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COPOLYMERIZATION

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CHAPTER X. COPOLYMERIZATIONS EMPLOYING VINYL CHLORIDE OR VINYLIDENE CHLORIDE AS PRINCIPAL COMPONENTS

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I. Copolymers Predominantly Vinyl Chloride

The copolymerization of vinyl chloride with other monomers obtained its original impetus because of the belief that the intractible nature and thermal instability of polyvinyl chloride provided a severe limitation to large scale exploitation of the homopolymer. The introduction of plasticizing side chains by copolymerization minimized these problems by decreasing the softening point of the polymer.

In more recent years the emergence of easy processing homopolymers of vinyl chloride was made possible through improved techniques of molecular weight regulation and the development of improved stabilizers and plasticizers. This has eliminated much of the original need for internally plasticized resins, but copolymers are still important in applications where superior melt flow characterisities are desirable and little or no external plasticizer can be tolerated.

II. Copolymers of Vinyl Chloride and Vinyl Acetate

The copolymer of vinyl chloride and vinyl acetate is by far the most important of the commercially available class of copolymers comprised principally of vinyl chloride. Copolymers containing from 3–40% vinyl acetate are offered for sale. Many of these resins are also available over a range of molecular weight to suit the particular needs of the consumer. In general, however, the vinyl acetate content of the copolymer is the more important end use con-

sideration. Polymers containing 13% or more vinyl acetate are used in protective coatings, vinyl asbestos floor tile, flexible films, and compression molding where exceptional melt flow characteristics are important. Higher molecular weight copolymers with lower amounts of copolymerized vinyl acetate are useful for the preparation of a wide range of products including rigid sheeting, extruded rods and shapes, and calendered articles.

In addition to the wide range of copolymers of this class available to the plastics industry, a number of modified vinyl chloride–vinyl acetate resins are used in protective coatings and decorative finishes where special properties are desired. Two of the more important resins of this class are modified by incorporation of a small amount of interpolymerized carboxyl compound such as maleic anhydride or by hydrolysis of a fraction of the acetate groups to provide hydroxyl groups along the polymer chain. The manufacture and application of these copolymers will be treated in the general discussion of chloride–acetate copolymers except for areas where specific differences are important.

1. Preparation

Vinyl chloride and vinyl acetate copolymerize at moderate temperatures to high conversions. Polymerization is usually initiated by a free-radical mechanism and the reactions may be carried out in mass, solution, suspension, or emulsion systems. Initiators most commonly employed are monomer soluble dialkyl or diaryl peroxides and diazo compounds such as azobisisobutyronitrile. The choice of catalyst usually depends on the polymerization temperature chosen and determines to a large extent the duration of the reaction cycle. The use of acetyl benzoyl peroxide has been specified for polymerizations conducted at temperatures of 30–40°C. (256), while lauroyl or benzoyl peroxide is usually employed for polymerizations conducted at 50–70°C.

Most producers use either aqueous suspension or continuous solution techniques. Emulsion systems are not commercially employed in the United States because of difficulties inherent in the removal of relatively large quantities of emulsifying agents and buffering salts which have a marked effect on the color and clarity of the end products. Mass or bulk polymerizations, although capable of providing high purity resin, present a difficult engineering problem due to the highly exothermic nature of the reaction (30,000 BTU/lb./mol. of monomer) in polymerizing an undiluted mass of monomers.

Solution Polymerization. Early development of vinyl chloride-vinyl acetate copolymers by the solution technique was initiated by the Union Carbide Chemicals Co. in about 1928. The earliest patent in the field was issued to Reid (239) in 1933. It described a copolymer of 22 parts vinyl chloride and 25 parts vinyl acetate prepared in the presence of 3 parts acetaldehyde and 50 parts solvent. A later patent issued to Douglas in 1937 (78) described the preparation of copolymers of vinyl chloride and vinyl acetate in the ratio of about 4:1 by a continuous polymerization in a hydrocarbon which was a solvent for the monomers and a nonsolvent for the polymer.

The monomers were charged to a lead-lined autoclave containing 4 parts butane to 1 part combined monomer and fitted with a pump capable of circulating the reaction mass through parallel filter presses. Polymerization was initiated with 0.5% benzoyl peroxide at a temperature of 40°C. As the copolymer formed in the system it was contained on one of the filter presses while additional monomers and initiator were added at a rate equivalent to monomer consumption. Filter presses were changed as they became loaded with polymer permitting uninterrupted continuation of the reaction. The finished polymer was dried by allowing residual butane to evaporate. The copolymer produced by this procedure was said to have unusually good color because washing with water with subsequent lengthy drying at elevated temperature was avoided and thermal degradation was minimized.

In theory it is possible to carry out solution copolymerization in diluents which are solvents for both the monomer and polymer, as well as in solvents which dissolve the monomer but precipitate the polymer. Polymerization in polymer solvents is not generally practical because of the very slow polymerization rates due to solvent activity. Preparation of most production solution resins is believed to be made in diluents which are nonsolvents for the copolymer.

Copolymers prepared by the solution precipitation method are more generally homogeneous in composition than copolymers prepared in batch systems and because of this they are more suitable for solution applications. The copolymers are free from residual quantities of suspending agents and emulsifiers and this advantage along with

lower production and finishing temperatures provides resins with good color and clarity. The diluent solvents desirably control molecular weights because polymer chain growth is essentially terminated when precipitation occurs and because the solvent provides some solvent to radical chain transfer. Perhaps the most important advantage of the solution process is its ease of adaptability to convenient continuous polymerization techniques.

Solution polymerization has several disadvantages and these may have limited adoption of the technique by more manufacturers although the original Carbide patents expired about 1954. The resins are somewhat more expensive than those prepared in aqueous suspension because of generally slower reaction rates and costs involved in recovering and purifying the usually flammable diluent. The choice of monomer solvents is also limited by the tendency of many otherwise desirable compounds to act as polymerization inhibitors. In order to minimize such solvent effects it is often necessary to conduct the polymerizations at low reaction temperatures. This lengthens reaction cycles, or in the case of continuous polymerization decreases the overall production rate.

Suspension Polymerization. All aqueous suspension copolymerizations of vinyl chloride and vinyl acetate are probably carried out batchwise, although several patents describe continuous suspension processes (122,307). Suspension of the monomer droplets present in the water as a disperse phase is maintained by the use of vigorous agitation and suspension stabilizers or protective colloids. The water-soluble suspending agents are usually polymers such as gelatin, polyvinyl alcohol, methyl cellulose, carboxymethyl cellulose, and any number of other naturally occurring or synthetic macromolecular materials. Frequently, surface-active agents are used in minor quantities as secondary emulsifiers to assist in uniform dispersion of the suspension stabilizer and provide some control over the particle size of the finished product. During the reaction some dehydrohalogenation of vinyl chloride and hydrolysis of vinyl acetate generates hydrochloric and acetic acids so buffering agents are usually added to maintain a near neutral pH.

In a typical suspension polymerization the suspension stabilizers, buffering agents, and initiator are dissolved in water and charged to a glass-lined autoclave, the largest of which is thought to be about 3,700 gallons. The reactor is closed and purged with an inert gas

or monomer and then evacuated. The monomers are bled into the evacuated system from weigh tanks, and the reaction started by quickly raising the temperature of the system to the desired operating level. Because of the highly exothermic nature of the reaction, precautions must be exercised by control of the reaction rate and water to monomer ratio so that the cooling capacity of the reactor jacket cooling water is not exceeded. After a period of between 8 and 24 hr. and about 90% conversion of monomer to polymer, the reactor pressure starts to drop quickly and the reaction is usually terminated. Excess monomer is stripped off under vacuum and the product is transferred to blending tanks. Finishing is accomplished by washing the polymer and removing excess water on a continuous centrifuge and then drying in a rotary dryer.

III. Copolymer Composition

Copolymers of the same average composition and the same average molecular weight are commercially available from several manufacturers but the physical properties of some resins make them more suitable in certain applications than other apparently identical resins.

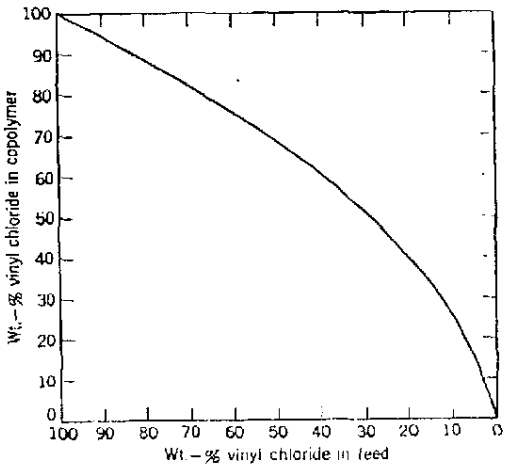

Fig. 1. Copolymerization of vinyl chloride with vinyl acetate. Instantaneous relation of feed to copolymer composition.

