer must be free of metallic impurities to prevent an adverse effect on the thermal stability of the polymer.

Emulsion Polymerization. Emulsion polymerization is used commercially to make VDC copolymers. In some applications, the resulting latex is used directly, usually with additional stabilizing ingredients, as a coating vehicle to apply the polymer to various substrates. In other applications, the polymer is first isolated from the latex before use. When the polymer is not used in latex form, the emulsion/coagulation process is chosen over alternative methods. The polymer is recovered in dry powder form, usually by coagulating the latex with an electrolyte, followed by washing and drying. The principal advantages of emulsion polymerization are twofold. First, high molecular weight polymers can be produced in reasonable reaction times, especially copolymers with VC. The initiation and propagation steps can be controlled more independently than in the suspension process. Second, monomer can be added during the polymerization to maintain copolymer composition control.

The disadvantages of emulsion polymerization result from the relatively high concentration of additives in the recipe. The water-soluble initiators, activators, and surface-active agents generally cause the polymer to have greater water sensitivity, poorer electrical properties, and poorer heat and light stability. These agents promote degradative dehydrochlorination during polymerization.

A typical recipe for batch emulsion polymerization is shown in Table 16. A reaction time of 7–8 h at 30°C is required for 95–98% conversion. A latex is produced with an average particle diameter of 100–150 nm. Other modifying ingredients may be present, eg, other colloidal protective agents such as gelatin or carboxymethylcellulose, initiator activators such as redox types, chelates, plasticizers, and stabilizers; and chain-transfer agents.

Commercial surfactants are generally anionic emulsifiers, alone or in combination with nonionic types. Representative anionic emulsifiers are the sodium

Table 16. Recipe for Batch Emulsion Polymerization^a

Ingredient	Parts by weight
Vinylidene chloride	78
Vinyl chloride	22
Water	180
Potassium peroxy sulfate	0.22
Sodium bisulfite	0.11
Aerosol MA, ^b 80 wt%	3.58
Nitric acid, 60 wt%	0.07

^aRef. 180.^bAerosol MA (American Cyanamid Co.) = dihexyl sodium sulfosuccinate.

alkylaryl sulfonates, the alkyl esters of sodium sulfosuccinic acid, and the sodium salts of fatty alcohol sulfates. Nonionic emulsifiers are of the ethoxylated alkylphenol type. Free-radical sources other than peroxy sulfates may be used, eg, hydrogen peroxide, organic hydroperoxides, peroxyborates, and peroxy carbonates. Many of these are used in redox pairs, in which an activator promotes the decomposition of the peroxy compound. Examples are peroxy sulfate or perchlorate activated with bisulfite, hydrogen peroxide with metallic ions, and organic hydroperoxides with sodium formaldehyde sulfoxylate. The use of activators causes the decomposition of the initiator to occur at lower reaction temperatures, which allows the preparation of a higher molecular weight polymer within reasonable reaction times. This is an advantage, particularly for copolymers of VDC with VC. Oil-soluble initiators are usually effective only when activated by water-soluble activators or reducing agents.

To ensure constant composition, the method of emulsion polymerization by continuous addition is employed. One or more components are metered continuously into the reaction. If the system is properly balanced, a steady state is reached in which a copolymer of uniform composition is produced (181). A process of this type can be used for the copolymerization of VDC with a variety of monomers. A flow diagram of the apparatus is shown in Figure 12; a typical recipe is shown in Table 17. The monomers are charged to the weigh tank A, which is kept under a nitrogen blanket. The emulsifiers, initiator, and part of the water are charged to tank B; the reducing agent and some water to tank C. The remaining water is charged to the reactor D, and the system is sealed and purged. The temperature is raised to 40°C and one tenth of the monomer and initiator charges is added, and then one tenth of the activator is pumped in. Once the reaction begins, as indicated by an exotherm and pressure drop, feeds of A, B, and C are started at programmed rates that begin slowly and gradually increase. The emulsion is maintained at a constant temperature during the run by cooling water that is pumped through the jacket. When all components are in the reactor and the exotherm begins to subside, a final addition of initiator and reducing agent completes the reaction.

Suspension Polymerization. Suspension polymerization of VDC is used commercially to make molding and extrusion resins. The principal advantage of the suspension process over the emulsion process is the use of fewer ingredients that might detract from the polymer properties. Stability is improved and water

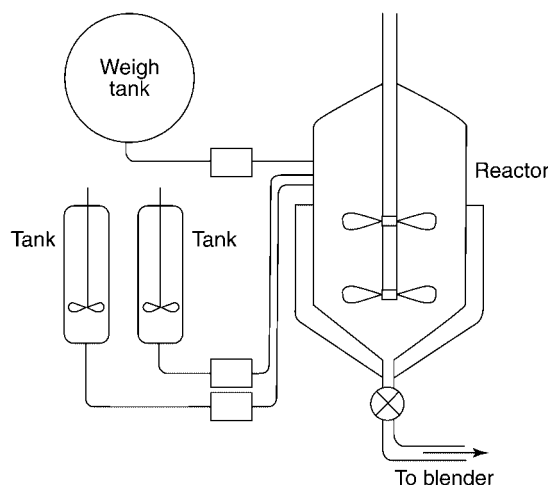


Fig. 12. Apparatus for continuous-addition emulsion polymerization of a VDC-acrylate mixture (181).

sensitivity is decreased. Extended reaction times and the difficult preparation of higher molecular weight polymers are disadvantages of the suspension process compared to the emulsion process, particularly for copolymers containing VC.