The difference between such copolymers, assuming an equivalent degree of polymerization, is largely a difference in the degree of copolymeric homogeneity attained during the manufacturing process. During any copolymerization of two vinyl monomers different degrees of reactivity exist between the radical chain ends and the two monomers. Mayo et al. showed that in the copolymerization of vinyl chloride and vinyl acetate, the vinyl chloride monomer is more reactive toward the growing chain regardless of whether the radical end

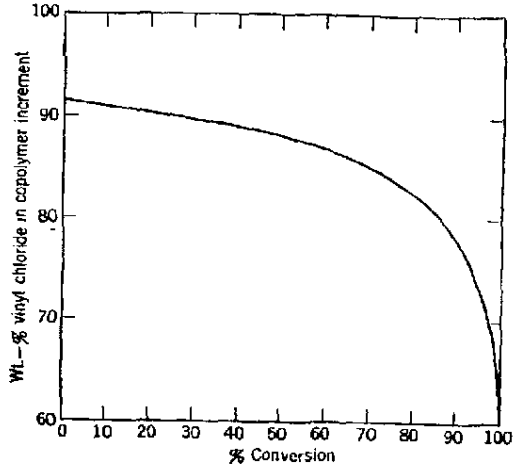

Fig. 2. Copolymerization of vinyl chloride with vinyl acetate. Instantaneous composition of the copolymer *vs.* conversion for a batch system charged with 85 parts vinyl chloride and 15 parts vinyl acetate.

was derived from vinyl chloride or vinyl acetate (201). Therefore, in copolymerization of these two monomers, the polymer is always richer in vinyl chloride up to 100% conversion of both monomers. This relationship is shown in Figure 1. As polymerization proceeds in a batch reaction, the composition of the copolymer molecules being formed undergoes a progressive change. This effect is illustrated in Figure 2 calculated from reactivity data and an integral form of the copolymerization equation. The charge composition employed was 85 vinyl chloride/15 vinyl acetate.

In many copolymer applications, uniform chemical composition is important. A resin with a very wide spectrum of compositions from molecules very low in vinyl acetate to others very rich in vinyl acetate may be difficult to process. It may also be insufficiently soluble for use in solution applications. Relatively homogeneous copolymers may be readily prepared by solution polymerization. In this system, the monomer composition of the reaction solution is held constant by continual addition of fresh monomer and removal of finished polymer. When steady-state conditions are attained all polymer molecules are initiated, propagated, and terminated in an environment of nearly constant composition. Molecular weights also tend to be distributed over a narrower range because of limits imposed on the solution or dissolution of polymer molecules by the solvent and because termination occurs in a system nearly constant with regard to chain transfer.

Homogeneity of composition may be improved in batch copolymerization by continuous addition of one, or a mixture, of both of the monomers. The "proportioning" is regulated at a given temperature by maintaining reactor pressures consistent with the vapor pressure of the desired monomer mixture.

Thomas and Hinds calculated (294) the initial monomer charge and the amount of vinyl chloride to be proportioned to give a chemically uniform copolymer of several compositions. Their data are reproduced here:

Theoretical Monomer Loading and Operating Conditions for Forming Chemically Homogeneous Copolymers at 60°C.

Desired copolymer composition, %		Initial monomer charge parts/wt.		Vinyl chloride to be proportioned	Equilibrium pressure lb./in.²
Vinyl chloride	Vinyl acetate	Vinyl chloride	Vinyl acetate		
97	3	57	3	40	142
94	6	54	6	40	136
91	9	51	9	40	131
88	12	48	12	40	125
85	15	46	15	39	120
82	18	44	18	38	115
80	20	43	20	37	112

1. Physical Properties

The physical properties of vinyl chloride/vinyl acetate copolymers depend mainly on the composition of the copolymer. Molecular weight also contributes to the processing characteristics of the resins, although separation of the two effects is difficult to assess. Homogeneity, already discussed, also affects resin processibility.

Copolymers have a lower softening point and a lower melt viscosity than homopolymers of equivalent molecular weight. They are also more subject to chemical attack by ketones. Both of these properties are directly dependent on the vinyl acetate content and its plasticizing effect on the molecule. The homopolymer of vinyl chloride is described as pseudo-crystalline because of its tendency to contain stereoregular sequences of appreciable length. The close chain packing made possible by such molecular regularity raises the fusion point and decreases the solubility of the resin. Copolymerization with vinyl acetate introduces side chains which prevent such tight chain packing therefore decreasing inter- and intra-molecular bonding forces. In this way, the comonomer acts as an internal plasticizer and the copolymer may be processed at lower temperatures.

Copolymers also have slightly higher tensile strength, lower rigidity and heat distortion temperature, and poorer abrasion resistance than homopolymers of nearly the same molecular weight. These deficiencies increase in proportion to the vinyl acetate content. The greater solubility of vinyl chloride–acetate copolymers in ketones has made the copolymers useful in a wide range of coating applications.

Typical physical properties of a copolymer composed of 85% vinyl chloride and 15% vinyl acetate are compared in the following table with the physical properties of a copolymer containing only 3% vinyl acetate.

Properties of Rigid Press-Polished Sheet, Vinyl Chloride-Vinyl Acetate Copolymers

Acetate content	3%	15%
Mill roll temp., °F.	340	250
Rockwell hardness M scale	60	50
Notched impact, ft.-lb./in.	.65	.20
Abrasion loss % in 2000 cycles	.02	.13
Heat distortion °C., 66 psi	67	57
Tensile strength, psi	8,200	8,500
Stress of yield, flex. psi	12,800	12,200

2. Applications

Reliable consumption figures for chloride–acetate copolymers are difficult to obtain. The U.S. Tariff Commission does not distinguish between vinyl chloride homopolymer uses and chloride–acetate copolymers, and in many instances, companies producing copolymers do not know what the resin is being used for.

The following table, however, represents a reasonable estimate of the consumption and applications of chloride-acetate copolymers during 1961 and 1962.

Consumption (Millions of Pounds) 1961	1962	Application
85	106	Flooring
60	68	Records
25	19	Calendered sheet
30	40	Protective coatings
25	27	Films, sheeting, and extrusion
25	25	Export
250	295	

Of the total consumption, approximately one-half is thought to be of copolymers containing 13 to 15% bound vinyl acetate. Most of the remaining volume is made up of copolymers with lower amounts of vinyl acetate.

Flooring. In 1961 and 1962, the flooring industry was the largest consumer of chloride–acetate copolymers. Approximately 85 million pounds of copolymer was used mainly in the production of vinyl asbestos flooring in 1961 and a somewhat higher volume was consumed in 1962. Growth is expected to continue in this application, mostly at the expense of asphalt flooring, due to the greater consumer appeal of the more decorative vinyl asbestos flooring. In addition to decorative superiority, vinyl asbestos tiles have greater flexural strength making possible the production of thin tiles (1/16 in.) which are generally easier to work with and, therefore, appealing to the do-it-yourself home owner. Cost has also been an important factor in the growth of vinyl asbestos flooring. The price of the copolymer to the flooring industry is about 16¢/lb. and the consumer can purchase the tiling through retail outlets for less than 22¢/ft.² in 1/16 in.

gage (about 12¢ per 9 in. × 9 in. tile). Asphalt tiles retail at prices ranging from 12.4¢/ft.² for dark materials to about 23¢/ft.² for the lighter tiles.

The copolymer content of a typical vinyl asbestos floor tile is generally less than 30% blended with asbestos and clay filler and a small amount of plasticizer and stabilizer. Copolymers are used rather than homopolymers, because their low melt viscosity permits easier and more rapid wetting of the highly filled stock.

The following is a typical basic flooring recipe:

Vinyl copolymer	100
Clay	115
Asbestos	115
DOP	20
Epoxidized oil	15
Barium–zinc stabilizer	5

Production techniques vary considerably from one manufacturer to the other, but the recipe components are usually blended in an intensive mixer such as a Banbury, and then dropped onto a heated mill. Some manufacturers use more than one milling operation, but the final step in the procedure is usually made on a 3-roll calender, followed by a cutting step to reduce the calendered sheet to the desired tile size. Pigments and colorants may be added during the milling or calendering steps to provide the desired decorative effect.

Phonograph Records. The phonograph record industry was second only to the flooring industry in volume consumption of copolymer in 1961 and 1962, with a total volume of 60–68 million pounds. Nearly all of this was copolymer containing 13% vinyl acetate and 87% vinyl chloride. Virgin resin is used for the production of 12 in. high fidelity records, while scrap generated in the production is sometimes used to prepare the smaller 33 r.p.m. records.

No other commercial application makes such exacting demands on the mold fidelity of a polymer. Compression molding of phonograph records with over 1000 highly complex grooves to fill demands a resin with a very low melt viscosity as well as one which has excellent resistance to shrinkage on cooling. These demands are well met by vinyl chloride–acetate copolymers. Such records are also highly resistant to water and changes in humidity and temperature. They are also essentially nonbreakable and have reasonably good scratch resistance

A typical phonograph record formulation contains:

Vinyl copolymer resin (85/15)	97.50
Black pigment	1.00
Lead stabilizer	1.50

Several procedures are used in preparing compounds for phonograph records. Usually the resin, pigment, and stabilizer are dry-blended and Banbury-mixed at some temperature lower than 300°F. The mixed compound is fed to a calender and then scored into biscuits. The biscuits are preheated on steam tables and molded at 300–350°F. at a pressure of about 1500 psi. After molding, the discs are quickly cooled and removed from the presses to prevent warping and distortion.

Protective Coatings. Vinyl copolymer surface coatings consume large quantities of resin. The coatings are resistant to most chemicals, including acids, alkalies, greases, oils, alcohols, and hydrocarbons. They are, of course, attacked by solvents such as ketones and esters. The coatings are odorless, tasteless, nontoxic, and nonflammable and have excellent resistance to weathering. Because the polymer films are colorless, they can be pigmented in a wide variety of colors including the lightest pastel shades. The coatings are also tough, flexible, and have good wearing qualities.

Nearly all of the resins used in the preparation of vinyl coatings are chloride–acetate copolymers with vinyl acetate contents varying from 5 to 40%. The acetate content of the copolymer and its degree of polymerization or molecular weight are important to the toughness, strength, and chemical resistance of the deposited coating and to the solubility of the polymer. In most applications copolymers containing about 15% vinyl acetate with a medium average molecular weight are satisfactory. Such copolymers represent the largest volume of vinyls used in surface coatings. Copolymers with a lower molecular weight or a higher acetate content are used when low solution viscosity or higher diluent tolerance is desired. The coatings have consequently less toughness and strength and are softer and more subject to chemical attack.

In many applications, such as metal coating, vinyl copolymers suffer from poor adhesion. To overcome this problem, special primers must be used, or the copolymer must be modified to contain a built-in

anchoring agent. The most commonly used anchoring agents are monomers containing carboxylic acid groups such as maleic anhydride, methacrylic acid, or itaconic acid. A typical copolymer described as having improved adhesion to metal has the composition vinyl chloride (85%), vinyl acetate (13%), and maleic anhydride (2%). Other copolymers are commercially available containing hydroxyl groups obtained by partial hydrolysis of the acetate groups in the copolymer. Such resins as these are usually not used as the primary coating but are more often mixed with conventional copolymer solution resins in amounts sufficient to give the desired degree of adhesion.

The most common and best solvents for vinyl chloride–acetate copolymers are ketones; and the most commonly used ketones are acetone, methyl ethyl ketone, and methyl isobutyl ketone. The copolymers also have appreciable solubility in certain alkyl acetates, nitroparaffins, and chlorinated hydrocarbons. Ketones are preferred, however, because of their ability to solvate greater amounts of polymer. The solutions have low viscosities, are more stable to aging and can tolerate larger quantities of diluent. Ketones are also noncorrosive and relatively nontoxic. Chlorinated hydrocarbons are used in special nonflammable lacquers, but the toxicity of these solvents makes extensive ventilation necessary. Diluents, such as toluene or xylene, are added to coating formulations to retard evaporation rates, reduce cost, thin the lacquers, improve brushability, and to simplify solution of the resin.

Copolymer solutions are readily prepared by careful addition of the polymer to the solvent system. High shear agitation is desirable to prevent clumping of the resin. It also reduces the solution viscosity because the resins are "shear thinning." When diluents are used it is often desirable to disperse the polymer in them first, and then add the solvent. This procedure usually makes solution times shorter.

In certain applications where penetration of the coating into porous materials is desirable, or where higher solids contents are desired, chloride–acetate copolymers may be applied as oil-in-water emulsions. The emulsions are prepared by dispersing a dissolved resin in water with agitation and then passing the emulsion through a colloid mill to reduce the size of the lacquer droplets. Small amounts of surface active agents are added to reduce coalescence and stabilize the emulsion. On application of the emulsion the water evaporates and the suspended droplets coalesce and become the continuous phase. Emulsion coatings offer the advantages of low cost, high solids content, low surface penetration, improved brushing characteristics, and low flammability. The coatings, however, are difficult to pigment, slow-drying, and cannot be used on surfaces that are corroded by or undergo dimensional changes on contact with water.

Vinyl copolymers are used as surface coatings in a wide variety of applications, as: metal finishes, cement finishes, coatings for aluminum house siding, paper coating, wood finishes, artificial leather finishes, and textile sizing.

The gradual acceptance of synthetic materials by the building industry provides an area for continued growth of vinyl surface coatings. In 1959 an estimated 275,000 homes were covered with vinyl-coated aluminum siding. Vinyl coatings are also used on gutters, downspouts, and ducting. Application to traditional structural materials such as cement, interior panels, and wood flooring is used for protection against weathering, decorative effects, sound deadening qualities, insulation, and waterproofing.

In the food packaging industry vinyl surface coatings are used on the inside of cans, frequently over other resinous materials, to protect the product from flavor-contaminating impurities.

Film and Sheeting. The increasing demand for unplasticized sheeting and film has created a growing market for polyvinyl chloride acetate copolymers with an ester content generally lower than 13%. Converters prefer to use copolymers containing the least amount of vinyl acetate consistent with satisfactory product processing in order to approach the higher heat distortion temperature and superior heat stability of homopolymers. Copolymers containing as little as 3% vinyl acetate are used in applications where rigidity, chemical resistance, and hardness are important. Copolymers with higher acetate contents are used when flexibility and easy thermal processing are necessary.

Impressive growth occurred during 1961–1962 in the use of copolymer for the preparation of calendered rigid sheeting. The material is used for playing cards, identification cards, templates, graphic arts, ring binders, ducts, and pipes. One manufacturer supplies copolymeric sheeting for use in the curved plate structure of printing

TABLE I
Physical Properties of Vinyon HH and Dynel Fibers

	Vinyon HH	Dynel
Composition	88% Vinyl chloride/ 12% vinyl acetate	60% Vinyl chloride/ 40% acrylonitrile
Molecular structure	Amorphous	Slightly crystalline
Transition temperature	—	T_g = 195°F.
Fiber cross section	Round	Irregular
Dry tensile, psi	12,000–17,000	40,000–57,000
Dry and wet tenacity, g./den.	0.7–1.0	2.5–3
Dry and wet elongation	100–120%	42–30%
Initial stiffness, g./den.	—	30
Elastic recovery	—	94% from 2% extension
Specific gravity	1.33–1.35	1.30
Moisture regain, % at 70°F., 65% RH	Less than 0.1	0.4
Shrinkage, % in boiling water	60–70	2.0
Shrinkage, % in 300°F. air	—	45.0
Moth and mildew resistance	Unattacked	Unattacked
Chemical resistance	Excellent to acids, 30% caustic, alcohols and aliphatic hydrocarbons	Good to acids and alkalies—poor to ketones
Solvents	Chloroform, acetone, methylene chloride	Acetone, higher ketones, cyclic ethers

presses. Other uses of rigid extruded stock are expected to develop in the building industry.

Fibers. The production of staple fibers is a relatively small, but interesting, application for polyvinyl chloride–acetate copolymers. Since 1939 such fibers have been produced by American Viscose as Avisco Vinyon (Vinyon HH). The copolymer is spun from acetone solution and is believed to be 88% vinyl chloride and 12% vinyl acetate. Vinyon fibers have similar physical properties (Table I) to polyvinyl chloride homopolymers made in Europe (Rhovyl, Fibrovyl, Isovyl) except for a slightly lower softening point. This property is used to advantage in the preparation of bonded fiber batting, felts, and heat sealable wet strength papers.

IV. Copolymers of Vinyl Chloride and Acrylonitrile

1. Copolymerization

Vinyl chloride copolymerizes with acrylonitrile but the much faster polymerization rate of acrylonitrile with radicals of its own type or radicals derived of vinyl chloride, makes homogeneous copolymerization difficult. The instantaneous copolymer composition curve (Fig. 3) for vinyl chloride and acrylonitrile was calculated using reactivity ratios determined by Lewis et al. (186). The curve shows that any mixture of the two monomers results in a copolymer relatively richer in acrylonitrile. If the monomers are charged batchwise, the composition distribution of polymer molecules will vary over a wide range from chains high in acrylonitrile to chains containing very little acrylonitrile. To overcome this problem an initial monomer charge is chosen to give a copolymer of the desired composition. The faster reacting monomer is then added continuously or portion wise during the polymerization.

In 1947 a commercial process was revealed for the copolymerization of vinyl chloride and acrylonitrile (235). The polymerization was

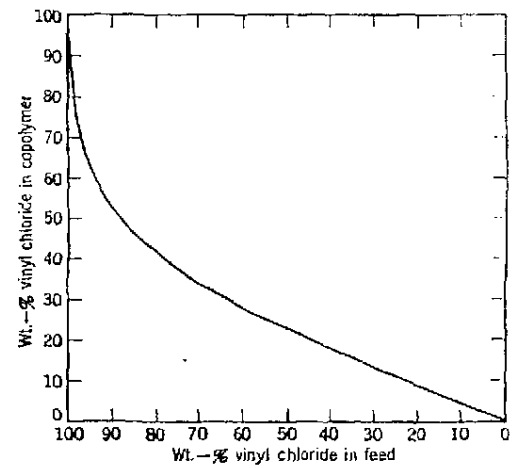

Fig. 3. Copolymerization of vinyl chloride with acrylonitrile. Instantaneous relation of feed to copolymer composition.

carried out in an emulsion system as follows: 90 parts vinyl chloride, 10 parts acrylonitrile, 5 parts acetaldehyde, and 1 part potassium persulfate were emulsified in 400 parts water containing 1 part 2-ethylhexyl sulfosuccinate. The polymerization was conducted in an autoclave at 40°C. and the remaining acrylonitrile was added during the polymerization. A 53% yield of polymer was obtained after 33 hr. Improved rates were obtained in later polymerizations using redox catalyst systems (10).