A typical recipe for suspension polymerization is shown in Table 18. At a reaction temperature of 60°C, the polymerization proceeds to 85–90% conversion in 30–60 h. Unreacted monomer is removed by vacuum stripping; then it is condensed and reused after processing. The polymer is obtained in the form of small [150–600 μm (30–100 mesh)] beads, which are dewatered by filtration or centrifugation and then dried in a flash dryer or fluid-bed dryer. Suspension polymerization involves monomer-soluble initiators, and polymerization occurs inside suspended monomer droplets, which form by the shearing action of the agitator and are prevented from coalescence by the protective colloid. It is important that the initiator be uniformly dissolved in the monomer before droplet formation. Unequal distri-

Table 17. Recipe for Emulsion Polymerization by Continuous Addition^a

Ingredient	Parts by weight
Vinylidene chloride	468
Comonomer	52
Emulsifiers	
Tergitol ^b NP 35	12
Sodium lauryl sulfate, 25 wt%	12
Initiator ammonium peroxydisulfate	10
Sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), 5 wt%	10
Water	436

^aRef. 181.

^bNonionic wetting agent produced by Union Carbide.

Table 18. Recipe for Suspension Polymerization^a

Ingredient	Parts by weight
Vinylidene chloride	85
Vinyl chloride	15
Deionized water	200
400 mPa·s (=cP) methyl hydroxypropylcellulose	0.05
Lauroyl peroxide	0.3

^aRef. 182.

bution of initiator causes some droplets to polymerize faster than others, leading to monomer diffusion from slow-polymerizing to fast-polymerizing droplets. The fast-polymerizing droplets form polymer beads that are dense, hard, glassy, and extremely difficult to fabricate because of their inability to accept stabilizers and plasticizers. Common protective colloids that prevent droplet coalescence and control particle size are PVC, gelatin, and methylcellulose. Organic peroxides, peroxycarbonates, and azo compounds are used as initiators for VDC suspension polymerization.

The batch-suspension process does not compensate for composition drift, whereas constant-composition processes have been designed for emulsion or suspension reactions. It is more difficult to design controlled-composition processes by suspension methods. In one approach (183), the less reactive component is removed continuously from the reaction to keep the unreacted monomer composition constant. This method has been used effectively in VDC–VC copolymerization, where the slower reacting component is volatile and can be released during the reaction to maintain constant pressure. In many other cases, no practical way is known for removing the slower reacting component.

Economic Aspects

Vinylidene chloride monomer is produced commercially in the United States by The Dow Chemical Co. and PPG Industries. The monomer is produced in Europe by Imperial Chemical Industries, Ltd. and Solvin. The monomer is produced in Japan by the Asahi Chemical Co., Kureha Chemical Industries, and Kanto Denka Kogyo Co. Commercial suppliers of VDC copolymers include The Dow Chemical Co. in the United States and Solvin in Europe. Asahi Chemical Co. and Kureha Chemical Industries are suppliers of VDC resins in Japan. Additional manufacturers of exclusively VDC latexes include W. R. Grace and Rohm & Haas in the United States, and Scott-Bader in Europe. Local suppliers of VDC resins have also been reported in Russia and the People's Republic of China.

Although Saran is a generic name for VDC copolymers in the United States, it is a Dow trademark in most foreign countries. Other trademarks include Daran (W. R. Grace) and Serfene (Rohm & Haas) in the United States; Diofan and Ixan (Solvin) and Polyidene (Scott-Bader) in Europe; and Kurehalon (Kureha) in Japan. In addition, B. F. Goodrich Chemicals (GEON) and Avecia (Haloflex) supply non-barrier VDC copolymers.

Applications

Melt Processing. Vinylidene chloride copolymers are melt processed via a variety of fabrication techniques. These include molding, monofilament fiber extrusion, monolayer blown film extrusion, multilayer cast- and blown-film extrusion, and multilayer sheet extrusion. There are a number of elements of melt processing and melt-processing equipment that are common to all of these fabrication techniques (184–187). These include proper equipment design and materials of construction, proper and accurately controlled operating conditions, and a properly formulated resin.

Because of their high crystalline melting point, VDC copolymers are generally melt fabricated near their thermal stability limits. Products of degradation are corrosive to equipment and given sufficient time will generate a char or carbon. Also, at temperatures of about 130°C and above, a number of metals, including iron, zinc, copper, and aluminum, catalyze the degradation of VDC resins. As a consequence the correct materials of construction are essential for melt processing VDC resins. High nickel alloys that are both corrosion resistant and do not catalyze resin degradation are preferred for all surfaces that are in direct contact with the polymer melt. For example, the extruder barrel liner may be made from Xaloy 306 or other high nickel, low iron containing alloy. Extruder screws may be made from Duranickel 301 with Colmonoy 56 flight lands. Other parts in direct contact with polymer melt should also be made out of Duranickel or similar material. Instruments such as melt thermocouples or pressure transducers could be Hastelloy C.

Degradation of VDC resins is a product of time at temperature. Both of these aspects should be controlled to optimize melt-processing performance. Extruders in the range of 18:1 to 24:1 length-to-diameter ratio are commonly used. Melt channels should be designed with a smooth flow pattern to minimize dead spots where polymer may degrade excessively or permit carbon buildup. The clearance between the screw tip and the extruder nosepiece should be minimized. Screen packs are also not recommended for melt-processing VDC resins. Proper instrumentation, including multiple melt thermocouples and pressure transducers, amperage or torque measurement for the extruder, and accurate screw speed measurement, is also critical.

Heat management is an important factor in melt-processing VDC resins. Screw design (188) and resin formulation combine to affect the amount of heat generated during melting and the eventual melt temperature. Vinylidene chloride polymer powders exhibit a relatively high level of frictional heating and also contain a large amount of entrained air (189). Screws are typically designed to be low work to minimize frictional and viscous heating. They must also be designed to eliminate air entrapment. Screws greater than 6.35-cm (2.5-in.) diameter for VDC resin processing also generally have two-zone cooling capability for further heat management.

Vinylidene chloride resins for melt processing are generally supplied formulated or unformulated. Formulated resins may be melt processed as supplied or with some additional additives. Unformulated resins require additives prior to melt processing. Processing additives for VDC resins include plasticizers, lubricants, and other process aids designed to control heat generation and residence

time in melt processing. Patent literature cites a wide variety of lubricants and processing aids, including acids, esters, amides, and metal salts of fatty acids; polyolefins or polyolefin waxes; and inorganic stabilizers such as magnesium hydroxide or tetrasodium pyrophosphate (190). Some of these processing aids are common to PVC melt processing as well. However, it should also be noted that some PVC melt-processing additives are incompatible with VDC resins and will actually degrade melt-processing performance.

Molding. Molded articles were among the earliest applications for VDC copolymers (184,191). Vinylidene chloride–vinyl chloride copolymers were originally developed for thermoplastic molding applications, and small amounts are still used for this purpose. When properly formulated with plasticizers and heat stabilizers, the resins can be fabricated by common methods, eg, injection, compression, or transfer molding. Conventional or dielectric heating can be used to melt the polymers. Rapid hardening is achieved by forming in heated molds to induce rapid crystallization. Cold molds result in supercooling of the polymer. Because the interior of the molded part remains soft and amorphous, the part cannot be easily removed from the mold without distortion. Mold temperatures of up to 100°C allow rapid removal of dimensionally stable parts. The range of molding temperatures is rather narrow because of the crystalline nature of the resin and thermal sensitivity. All crystallites must be melted to obtain low polymer melt viscosity, but prolonged or excessive heating must be avoided to prevent dehydrochlorination.

The metal parts of the injection molder, ie, the liner, torpedo, and nozzle, that contact the hot molten resin must be of the noncatalytic, corrosion-resistant type previously described. The injection mold need not be made of noncatalytic metals; any high grade tool steel may be used because the plastic cools in the mold and undergoes little decomposition. However, the mold requires good venting to allow the passage of small amounts of acid gas as well as air. Vents tend to become clogged by corrosion and must be cleaned periodically.

Molded parts of VDC copolymers are used to satisfy the industrial requirements of chemical resistance and extended service life. They are used in such items as gasoline filters, valves, pipe fittings, containers, and chemical process equipment. Complex articles are constructed from molded parts by welding; hot-air welding at 200–260°C is a suitable method. Molded parts have good physical properties but lower tensile strength than films or fibers, because crystallization is random in molded parts. Higher strength is developed by orientation in films and fibers. Physical properties of a typical molded VDC copolymer plastic are listed in Table 19.

Monofilament Fiber Extrusion. Monofilament fiber extrusion was another early application for VDC resins (184,191,193). Monofilament applications have included automotive seat covers, window screens, and upholstery fabrics, where the durability and ease of cleaning were important. Fabrics made from VDC copolymer monofilaments are still used today in applications such as filter fabrics, light screens, greenhouse covers, pool or bath fabrics, and shoe insoles (194). Such fabrics claim excellent resistance to flame, chemicals, uv light, moisture, and microbial attack.