2. *Preparation*

Fibers: Vinyon N and Dynel. Copolymers of vinyl chloride and acrylonitrile have rather unusual physical properties. At low concentrations of acrylonitrile (10% or less), the resins behave much like polyvinyl chloride with respect to their use in solution and in thermal processing operations. As the acrylonitrile content is increased to 40–45%, the polymer becomes difficult to process because of the poor melt flow characteristics typical of polyacrylonitrile. Compression-molded articles can be made but they are fibrous in nature and generally non-isotropic. Some processing improvement is obtained with plasticizers such as *p*-toluene ethyl sulfonamide, but the polymer is generally incompatible with most other plasticizers. Heat treatment leads to considerable darkening in processed articles, but unlike polyvinyl chloride the vinyl chloride–acrylonitrile copolymer becomes lighter colored on aging.

Although poor melt flow characteristics limited the use of these copolymers in thermoplastic processing, their solubility in acetone and their high molecular weight made them useful resins for the preparation of synthetic fibers. In 1948 Union Carbide Chemicals Co. introduced a continuous filament called Vinyon N prepared from a 60/40 vinyl chloride–acrylonitrile copolymer. In 1950 the continuous filament was withdrawn in favor of staple fiber, and the name of the product was changed to Dynel.

Vinyl chloride copolymers containing 40% acrylonitrile are sufficiently soluble in acetone to permit fiber spinning from 25% polymer in solvent solutions. It is interesting, however, that on aging at elevated temperature the solubility of the copolymer in acetone decreases, and its heat distortion temperature rises. Fibers spun from acetone solution may be heat-treated at 150°C. for 1 to 2 hr. to reduce their acetone solubility from 100% to less than 10%. The heat distortion temperature of molded articles rises from 85°C. to 90°C. with the same heat treatment.

Fabrics prepared from Dynel have a warm pleasant hand, good drape, and the resiliency and wrinkle resistance characteristic of fibers containing high levels of acrylonitrile. They also develop a high luster on heating and, due to their thermoplastic nature, they can be heat formed to prepare shaped fabrics such as felts used in men's hats. The high luster of the fibers makes them useful for the preparation of synthetic fleeces and furs. The fibers do not support combustion making them useful in drapery materials and other articles where flame resistance is desired. The chemical resistance of the fibers, especially to acids and alkalies, is desirable for preparation of protective clothing, wet and dry filtration fabrics, anode bags, overlays for glass fiber laminates, and many other applications.

The physical properties of Dynel fibers are shown in Table I.

V. Copolymers of Vinyl Chloride and Vinylidene Chloride

When small amounts of vinylidene chloride (less than 5%) are copolymerized with vinyl chloride the copolymer is somewhat more soluble and processes at a lower temperature than a PVC homopolymer prepared under equivalent conditions. Vinylidene chloride polymerizes at a faster rate than vinyl chloride with radicals derived of either monomer and it is usually metered to the system continuously during polymerization in order to obtain copolymers of reasonable composition uniformity.

A relatively small quantity of vinyl chloride–vinylidene chloride copolymer is produced each year. The resin is used mainly as a plastisol extender.

VI. Other Copolymers Predominantly Vinyl Chloride

Vinyl chloride has been copolymerized with a large number of compounds and combinations of compounds. The reasons for preparing such resins vary, but most of the copolymers reported in the literature were prepared to improve the processability of polyvinyl chloride by lowering its melt viscosity through internal plasticization. Copolymers are also described which have improved solubility, adhesion and a wide spectrum of other advantageous properties. In general, an ideal copolymer of vinyl chloride would process without breakdown

TABLE IIA
Copolymers of Vinyl Chloride[a]

Type	Ref.
Aromatic Compounds	
Allyl carbonate derivatives of aromatic hydroxy esters	243
Aromatic acid amides of aminoalkyl vinyl ethers	319
Styrene and substituted styrenes	52,127,180,185, 299,300
Tetrahydro-*endo*-methylene phthalates	280
Epoxy Compounds	
Allyl 3,4-epoxy-2-hydroxybutyrate	154
Allyl glycidyl ether	90,162
3,4-Epoxycyclohexane methanols	113,155,156
Unsaturated esters of epoxy fatty acids	157
Vinyl 9,10-epoxystearate	258,306
Heterocyclic Compounds	
N-Isopropenyl derivatives of 2-oxazinones and 2-oxazolidinones	14
N-2-Norcamphanyl acrylamides	36
Tetrahydrofuran	181
N-Vinyloxazolidinone	23
N-Vinylpyrrolidinone	173
Miscellaneous Compounds	
Acrylamides	190,334
Acrylonitrile	1,108,117,118,216, 222,255,257
Allyl, methallyl chloride	203
Allyl sulfide	195
Butadienes	38,172
2-Chloroallylidine diacetate	297,298
Isopropenyl acetate	130
Maleic anhydride	315
Maleimide derivatives	290
β-Methylene-β-propiolactone	46
Octafluoro-1,3-cyclohexadiene	138
Phosphorus derivatives	75,171,316
Silicon derivatives	13,228,234,265,290
Succinic anhydride	329
Sulfates and sulfonates	7,51,213,226
Vinyl acetals	292
Vinylene carbonate	120,131,132

TABLE IIA (*continued*)

Type	Ref.
Olefinic Compounds	
Chlorinated polyethylene	111
1-Chloro-1-fluoroethylene	37,332
ω-Chloro-1-olefins	183
Chloroprene	47,158
Chlorotrifluoroethylene	93,134,167,174, 223,224,287,288, 295
1,1-Dichloro-2,2-difluoroethylene	251
Dichlorohexafluorobutenes	188
Ethylene	32,33,105,242
Fluorohaloethylenes (general)	245
Fluoroolefins (general)	4
Fluoroprene	139
Isobutylene	15,31,85,119
Olefins (general)	100
Tetrafluoroethylene	128,141,193
Trichloroethylene	40
3,3,3-Trifluoropropene	22
Vinyl bromide	253
Vinyl fluoride	204,293
Unsaturated Acids and Esters	
Acrylic derivatives (general)	95,248
Alkyl aconitates	60
Alkyl acrylates	2,68,98,110,175, 176,184,301
Alkyl carbonates of 2-hydroxyethyl acrylate	61
Alkyl citraconates or mesaconates	49
Alkyl fumarates	9,83,84,96,241
Alkyl itaconates	27,64,210,211
Alkyl maleates	3,11,12,39,94, 163–165,279
Alkyl methacrylates	68,69,187,302
Allyl acrylate	261
Allyl trifluoroacetate	53
2-(2-Chloroacetamido) acrylates	55
Cyano ether esters of acrylic or methacrylic acid	205
Diamidophosphoroacrylates	56
Diethyl chloromaleate	121
3,3-Difluoroacrylates	76

(*continued*)

TABLE IIA (*continued*)

Type	Ref.
Ethylene dicarboxylic acids, esters, and derivatives	87,97
Hydronopyl acrylate	199,259
Methyl 2-chloroacrylate	330
1-Propen-2-ol acetate	126
Unsaturated carboxylic acids and esters (general)	72,95,291
VINYL ESTERS	
Methyl carboxylic vinyl esters	231
Vinyl 3-alkoxybutyrates	25
Vinyl benzoate	302
Vinyl carboxylic esters (general)	159–161,197,233
Vinyl levulinate	182
Vinyl pinoate	200
Vinyl propionate	252
Vinyl stearate	232
VINYL ETHERS	
Alkoxymethoxyalkyl vinyl ethers	91
Butyl vinyl ether	212,335
Decahydro 2-naphthyl vinyl ether	34
Isobutyl vinyl ether	8,335
Methyl vinyl ether	166
Trifluoroethyl vinyl ether	249,250
Vinyl ethers (general)	5,6,244

* Limited to those copolymers containing at least 50% vinyl chloride, and not including copolymers with vinyl acetate and vinylidene chloride.

at relatively low temperatures with melt flow characteristics sufficiently fluid to minimize power requirements. The processed polymer would, however, have the high heat distortion temperature, toughness, strength, and chemical resistance of the homopolymer. No such ideal copolymer of vinyl chloride has been prepared. Many attempts have been made to improve on the processing and physical characteristics of polyvinyl chloride–acetate copolymers but no copolymer has been developed commercially which provides sufficient superiority to offset the low cost and versatility of vinyl acetate.