Vinylidene chloride copolymer monofilaments typically range from 0.15- to 1.5-mm (0.006- to 0.06-in.) diameter. To produce these monofilaments, a molten

Table 19. Properties of Resin for Injection-Molding Applications^a

Typical resin properties	Test method	Value
Ultimate tensile strength, MPa ^b	ASTM D638	24.1–34.5
Yield tensile strength, MPa ^b	ASTM D638	19.3–26.2
Ultimate elongation, %	ASTM D638	160–240
Modulus of elasticity in tension, MPa ^b		345–552
Izod impact strength, J/m ^c of notch	ASTM D256	21.35–53.38
Density, g/cm ³	ASTM D792	1.65–1.72
Hardness, Rockwell M	ASTM D785	50–65
Water absorption, % in 24 h	ASTM D570	0.1
Mold shrinkage, cm/cm (injection-molded)	ASTM D955	0.005–0.025
Limiting oxygen index, %	ASTM D2863	60.0 ^d
UL-94	UL-94 Test	V-O ^d

^aRef. 191.^bTo convert MPa to psi, multiply by 145.^cTo convert J/m to ft-lbf/in. of notch, divide by 53.38.^dThe results of small-scale flammability tests are not intended to reflect the hazards of this or any other material under actual fire conditions.

VDC copolymer extrudate is quenched to about room temperature in a supercooling tank to produce an amorphous polymer strand (184,191,193). This strand is then wrapped several times around smooth take-off rolls, and then wrapped several times around orienting rolls, which operate at a higher speed than the take-off rolls. The difference in roll speeds produces mechanical stretching, orienting the filament along the longitudinal axis while the polymer is crystallizing. A typical stretch ratio for this process is about 400%. The orientation process increases the fiber strength from about 55 MPa (8000 psi) to as high as 414 MPa (60,000 psi). Much of the increased tensile strength is obtained as the stretch ratio approaches 400%. Heat treatment may be used during or after stretching to affect the degree of crystallization and control the physical properties of the oriented filaments.

Monolayer Blown-Film Extrusion. One of the major applications for VDC resins is monolayer film produced via a blown-film extrusion process. Previously, VDC copolymer film extrusion was limited to just a few experts in the field. However, over the last several years, production of VDC-containing films has greatly expanded (195,196). Monolayer VDC copolymer blown-film lines are now commercially available from a number of manufacturers and a considerable number of lines have been recently installed around the world, particularly in the People's Republic of China.

Figure 13 illustrates a monolayer blown-film process for VDC resin. In this process (185,197–200) a tube of molten VDC resin is extruded downward and is immediately quenched in a cold-water supercooling bath. This bath cools the polymer melt to create a leathery polymer tube which is essentially amorphous VDC copolymer. The low temperature of the bath also controls nucleation of the crystallites and thus impacts the subsequent film-formation processes. After the supercooling bath, the amorphous tube is passed through a warming or reheat bath. This bath increases the resin temperature, which in turn will make the film more pliable and increase the rate of crystallization propagation during the

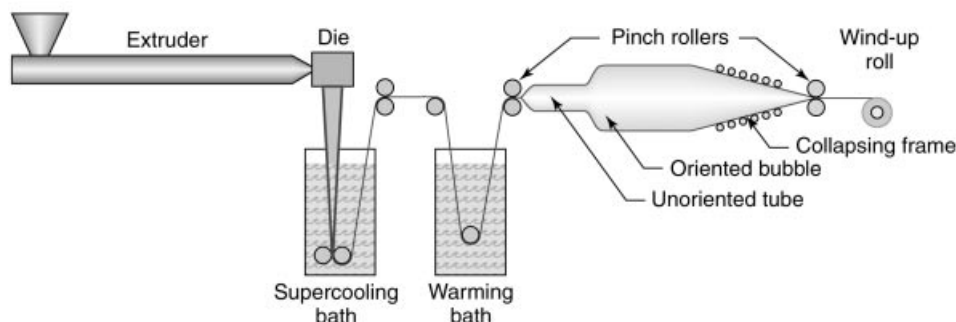


Fig. 13. Monolayer blown-film process for VDC resins (196).

subsequent film-blowing process. Exiting the warming bath, the tube passes through two sets of pinch rolls, which are arranged so that the second set of rolls travels faster than the first set. Between the two sets, air is injected into the tube to create a bubble that is entrapped by the pinch rolls. The entrapped air bubble remains stationary while the extruded tube is oriented as it passes around the bubble. In this manner, orientation is produced simultaneously in both the transverse and the longitudinal directions.

As the tube expands and orients, the amorphous polymer begins to crystallize rapidly, eventually limiting the diameter of the bubble. Adding additional air to the bubble at this point will only lengthen the bubble but will not change its overall diameter. Crystallization rate and thus bubble diameter or "blow up ratio" is controlled by a number of factors, including temperatures of the supercooling and warming baths, room temperature, polymer composition, and amount and type of plasticizer additives. These parameters as well as variables such as extrusion rate, die diameter, die gap, and drawdown ratio are combined to make a wide variety of film types and sizes. Films produced via this process generally have some shrink properties, which in many cases are advantageous. Where shrink is not desirable, films can be preshrunk via controlled heat application prior to the winding process.