Among the copolymers offered over the years was the copolymer of vinyl chloride and vinyl formate developed by I. G. Farben, but never commercialized (284). Copolymers of vinyl chloride with vinyl stearate (232) were developed and sold as internally plasticized resins. These polymers suffered a tendency to bloom, and may not have been

true copolymers. Alkyl esters of maleic and fumaric acid copolymerized with vinyl chloride (136,241) are said to be insolubilized and crosslinked by the addition of an organic peroxide and exposure to actinic light (65). Copolymers containing 1-20% 2-ethyl hexyl fumarate are said to be processable without plasticizer and possess greatly increased shock and impact resistance (81). Cyano ether esters such as 2-(2-cyanoethoxy) ethyl acrylate may be copolymerized with vinyl chloride in emulsion and provide tough flexible films (205). Copolymerization of vinyl chloride with a wide range of alkyl acrylates and methacrylates has been reported. Preparation of homogeneous copolymers of vinyl chloride with acrylates or methacrylates requires monomer proportioning due to the much higher reactivity of the acrylics (69,247). The polymers are usually prepared by emulsion techniques using redox catalyst systems. Physical properties of copolymers containing methyl acrylate are similar to vinyl chloride–acetate copolymers with the same ester content. Copolymers of vinyl chloride with methyl methacrylate are reported to have a higher softening point than polyvinyl chloride alone (103), greater flexural strength and superior optical properties (247). Although no vinyl chloride–acrylic copolymers have industrial importance in the United States, copolymers with methyl acrylate were sold in Germany as Igelit MP-A and Igelit MP-K. Igelit MP-A was fabricated into clear press polished sheets sold under the trade name Astralon and Igelit MP-K was used for wire and cable insulation.

Among the more recent copolymers of interest is a graft copolymer of vinyl chloride onto polyvinyl alcohol developed by Toyo Chemical Co. of Japan (41). The composition of the polymer has not been revealed, but it is expected to find applications in the fiber industry as a replacement for silk. Pilot plant production was expected early in 1963. Fibers prepared from the copolymer have elasticity, dyeability, moisture absorption, and heat resistance which compare well with established fibers.

Other examples of polyvinyl chloride block and graft copolymers are polyvinyl chloride grafted with acrylonitrile (54), polyvinyl chloride grafted with methyl acrylate (237), and polyvinyl chloride block copolymerized with vinyl acetate, acrylonitrile, or vinylidene chloride (66).

Other copolymers reported in *Chemical Abstracts* from 1927 through June 1962 are contained in Table II.

TABLE IIB. Terpolymers of Vinyl Chloride[a]

Second monomer	Third monomer	Ref.
Acrylic acid	Methyl acrylate	220
Acrylic or methacrylic compounds	Vinylidene halides	67
Acrylic acid	Methyl methacrylate	305
Acrylonitrile	Vinyl acetate or pyrrolidone	106
	Vinyl chloroacetate	217
	Vinyl pyridine	63
Alkyl acrylates	Acrylonitriles	325
	Dibasic acid monovinyl esters	322
	Divinyl aromatic hydrocarbons	323
	Hydroxyalkyl acrylates	327
	Isoolefins	321
	Olefinic dicarboxylic acid dialkenyl esters	324
	Styrene	328
	Vinyl aromatic esters	320
	Vinylidene chloride	260
Alkyl esters of unsaturated dicarboxylic acids	Styrene	310
Alkyl maleates	Vinyl esters of fatty acids	308, 309
Allyl esters of hydroxyalkanoic acids	Allyl glycidyl ethers	89
Allyl glycidyl ether	Allyloxalkanoic acids	92
Allyl maleate or triallyl cyanurate	Vinyl acetate	116
Butadiene	Vinyl esters of soybean acids	42
	Vinylidene chloride	269
Diallyl maleate	Diallyl fumarate	194
Dibutyl maleate	Methyl acrylate	221
Diethyl maleate	Vinyl acetate	135
2-Ethylhexyl acrylate	Vinyl acetate	326
α-Fluoroacetoxyacrylonitrile derivatives	Styrene	77
Fumaric acid	Vinyl acetate	21
Isopropyl vinyl ether	Vinyl acetate	313
Maleic acid esters	Vinyl acetate	215
Maleic anhydride	Vinyl acetate	20, 214, 263
	Vinylidene chloride	218
Maleic esters of alcohols from soybean oil reduction	Vinyl acetate	43
Maleic acid	Tetrahydrophthalic half-esters	229
Methacrylic acid	Vinyl acetate	189
Styrene	Vinylidene chloride	16
	TETRAPOLYMER	
Maleic acid	Methyl methacrylate–polyvinyl acetate	145

[a] Limited to those terpolymers containing at least 50% vinyl chloride.

VII. Copolymers Predominantly Vinylidene Chloride

The polymerization of vinylidene chloride (1,1-dichloroethylene) was first observed by Regnault in 1838 (238), but no detailed investigation was made until nearly 100 years later when the reaction was studied by Feisst (102) and then by Staudinger et al. (277). The intractibility and general instability of vinylidene chloride homopolymers was quickly recognized, and copolymerization was investigated as a means to obtain a useful plastic material. Intensive research work in the United States, particularly at the Dow Chemical Co., led to the introduction, in 1940, of the family of copolymers of vinylidene chloride and vinyl chloride now known as Saran.

VIII. Copolymers of Vinylidene Chloride and Vinyl Chloride

1. Preparation

Vinylidene chloride may be copolymerized with a variety of comonomers by suspension processes, batch and continuous emulsion, solution precipitation, and bulk, although it is doubtful that bulk techniques are ever used commercially. The various techniques of polymerization form the basis for a number of patents too numerous to detail here, but in general copolymers of vinylidene chloride with vinyl chloride may be prepared in the same type of equipment used for chloride-acetate copolymers. Copolymerization techniques are also similar. Vinyl chloride polymerizes at a slower rate than vinylidene chloride in mixtures of the two monomers, and homogeneous copolymers may be made in batch processes by controlled monomer feeding or proportioning. Proportioning procedures to obtain homogeneity are also possible in emulsion systems. Emulsion resins may also be prepared quite readily by continuous polymerization, a technique which provides inherently uniform polymers by continuous proportioning of both monomers.

2. Suspension Polymerization

A typical preparation of a vinylidene chloride–vinyl chloride copolymer by the suspension method was described in a recent U.S. patent assigned to the Dow Chemical Co. (112). The reactor used was described as cylindrical with a capacity of 3,500 gallons. It was fitted with a coaxial agitator which turned at 45 r.p.m. during the

polymerization. The temperature of the reaction was 60°C. The following recipe was charged:

Water	200
Vinylidene chloride	85
Lauroyl peroxide	0.3
Vinyl chloride	15
400 cp. Methyl hydroxyl propyl cellulose	0.05

The finished resin, after filtration and drying had a particle size of 30–100 mesh and could be extruded to give haze-free film.

An earlier patent to Heerema (133) disclosed a procedure for preparation of more homogeneous resins. In this system, the more volatile vinyl chloride was overcharged and then vented off during the run to maintain a predetermined pressure. A glass-lined reactor was charged with 78 parts vinylidene chloride and 22 parts vinyl chloride. The reaction temperature was maintained at 60°C. ± 0.5°. After an induction period of about an hour the reactor pressure rose to 60 lb. psig. As the reaction proceeded the tendency of the gauge pressure to increase, due to the faster consumption rate of vinylidene chloride, was offset by venting vinyl chloride. After 32 hr. the reactor pressure dropped below 60 lb. indicating essential completion of the polymerization. The resulting polymer was 90.8% vinylidene chloride and 9.2% vinyl chloride. Only 0.39% of the resin was soluble in acetone indicating a homogeneous composition. A similar resin prepared in an unvented system was 5.9% soluble in acetone. Polymers prepared in this way crystallized at a faster rate than less homogeneous resins.

3. *Emulsion Polymerization*

An interesting variation of the above procedure was revealed in a U. S. patent assigned to W. R. Grace & Co. (142). In this disclosure a copolymer containing 78% vinylidene chloride and 22% vinyl chloride was obtained in an emulsion system by initially charging 60 parts vinylidene chloride (33% of the total vinylidene chloride) and 40 parts vinyl chloride (100% of total vinyl chloride) to a stirred and evacuated reactor at 30°C. Water, emulsifier, initiator, and buffer were charged before the monomers were added. The reactor pressure at this point was 28 psig. When it rose to 29 psig addition of the remaining 120 parts vinylidene chloride was started. A proportioning pump maintained a feed of vinylidene chloride sufficient

to hold the pressure at 29 psig to within ±0.2 psig. After 7 hr. a pressure drop occurred and the vinylidene chloride flow was stopped automatically. The latex containing 33% solids was then coagulated, washed and dried. Resins produced by this technique were said to form films having improved tensile strength, greater clarity and heat stability, and were less brittle than films prepared in a nonproportioned batch process on an otherwise identical recipe. The recipe used in this system is shown below and is reasonably typical for the preparation of vinylidene chloride copolymer latexes.