Monolayer blown-film processes generally use a VDC-VC copolymer. Such resins have the combination of performance properties and optimum crystallization rate necessary for this process. Resins are generally formulated with plasticizers, lubricants, and other additives to affect performance during the extrusion process as well as in the final film applications.

Applications for VDC copolymer monolayer films fall into three major categories: household wrap, food and medical packaging, and industrial films. Food packaging includes packaging of processed meats, cheese and other dairy products, and bakery goods. Packaging types include film overwraps, shrinkable films, chub packaging, and unit packaging. Performance attributes of VDC copolymer films that are important to these applications include high barrier to oxygen, water, and other permeating molecules; clarity; resistance to fats and oils; dimensional stability; ability to be sealed and printed; and ability to withstand retort and microwave oven temperatures. Typical film properties are shown in Table 20.

Table 20. Physical Properties of PVDC Copolymer Films^a

Properties ^b	Overwrap film	Chub packaging film A	Chub packaging film B	Unit packaging film A	Unit packaging film B	High barrier packaging film	Test methods
Average thickness, μm^c	15	25	25	51	152	25	—
Yield, m^2 film/kg resin ^d	38	23	23	12	4	23	Calculated
Water vapor transmission rate at 90% RH and 38°C, $\text{nmol}/(\text{m}\cdot\text{s})^e$	0.09	0.09	0.1	0.06	0.06	0.01	Permatran W
Oxygen transmission at 100% RH and 23°C, $\text{nmol}/(\text{m}\cdot\text{s}\cdot\text{GPa})^f$	2.6	2.6	3.8	2.9	2.9	0.16	ASTM D3985-81
Ultimate tensile strength, MPa^g							ASTM D882-81
MD	76	97	83	111	111	83	
TD	124	138	117	133	95	128	
Ultimate elongation, %							ASTM D882-81
MD	75	90	90	95	80	100	
TD	55	60	75	80	70	50	
2% secant modulus, MPa^g							ASTM D882-81
MD	690	690	607	690	655	1103	
TD	621	593	530	615	615	965	
Unrestrained shrink, 10 min at 100°C in air, %							ASTM D1204
MD	16	16	20	8	12	6	
TD	9	9	11	4	7	4	
Haze, %	1	5	5	3	3	2.5	ASTM D1003-61 (77)
45° gloss	115	92	90	105	105	110	ASTM D2457-60 (77)
Clarity, %	86	65	52	73	73	80	ASTM D1746-70 (78)
Film block, unconditioned, g	114	—	—	—	—	—	ASTM D3354-89
Film cling, unstretched, g	65	—	—	—	—	—	ASTM D4649-87
Kinetic coefficient of friction, film-to-metal	—	0.29	0.30	0.30	0.30	—	ASTM D1894

^aRef. 201.^bMD is machine direction; TD is transverse direction.^cTo convert μm to mil, divide by 25.6.^dTo convert m^2 film/kg resin to in^2 film/lb resin, multiply by 704.^eTo convert $\text{nmol}/(\text{m}\cdot\text{s})$ to $(\text{g}\cdot\text{mil})/(\text{100 in}^2\cdot\text{d})$, multiply by 4.^fTo convert $\text{nmol}/(\text{m}\cdot\text{s}\cdot\text{GPa})$ to $(\text{cc}\cdot\text{mil})/(\text{100 in}^2\cdot\text{d}\cdot\text{atm})$, divide by 2.^gTo convert MPa to psi, multiply by 145.

Multilayer Cast- and Blown-Film Extrusion. A significant application for VDC copolymer resins is in the construction of multilayer film and sheet (202,203). This permits the design of a packaging material with a combination of properties not obtainable in any single material. A VDC copolymer layer is incorporated into multilayer film for perishable food packaging because it provides a barrier to oxygen. A special high barrier resin is supplied specifically for this application. Typically, multilayer packaging films contain outer layers of a tough, low cost polymer such as high density or linear low density polyethylene with VDC copolymer as the core layer. Cast and blown films are produced on conventional film lines with one extruder and die designed to handle the heat-sensitive nature of VDC resin. The properties of a 0.05-mm (39-mil) multilayer cast film are listed in Table 21.