Water	180
Vinylidene chloride	78
Vinyl chloride	22
Potassium persulfate	0.22
Sodium bisulfate	0.11
Aerosol MA (80%) (Dihexyl sodium sulfo-succinate)	3.58
Nitric acid (69%)	0.07

4. *Physical Characteristics*

The homopolymer of vinylidene chloride and copolymers comprised principally of vinylidene chloride are thermoplastic in nature, but differ from other thermoplastics in their strong tendency to crystallize. The high softening temperatures and relatively sharp melting points of the crystalline resins markedly affects the processing characteristics and physical properties of the polymers.

The crystallinity of polyvinylidene chloride is due to its regular molecular structure, which coupled with chain linearity results in lattice-like chain packing. Staudinger concluded that polymeriza-

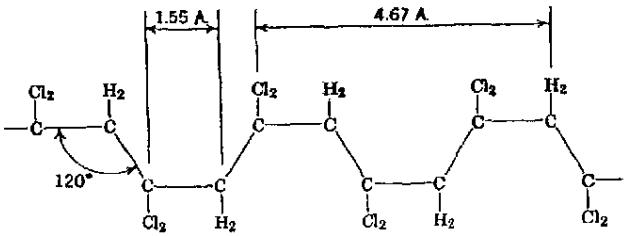

Fig. 4. Chain structure of polyvinylidene chloride.

tion occurs exclusively in a head-to-tail manner (276). Later workers (114,240) assigned the configuration shown in Figure 4 as the most probable chain structure and suggested a serpentine arrangement of the carbon atoms.

In this arrangement, with a carbon valence bond angle of 120° and a carbon to carbon distance of 1.55 A., an identity period of 4.67 A. results and is in agreement with observed values. Other chain conformations such as the planar zigzag or the trough arrangement proposed by German investigators (179) require orientation of the C–Cl dipoles in an energetically unstable configuration. Based on x-ray analysis, the unit cell of polyvinylidene chloride is described as monoclinic and has the following dimensions (240):

a	$= 13.69 \pm 0.05$ A.
b	$= 4.67 \pm 0.01$ A.
c	$= 6.296 \pm 0.010$ A.
$\sin \beta$	$= 0.8212 \pm 0.015$ A.
Volume of cell	= 330.6 A.

Polyvinylidene chloride and its copolymers are obtained in a partially crystalline state in which the polymer chains in the amorphous regions are randomly distributed. Areas of crystallinity or lattice-like packings of molecular segments occur as poorly defined centers, with the long-chain molecules traversing both crystalline and amorphous regions. The extent of crystallinity in such polymers is affected by the amount of comonomer and by the nature of the comonomer, but even in the most highly crystalline samples the amorphous regions constitute the continuous phase. Small amounts of comonomer cause only minor discontinuity in crystalline areas, but as the amount is increased the reduced ability of the polymer to exist in uniformly packed lattices decreases the number of crystalline centers and the polymer becomes more amorphous. The nature of the comonomer is also important. Copolymerization with monomers containing bulky side chains, such as butyl acrylate or styrene cause much more severe geometric limitations to the formation of crystalline areas than more compact comonomers such as vinyl chloride.

On application of heat the polymer softens, and a few degrees above the softening point a sharp reproducible crystalline melting point may be observed by the use of crossed polaroids. At this point sufficient thermal energy has been supplied to the crystallites to destroy the cohesive bonding forces and a totally amorphous, low viscosity polymer melt develops. If this melt is quickly chilled it will remain amorphous for a period of time determined mainly by the temperature, and to a lesser extent, by copolymer composition and amount of plasticizer. The relation of temperature to the crystallization induction period, or time that the polymer remains totally amorphous, was reported by Reinhardt (240) and is reproduced in Figure 5.

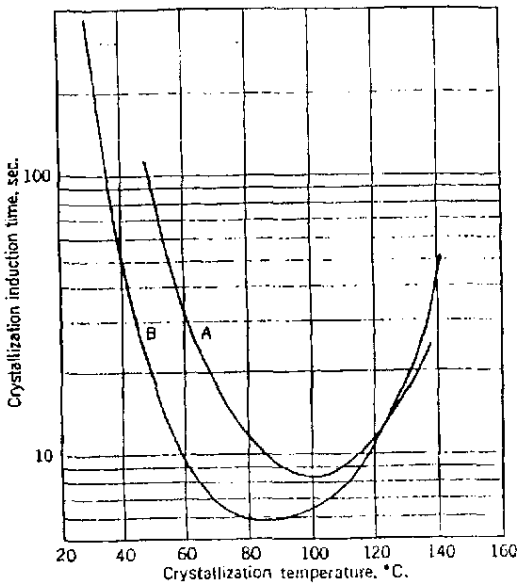

Fig. 5. The effect of temperature on the crystallization rate of a typical crystalline vinylidene chloride–vinyl chloride copolymer.

It is interesting that a plasticized compound (curve B) has a shorter induction period than the same compound without plasticizer. The effect is due to the increased chain mobility provided by the plasticizer which allows the polymer chains to slip more readily into positions of alignment. Above 150 to 160° or the crystalline melting

point of the particular copolymer, no recrystallization occurs because of high molecular activity. At temperatures of 30° or below, the polymer mass is supercooled and crystallite growth is essentially stopped by high internal viscosity.

The transition of polyvinylidene chloride and its copolymers from the amorphous state to the crystalline modification causes marked changes in the physical properties of the polymer mass. The polymer becomes harder, more dense and much more resistant to plastic deformation. The chemical resistance of the material to solvents increases and a change is observed in electrical conductivity. The heat of crystallization for the transition has been measured as 3.5 cal./g.

The ability of polyvinylidene chloride and its copolymers to be cold-worked while in an amorphous state makes them unique among thermoplastics and forms the basis for the production of many commercially important products. Vinylidene chloride copolymers can be stretched and oriented somewhat while at temperatures higher than their crystalline melting points, but if the polymer is first supercooled and then worked, a high degree of orientation results. The effect of the orientation is to create molecular alignment parallel to the direction of force. The lateral order so created extends existing crystalline regions and places polymer chains in positions conducive to the formation of new areas of crystallinity. The growth of crystallinity in specimens of polyvinylidene chloride oriented 200–250% manifests itself by slight additional elongation without application of additional load. Although this phenomenon attributable to additional molecular alignment through Brownian movement can occur in all linear polymers containing lateral bonding capacity, the effect is most pronounced with polymers of vinylidene chloride.

Polyvinylidene chloride and copolymers which are predominantly vinylidene chloride exist in three distinctly different modifications. The polymer as prepared is semicrystalline with a continuous amorphous phase indicated by an x-ray pattern of sharply defined concentric rings on a diffuse background. The supercooled amorphous modification has a poorly defined x-ray pattern, characteristic of randomly distributed systems, while the highly oriented and internally crystallized modification has the sharply defined spot pattern characteristic of crystalline materials. The x-ray diffraction patterns of even the most crystalline modification show some background scattering. This is due to the fact that although in principle the polymeric chains have sufficient regularity to completely crystallize, they never do. Crystallization starts at many random points throughout the polymer mass and grows from these points rather than from a single point. The crystalline areas grow against each other in a random fashion, and are connected by regions which must therefore remain noncrystalline for purely geometric reasons.

5. *Heat Stability*

Polymers and copolymers of vinylidene chloride have remarkable stability to the degradative effects of sunlight, but at temperatures above 100°C. they are thermally unstable and turn yellow on aging. At higher temperatures thermal decomposition proceeds with the evolution of hydrogen chloride. This effect is accelerated by the influence of certain metals such as iron. Boyer (24) proposes that the random loss of a molecule of hydrogen chloride from the polymer chain causes the chlorine atom adjacent to the newly formed double bond to acquire the activity of an allylic chlorine. This eases the departure of another molecule of hydrogen chloride from the chain with the formation of another double bond. Once started the process continues and a polyene sequence of alternating double bonds is formed. The length of the sequence determines the intensity of color formed. A completely satisfactory explanation of the initiating mechanism for hydrogen chloride elimination has not been made. Possible sites of initiation exist at the unsaturated ends of chains terminated by chain transfer. Other potential sites of instability are the tertiary carbon atoms which may be present due to branching or oxygen bridging, or the double bonds present along the polymer chain due to hydrogen chloride elimination during fabrication (278). Copolymerization with a stable comonomer is reported to be an effective means of increasing heat stability, or at least minimizing color formation. A monomer, such as ethyl acrylate, present in the vinylidene chloride chain acts as a block to autocatalytic dehydrohalogenation and effectively shortens the length of the color-contributing polyene sequences. Such comonomers also lower the softening temperature of the polymer and contribute to heat stability by decreasing the working temperature.