Multilayer films are produced by both cast- and blown-film coextrusion. One of the key enabling technologies in the manufacture of these multilayer films has been preencapsulation of the VDC resin (205). Preencapsulation means that the VDC resin extrudate is completely encapsulated with a more thermally stable polymer, such as an ethylene–vinyl acetate copolymer, prior to entering the coextrusion die. Using this technique, the VDC resin is not directly exposed to the

Table 21. Physical Properties^a of a Multilayer Barrier Film^b and a Polyethylene Film^c

Property ^d	Multilayer film	Polyethylene film	Test method
Yield tensile strength, MPa ^e			ASTM D882-61T
MD	14	12.1	
TD	13	9.7	
Ultimate tensile strength, MPa ^e			ASTM D882-61T
MD	24	20.0	
TD	17	17	
Tensile modulus, MPa ^e			ASTM D882-61T
MD	170	180	
TD	150	180	
Elongation, %			ASTM D882-61T
MD	400	325	
TD	400	550	
Elmendorf tear strength, g			ASTM D1922
MD	800	325	
TD	650	250	
Gas transmission at 24°C, nmol/(m ² ·s·GPa) ^f			ASTM D1434-63
Oxygen	6.6 × 10 ⁴	1.6 × 10 ⁷	
Carbon dioxide	11.1 × 10 ⁴	10.0 × 10 ⁷	
Nitrogen	0.8 × 10 ⁴	0.8 × 10 ⁷	
Water vapor transmission at 95% RH and 38°C, nmol/(m·s) ^g	2000	6400	ASTM E96-63T

^aRefs. 202 and 204.

^b0.05-mm total thickness with layers of polyethylene, adhesive, and vinylidene chloride copolymer.

^c0.05-mm polyethylene, 0.921 g/cm³ density.

^dMD is machine direction; TD is transverse direction.

^eTo convert MPa to psi, multiply by 145.

^fTo convert nmol/(m²·s·GPa) to cm³/(100 in.²·d·atm), divide by 7.9 × 10⁴.

^gTo convert nmol/(m·s) to g/(100 in.²·d), divide by 1 × 10⁴.

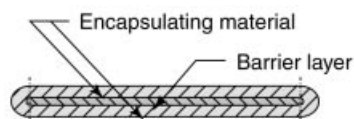


Fig. 14. Multilayer cast film showing a VDC copolymer barrier layer surrounded by a less thermally sensitive encapsulating material, such as ethylene–vinyl acetate (205). The edges are trimmed.

large surface area of the multilayer extrusion die, eliminating a greater potential for carbon formation and subsequent problems. Upon entering the die the encapsulated VDC resin is combined with other polymer layers, including tie and skin layers, to create the multilayer film.

The application of encapsulation technology to flat dies and cast film coextrusion is fairly easy to envision. As shown in Figure 14, the encapsulating material completely surrounds the VDC resin. When the edges are trimmed, a flat film with a continuous barrier layer is produced.

Blown-film coextrusion presents the added difficulty of obtaining a continuous barrier layer. A die with a crosshead mandrel is preferred over a die with a spiral mandrel, because the spiral mandrel tends to lead to long residence time in the spirals. A standard crosshead mandrel, however, results in a weld line where the barrier layer is not continuous. As shown in Figure 15, this problem is solved by providing an overlap of the barrier layer at the weld line (206). Although the barrier layer is not continuous across the weld line, sufficient overlap will create a tortuous path for permeation, and the barrier properties will be maintained.

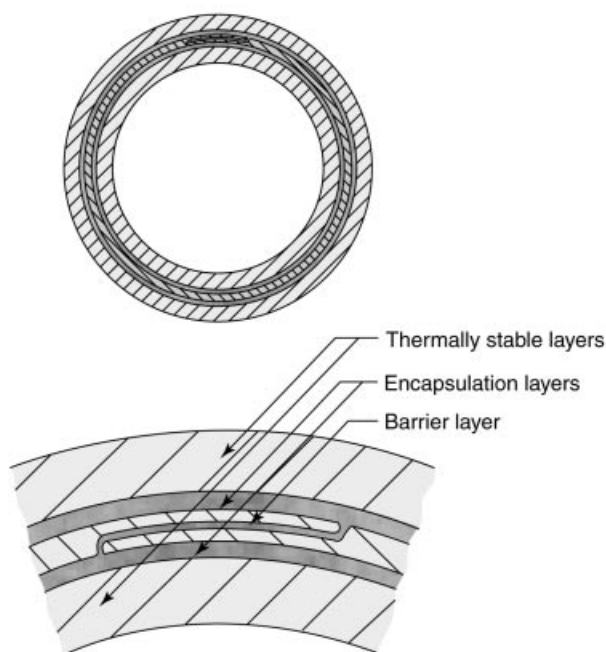


Fig. 15. Multilayer blown film with enlarged view showing overlap of barrier layer (206).

across the weld. This technology has only been recently applied to large blown-film dies. Five- to seven-layer blown-film dies up to 51-cm (20-in.) diameter have been demonstrated using this technology (207–210). These new blown-film dies also incorporate temperature isolation techniques that allow VDC resins to be co-extruded with resins such as nylon that require much higher melt temperatures. Similar to the monolayer films, multilayer films are used predominately in food packaging and medical applications.

Multilayer Sheet Extrusion. Rigid containers for food packaging can be made from coextruded sheet that contains a layer of a barrier polymer (211–213). A simple example is a sheet with five layers that has a total thickness of about 1.3 mm (50 mil). The outermost layers might be polypropylene, polyethylene, polystyrene, high impact polystyrene (HIPS), or other nonbarrier polymer having good mechanical properties. The innermost barrier layer is about 125 μm (5 mil) of a VDC copolymer. Adhesive layers connect the outer layers and the barrier layer. This coextruded sheet can be formed into containers by any of several techniques, including solid-phase pressure forming and melt-phase forming. The final container has a total wall thickness of about 500 μm (20 mil) and a barrier layer that is about 50 μm (2 mil) thick. Such a container is capable of protecting oxygen-sensitive foods at ambient temperatures for a year or more. These containers are lightweight, microwavable, nonbreakable, and attractive. More sophisticated containers may have more than five layers and improved economics by including a layer of scrap or recycled polymers in the structure.

Lacquer Resins. Vinylidene chloride copolymers have several properties that are valuable in the coatings industry: excellent resistance to gas and moisture vapor transmission, good resistance to attack by solvents and by fats and oils, high strength, and the ability to be heat-sealed (214,215). These characteristics result from the highly crystalline nature of the very high VDC content of the polymer, which ranges from ~80 to 90 wt%. Minor constituents in these copolymers generally are vinyl chloride, alkyl acrylates, alkyl methacrylates, acrylonitrile, methacrylonitrile, and vinyl acetate. Small concentrations of vinylcarboxylic acids, eg, acrylic acid, methacrylic acid, or itaconic acid, are sometimes included to enhance adhesion of the polymer to the substrate. The ability to crystallize and the extent of crystallization are reduced with increasing concentration of the comonomers; some commercial polymers do not crystallize. The most common lacquer resins are terpolymers of VDC–MMA–AN (216,217). The VDC level and the MMA–AN ratio are adjusted for the best balance of solubility and permeability. These polymers exhibit a unique combination of high solubility, low permeability, and rapid crystallization (218).

Acetone, methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, ethyl acetate, and tetrahydrofuran are solvents for VDC polymers used in lacquer coatings; methyl ethyl ketone and tetrahydrofuran are most extensively employed. Toluene is used as a diluent for either. Lacquers prepared at 10–20 wt% polymer solids in a solvent blend of two parts ketone and one part toluene have a viscosity of 20–1000 mPa·s (=cP). Lacquers can be prepared from polymers of very high VDC content in tetrahydrofuran–toluene mixtures and can be stored at room temperature. Methyl ethyl ketone lacquers must be prepared and maintained at 60–70°C or the lacquer forms a solid gel. It is critical in the manufacture of polymers for a lacquer application to maintain a fairly narrow compositional distribution in the polymer to achieve good dissolution properties.

The lacquers are applied commercially by roller coating, doctor and dip coating, knife coating, and spraying. Spraying is useful only with lower viscosity lacquers, and solvent balance is important to avoid webbing from the spray gun. Solvent removal is difficult from heavy coatings, and multiple coatings are recommended where a heavy film is desired. Sufficient time must be allowed between coats to avoid lifting of the previous coat by the solvent. In the machine coating of flexible substrates, eg, paper and plastic films, the solvent is removed by infrared heating or forced-air drying at 90–140°C. Temperatures of 60–95°C promote the recrystallization of the polymer after the solvent has been removed. Failure to recrystallize the polymer leaves a soft, amorphous coating that blocks or adheres between concentric layers in a rewound roll. A recrystallized coating can be rewound without blocking. Handling properties of the coated film are improved with small additions of wax as a slip agent and of talc or silica as an antiblock agent to the lacquer system. The concentration of additives is kept low to prevent any serious detracting from the vapor transmission properties of the VDC copolymer coating. For this reason, plasticizers are seldom, if ever, used.

A primary use of VDC copolymer lacquers is the coating of films made from regenerated cellulose or of board or paper coated with polyamide, polyester, polypropylene, poly(vinyl chloride), and polyethylene. The lacquer imparts resistance to fats, oils, oxygen, and water vapor (219). These coated products are used mainly in the packaging of foodstuffs, where the additional features of inertness, lack of odor or taste, and nontoxicity are required. Vinylidene chloride copolymers have been used extensively as interior coatings for ship tanks, railroad tank cars, and fuel storage tanks, and for coating of steel piles and structures (220,221). The excellent chemical resistance and good adhesion result in excellent long-term performance of the coating. Brushing and spraying are suitable methods of application.

The excellent adhesion to primed films of polyester combined with good dielectric properties and good surface properties makes VDC copolymers very suitable as binders for iron oxide pigmented coatings for magnetic tapes (222–224). They perform very well in audio, video, and computer tapes.

Vinylidene Chloride Copolymer Latex. Vinylidene chloride copolymers can be made in emulsion, and then isolated, dried, and used as coating or extrusion resins. Stable latices have been prepared and can be used directly for coatings (225–230). The principal applications for these materials are as barrier coatings on paper products and, more recently, on plastic films. The heat-seal characteristics of VDC copolymer coatings are equally valuable in many applications. They are also used for paints and as binders for nonwoven fabrics (231). Special VDC copolymer latices are used for barrier laminating adhesives, and the use of VDC copolymers in flame-resistant carpet backing is well known (232–235). VDC latices can also be used to coat poly(ethylene terephthalate) bottles to retain carbon dioxide (236).