Nonpolymerizable heat stabilizers may also be used effectively to minimize discoloration due to hydrogen chloride elimination re-

actions. Typical of the compounds used for this purpose are bis alpha methyl benzyl ether and glycidyl phenyl ether. The former is thought to form styrene at elevated temperatures which stabilizes the polymer molecule by reacting with labile groups to prevent elimination of hydrogen chloride. Compounds containing oxirane groupings such as glycidyl phenyl ether and many other basic organic compounds are thought to act as HCl acceptors. It is uncertain why hydrogen chloride acceptors stabilize these polymers. Hydrogen chloride has been thought by many workers to catalyze dehydrochlorination, while others have shown that thermal decomposition proceeds even when conditions are such that it cannot accumulate (123). Whatever the mechanism is, basic compounds are good heat stabilizers if they react irreversibly with hydrogen chloride, and if they are not so strong that they strip hydrogen chloride from the polymer chain.

6. *Processing*

Many of the commercially available copolymers of vinylidene chloride may be processed in conventional equipment, with minor modifications necessitated by their low melt viscosity, corrosive nature, and relatively poor thermal stability. Monofilaments, rods, tubes, and films may be prepared by extrusion. Injection molding and compression molding are also used, although injection molding is of more commercial importance. Other fabrication techniques such as vacuum forming, transfer molding, calendering, and various coating procedures are also employed.

Extrusion of vinylidene chloride copolymers should be made in equipment constructed of nonferrous metals in all heated areas contacting the resin. Iron catalyzes dehydrohalogenation very quickly resulting in severe fouling and corrosion of heated parts. Nickel, Hastelloy D, Duranickel, Xaloy 306, Stellite 10, magnesium alloys and nickel plate are recommended materials of construction for screws, dies, breaker plates, and cylinder liners.

The rather narrow temperature range between the crystalline melting point and the decomposition temperature makes a careful temperature program desirable in any type of thermal processing of this plastic. In extrusion and injection molding equipment, heating and cooling are best controlled by oil or steam jacketing. Electrical heaters may be used, but the response of such systems to temperature

adjustments is relatively slow. The heat sensitivity of the polymer also makes a shorter than usual screw design desirable, and the low thermal conductivity of the hot melt requires volumes to be kept small in the interest of uniform melting. Care should also be taken to design a highly streamlined fluid flow path to eliminate the formation of pockets where holdup can occur and result in thermal degradation of the polymer because of excessive residence time.

Extruded articles which do not require orientation such as chemically resistant pipe or rods emerge in a soft, rubbery state from the extruder, but may be quickly hardened by passing through a heated (60–100°C.) crystallizing zone. The length and temperature of heating necessary for recrystallization depends primarily on the composition of the copolymer.

Monofilaments, films, tapes, and other articles are frequently quenched after extrusion by immersion in cold water. This maintains the extrudate in an amorphous state and permits subsequent cold-working. Withdrawal of the soft, flexible, amorphous filament or tape over take-up rolls moving at carefully controlled but different speeds partially aligns the crystallites along the axis of orientation and causes a sharp increase in the tensile strength of the object. Heat treatment during the stretching process or at some other time while the extrudate is under tension is frequently used to "heat set" or preshrink the product. The cross-sectional area of the extruded tape or filament is directly related to the extent of elongation and can be controlled by the amount of stretching applied.

Biaxial orientation of films is necessary so that the product will have strength in all directions. Flat film extrudates may be oriented by a rolling operation applied after the quenching step, but only limited transverse orientation is obtained in this way. A more satisfactory technique involves simultaneous mechanical stretching along and transverse to the axis of withdrawal.

A commercially important way to prepare biaxially oriented film was described by Stephenson (285). The procedure involves extrusion of the copolymer in tubular form into a quenching bath where it is supercooled. Some control over wall thickness and diameter of the extruded tube as well as lubrication of its interior surface, is obtained by maintaining a constant head of oil in the tubing between the die orifice and a set of pinch rolls located in the cooling bath below the extruder die. The flattened tubing is then passed from the bath

to two sets of pinch rolls arranged so that the first set of rolls is traveling at a slower speed than the second set. Compressed air is introduced into the tubing at some point between the two sets of rolls. The injection is made with a hollow needle connected to a compressed air supply, and enough air is injected to blow a bubble of sufficient diameter to provide the desired degree of transverse orientation. It is important in this process that the extruded tubing be of uniform wall thickness and free of wall defects caused by poor die design. The bubble is flattened as it passes through the second pair of pinch rolls. The biaxially oriented film may then be passed through a programmed heat cycle to provide the film with the desired shrink characteristics. The final steps in the process are a slitting operation and winding of the finished film on rolls. A process of this type is used by Dow Chemical Co. to prepare "Saran Wrap."

Copolymers of vinylidene chloride may be compression molded although injection molding is a much more frequently used process. As in extrusion equipment, nonferrous metals are recommended for all heated parts in contact with the melted resin and careful streamlining should be employed to avoid polymer hold up. Conventional metals can be used in the dies because they can be operated either cold or hot. If the polymer is extruded into cold dies, it remains amorphous and can be reworked after ejection. Injection into heated dies speeds crystallization and hardening of the object, making shorter operating cycles possible. The ejected finished objects are strain-and warp-free, and dimensionally stable.

7. *Applications*

The literature reports a large and varied number of copolymers and terpolymers which are composed of more than 50% vinylidene chloride but only three basic types of copolymers have become commercially important. These are the copolymers of vinylidene chloride and vinyl chloride, vinylidene chloride and acrylonitrile, and certain copolymers and terpolymers containing alkyl acrylates. The copolymers containing vinyl chloride and those containing acrylonitrile are marketed by the Dow Chemical Co., while copolymers containing alkyl acrylates are manufactured by National Starch and sold as aqueous dispersions. The Dewey & Almy Division of W. R. Grace markets a latex which is thought to contain a high level of vinylidene chloride copolymerized with acrylonitrile and an acrylic ester.

Vinylidene chloride copolymers are odorless, tasteless, nontoxic, and flame-resistant. Toughness and abrasion resistance contribute to excellent wear properties. Oriented filaments, fibers, and films have tensile strengths of between 8,000 and 60,000 psi, depending on composition and the degree of orientation. Films of Saran are noted for their sparkling clarity and excellent vapor barrier properties. The molecular weight of commercial copolymers varies somewhat depending on composition but is generally thought to be around 20,000, with a maximum softening temperature in the range of 140°C.

Filaments and Fibers. Vinylidene chloride–vinyl chloride copolymers (Saran) are sold by Dow Chemical Co. for extrusion of monofilaments, multifilaments and fine fibers, and for extruded tubing, sheeting, and film. The resins are generally sold as compounds, containing plasticizer, heat and light stabilizer, and, in some cases, fillers and pigments. Filaments are used in the manufacture of high-quality outdoor furniture, automobile seat covers, and in practically indestructible window screening. Monofilaments and multifilaments are also used in carpeting, grill cloths, venetian blind tapes, acid-resistant filter cloths, dolls' hair, awnings, draperies, and bristles.

Molded Products. Injection-molded Saran parts achieved some prominence during the war years as replacements for strategic metals. Spray-gun handles with excellent solvent resistance were used in place of aluminum. Valve seats of Saran had superior abrasion resistance and seating qualities. Spinneret couplings and other parts for the rayon industry were chemically inert and replaced hard rubber.

Injection-molded parts still have certain specialty applications, but the total volume produced is small.

Film. The film market represents the largest outlet for vinylidene chloride–vinyl chloride copolymers. Basically, two types of film are sold. The familiar "Saran Wrap" contains about 15% copolymerized vinyl chloride, while films used in applications where greater heat shrinkage is desired probably contain up to 30–35% vinyl chloride. Both types of film are prepared by the blown film extrusion technique and are biaxially oriented.

Saran Wrap is offered by Dow Chemical Co. in several types, differing in transparency, surface, composition and shrinkage characteristics. For example, Saran Wrap 5 has the greatest cling and transparency, while Saran Wrap 17, with a rougher surface is intended

for machine overwrapping. The high vinylidene chloride content and crystalline nature of Saran Wrap makes the film highly resistant to oils and greases and useful for the packaging of a large variety of food products including cheese and other oleaginous products. The moisture and gas permeability of the film is lower than that of any other polymeric packaging film making it a superior overwrap where moisture retention is desired.

IX. Copolymers of Vinylidene Chloride and Acrylonitrile Protective Coatings

Copolymers of vinylidene chloride with acrylonitrile are used in protective coatings where moisture impermeability, chemical resistance, and solubility are important. They are sometimes modified with lesser amounts of other monomers to provide special properties such as adhesion to the coated object. The coatings are applied by solvent evaporation. Dispersion resins used for protective coatings do not need to be highly soluble and are usually copolymers with vinyl chloride or acrylic esters.

Aqueous dispersions, or emulsions, are supplied with a solids content of up to 50% by at least three manufacturers and are used mainly for paper coating, and to a lesser extent for cellophane coating and specialty paint applications. Dispersion coatings may be applied to the desired substrate by spray, dip, roller, doctor blade, and brush. They may be lightly plasticized to ease particle coalescence during the drying step. Small amounts of surface active agents are sometimes added to aid in wetting the substrate to ensure a continuous coating and a good surface bond. Additives should be held to a low level to prevent spewing and to maintain the efficiency of the polymer as a vapor barrier. Unfilled and unpigmented coatings dry on application of heat to a clear, glossy, tough film. Opaque and colored finishes may be obtained by the incorporation of suitable fillers and colorants and applied by similar procedures.

Vinylidene chloride–acrylonitrile copolymers are soluble in a number of inexpensive organic solvents providing the vinylidene chloride content of the polymer is not too high. Resins comprising 90% vinylidene chloride and 10% acrylonitrile are used in large volume for cellophane coating and in other applications where a very efficient moisture vapor barrier is required. The copolymers are readily soluble in tetrahydrofuran at room temperature and may be dissolved in methyl ethyl ketone at higher temperatures. As the vinylidene chloride content of the copolymer is decreased the resins become more soluble in ketones and other solvents. The moisture impermeability of the resin also decreases due to the increasing morphological disorder of the deposited film.

Solvent coatings may be applied in the same general way as the dispersion coatings. Preparation of the substrate material before the coating is applied is critical if satisfactory bonding is to be obtained. Concrete should be pretreated with a polysulfide rubber to ensure the integrity of the polyvinylidene chloride coating (59). Before steel items such as marine ballast and fuel tanks are coated, the metal should be carefully sandblasted. The coatings should be applied in thin layers to minimize pinhole formation which can be a problem in heavy films due to the slow solvent release of the impermeable resin film. Additional layers of coating should then be applied until the desired coating weight is obtained.

Polyvinylidene chloride coatings are costly because of their high density and relatively low solids content when applied from solvents. Substrate pretreatment and priming are also expensive. These problems are balanced by the high level of protection provided by relatively thin coatings.

X. Markets for Vinylidene Chloride Copolymers

The present market picture for copolymers based on vinylidene chloride is not clear. Most of the commercially available resins are produced by one manufacturer and consumption data are not included in the figures of the U. S. Tariff Commission. The following table, however, is thought to represent a reasonable estimate of production of such copolymers in 1963.

Production of vinylidene chloride copolymers

Use	Production (Millions of lb.)
Filament	8
Film	15
Shrinkable film	30
Coatings	20
Extrusions	3
Other	6
	82

TABLE IIIA
Copolymers of Vinylidene Chloride[a] (Excluding Vinyl Chloride)

Type	Ref.
Aromatic Compounds	
Allyl carbonate derivatives of aromatic hydroxy esters	318
Diallyl phthalate	262
Diesters of tetrahydro-*endo*methylene phthalic acid	280
9-Methylene fluorene	74
3-Methylene phthalide	57
Styrene and derivatives	29,35,101
Heterocyclic Compounds	
N-Isopropenyl derivatives of 2-oxazinones and 2-oxazolidinones	14
N-2-Norcamphanyl acrylamides	36
Vinylfuran	44,151
Vinyl oxazolidinone	129
Miscellaneous Compounds	
Acrylonitrile	17,18,26,82,118, 124,178,192,207–209,230,303
Aliphatic epoxides	275
Alkenyl silanes	234
Allyl-3,4-epoxy-2-hydroxybutyrate	153
Allyl esters of dicarboxylic acids	28
Butadienes	137,254,304
1,1-Dichloro-1,3-butadiene	62
N-Fluoroalkyl-*N*-vinyl amides	50
N-Hydroxymethyl maleimide	290
Isopropenyl isocyanate	143
β-Methylene-β-propiolactone	46
2,4,6-Triallyl-1,3,5-tricyclohexylborazine	125
2,4,6-Trivinyl-1,3,5-tricyclohexylborazine	227
Unsaturated esters of halo derivatives of acetic acid	30
Unsaturated ketones	140
Vinyl compounds (general)	286
Vinyl isocyanate	144
Vinylidene cyanide	109,117

(continued)

Best available data indicate that the filament market is declining because of competition from polypropylene, especially in outdoor furniture and automobile seat covers.

Saran film marketed by Dow as "Saran Wrap" is believed to be

TABLE IIIA *(continued)*

Type	Ref.
Olefinic Compounds	
Chlorotrifluoroethylene	134,107,174
Ethylene	86
Fluoroprene	139
Isobutylene	15,31,70,85,281, 282
Haloolefins (general)	169
Olefins (general)	115
Tetrafluoroethylene	128,141
3,3,3-Trifluoropropene	22
Unsaturated Acids and Esters	
Alkyl acrylates	79,88,104,148–150, 177,191,259,312, 317
Alkyl methacrylates	19,79,104,317
Allyl acrylate	261
Diamidophosphoroacrylates	56
Ethyl fumarate	313
Methyl 2-chloroacrylate	331
Sodium sulfopropyl acrylate	80
Trialkyl aconitates	198
Vinyl isothiocyanate	147
Vinyl Esters	
Butyl vinyl sulfonate	226
Vinyl acetate	168,264
Vinyl 3-alkoxybutyrates	25
Vinyl esters of carboxylic acids (general)	146,197
Vinyl Ethers	
Dodecyl vinyl ether	206
Trifluoroethyl vinyl ether	249

[a] Limited to those copolymers containing at least 50% vinylidene chloride.

declining in volume because of competition from less expensive polyethylene wrapping materials. These have inferior barrier properties but are apparently satisfactory in noncritical household applications. Industrial film is apparently growing in volume. Such film is used to overwrap cheese, meat, and candy.

Shrinkable film which generally contains higher levels of vinyl

TABLE IIIB
Terpolymers of Vinylidene Chloride[a]

Second Monomer	Third Monomer	Ref.
Acrylates or acrylonitrile	Isopropenyl acetate	58
Acrylic or methacrylic acid	Vinyl or acrylate esters	225
Acrylonitrile	Butadiene	273
	Methyl methacrylate	170
	α-Methylstyrene	272
	Vinylidene chloride	266
	5-Vinyl-2-picoline	236
α-Alkyl acrylates	Vinyl chloride	48
Alkyl maleates	Vinyl esters	107
Allyl chloride	Diallyl fumarate	289
1,3-Butadiene	Chloroprene	45
Butadiene	Ethyl acrylate	271
	Isobutylene	267
	Methyl methacrylate	274
	α-Methylstyrene	270
	Styrene	333
	Vinyl acetate	268
	Vinyl chloride	269
	Vinyl compounds	190
N-2-Formamidoethylacrylamide	Vinyl chloride	73
Isobutylene	Polymerizable substances	283
1-Chloro-1-bromoethylene	Vinylidene bromide	314
Glycidyl methacrylate	(2-Methacryloyloxyethyl) diethyl ammonium methyl sulfate	311
Methyl acrylate	Trichloroethylene	152, 219
	Vinyl chloride	202
Styrene	Vinyl chloride	16
Vinyl halides	Acrylic or methacrylic compounds	67
	TETRAPOLYMER	
Acrylic acid	Acrylonitrile Methyl methacrylate	99

[a] Limited to those copolymers containing at least 50% vinylidene chloride.

chloride than the Saran Wrap type shows good growth, especially for poultry packaging. This film is presently produced by the Dobeckman Division of Dow as Saran S and by Dewey and Almy Chemical Co. as Cryovac S. The films are usually supplied as bags and may be shrunk tightly around the packaged object by the application of heat.

Solution copolymers are slowly continuing to grow in volume mainly due to their increasing use as a moisture vapor barrier on cellophane. Dispersion coating of paper used to manufacture milk cartons, drinking cups, and other packaging materials which require protection from grease or oil is relatively new, and faced with the problem of penetrating the established market for polyethylene latexes. Some growth seems reasonable in applications where superior barrier properties are required.

A new use for polyvinylidene chloride copolymer emulsions was recently revealed by the Dow Chemical Co. The product is called Sarabond and the material shows growth potential in high bond masonry mortars. Dow claims that use of the new product will permit construction of high strength brick walls and other masonry assemblages of only half normal thickness thus more than offsetting the higher cost of the mortar over conventional cement-lime sand mortars.

XI. Other Copolymers Predominantly Vinylidene Chloride

As mentioned above, the only commercially important copolymers of vinylidene chloride are those containing vinyl chloride, acrylonitrile, and certain alkyl acrylates or methacrylates. Many other copolymers, terpolymers, and even more highly complex interpolymers are described in the patent literature intended for highly specific applications. As an example, a patent assigned to E. I. duPont (246) describes a dispersion coating resin prepared by the conjoint polymerization of vinylidene chloride, maleic anhydride, acrylonitrile, 2-ethyl hexyl acrylate, isopropenylacetate, acrylic acid, and methyl acrylate. The principal component of the resin was vinylidene chloride (90%). It was intended as a dispersion coating for cellophane. Ternary interpolymers of vinylidene chloride, butadiene, and ethyl acrylate are described in another patent (273). The resins are vulcanizable, rubberlike materials useful as abrasion-resistant and moisture-impermeable coatings. Still other patents describe alkyl acrylate modified vinylidene chloride, vinyl chloride interpolymers which are useful for the preparation of unsupported film (71).

A list of copolymers and more complex interpolymers of vinylidene chloride is contained in Table III. The table omits the large number of references pertaining to copolymers of vinylidene chloride with vinyl chloride or acrylonitrile.

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