Poly(vinylidene chloride) latices can be easily prepared by the same methods but have few uses because they do not form films. Copolymers of high VDC content are film-forming when freshly prepared but soon crystallize and lose this desirable characteristic. Because crystallinity in the final product is very often desirable, eg, in barrier coatings, a significant developmental problem has been to prevent crystallization in the latex during storage and to induce rapid

Table 22. Properties of a Typical Barrier Latex

Properties	Value
Total solids, wt%	54–56
Viscosity at 25°C, mPa·s (=cP)	25
pH	2
Color	Creamy white
Particle size, nm	ca 250
Density, g/cm ³	1.30
Mechanical stability	Excellent
Storage stability	Excellent
Chemical stability	Not stable to di- or trivalent ions

crystallization of the polymer after coating. This has been accomplished by using the proper combination of comonomers with VDC.

Most VDC copolymer latices are made with varying amounts of acrylates, methacrylates, and acrylonitrile, as well as minor amounts of vinylcarboxylic acids, eg, itaconic and acrylic acids. Low foam latices having high surface tension are prepared with copolymerizable sulfonate monomers (233,235–237). The total amount of comonomer ranges from about 8 wt% for barrier latices to as high as 60 wt% for binder and paint latices. The properties of a typical barrier latex used for paper coating are listed in Table 22. Barrier latices are usually formulated with antiblock, slip, and wetting agents. They can be deposited by conventional coating processes, eg, with an air knife (238,239).

Coating speeds in excess of 305 m/min can be attained. The latex coating can be dried in forced-air or radiant-heat ovens (240,241). Multiple coats are applied, particularly in paper coating, to reduce pinholing (242). A precoat is often used on porous substances to reduce the quantity of the more expensive VDC copolymer latex needed for covering (243). The properties of a typical coating are listed in Table 23.

Vinylidene Chloride Copolymer Foams. Low density, fine-celled VDC copolymer foams can be made by extrusion of a mixture of VDC copolymer and a blowing agent at 120–150°C (244). The formulation must contain heat stabilizers, and the extrusion equipment must be made of noncatalytic metals to prevent accelerated decomposition of the polymer. The low melt viscosity of the VDC copolymer formulation limits the size of the foam sheet that can be extruded.

Expandable VDC copolymer microspheres are prepared by a microsuspension process (245). The expanded microspheres are used in reinforced polyesters, blocking multipair cable, and in composites for furniture, marble, and marine applications (246–249). Vinylidene chloride copolymer microspheres are also used in printing inks and paper manufacture (250).

Vinylidene Chloride Copolymer Ignition-Resistant Applications. The role of halogen-containing compounds in ignition and flame suppression has been studied for many years (251–256). Vinylidene chloride copolymers are an abundant source of organic chlorine, eg, often above 70 wt%. Vinylidene chloride emulsion copolymers are used in a variety of ignition-resistant binding applications (257,258). Powders dispersible in nonsolvent organic polymer intermediates, eg, polyols, are used for both reinforcement and ignition resistance in polyurethane

Table 23. Film Properties of VDC Copolymer Latex

Property	Value
Water vapor transmission at 38°C and 95% RH, nmol/(m·s) ^a	0.012 ^b
Grease resistance	Excellent
Scorability and fold resistance	Moderate
Oxygen permeability at 25°C, nmol/(m·s·GPa) ^c	0.07
Heat sealability ^d	Good
Light stability	Fair
Density, g/cm ³	1.60
Color	Watery white
Clarity	Excellent
Gloss	Excellent
Odor	None

^aTo convert nmol/(m·s) to (g·mil)/(100 in.²·d), multiply by 4.

^bValues 0.37 g/(24 h·100 in.²) for 0.5 mil.

^cTo convert nmol/(m·s·GPa) to (cm³·mil)/(100 in.²·d·atm), divide by 2.

^dFace-to-face.

foams. Vinylidene chloride copolymer powder is also used as an ignition-resistant binder for cotton batt (259–261).

The halogenated polymers generate significantly more smoke than polymers that have aliphatic backbones, even though the presence of the halogen does increase the limiting oxygen index. Heavy-metal salts retard smoke generation in halogenated polymers (261,262). A VDC emulsion copolymer having a high AN graft can be used to make ignition-resistant acrylic fibers (263). A rubber-modified VDC copolymer combines good ignition resistance with good low temperature flexibility (264,265). The rubber-modified VDC copolymer has been evaluated in wire coating where better ignition resistance and lower smoke generation are needed.

Materials are also blended with VDC copolymers to improve toughness (265–268). Vinylidene chloride copolymer blended with ethylene–vinyl acetate copolymers improves toughness and lowers heat-seal temperatures (269,270). Adhesion of a VDC copolymer coating to polyester can be achieved by blending the copolymer with a linear polyester resin (271).

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