*Encyclopedia of Polymer Sceince and Technology*

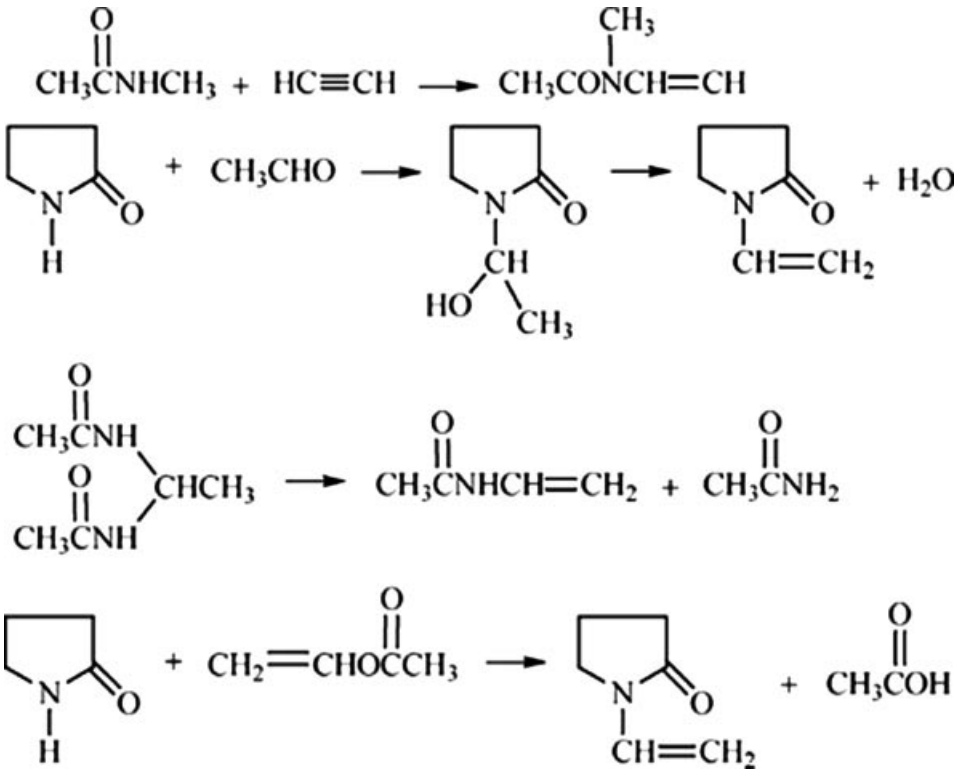

# *N*-VINYLAMIDE POLYMERS

## Introduction

*N*-Vinylamide-based polymers, especially the *N*-vinyllactams, such as poly(*N*-vinyl-2-pyrrolidinone) [9003-39-8] or simply polyvinylpyrrolidinone (PVP), continue to be of major importance to formulators of personal-care, pharmaceutical, agricultural, and industrial products because of desirable performance attributes and very low toxicity profiles. Because of hydrogen bonding of water to the amide group, many of the *N*-vinylamide homopolymers are water soluble or dispersible. Like proteins, they contain repeating (but pendant) amide (lactam) linkages and share several protein-like characteristics (1). Many studies have actually employed PVP as a substitute for proteins, eg, in simplifying the chemistry of the effects of radiation on polymers (2). Proteins are extremely complicated molecules with not only sequence distribution but tertiary bonding and structural complexity and it is an oversimplification to compare them to PVP, but the effects of radiation on PVP can be more readily studied. PVP can even be considered as a uniform synthetic protein-like analogue. By itself it does not enter into intermolecular hydrogen bonding, thus affording low viscosity concentrates, and also, unlike the proteins, PVP is soluble in polar solvents like alcohol. But even given these differences, the chemistry of PVP, the most commercially successful polymer of the class, is in many respects similar to that of proteins because of amide linkages sharing with them complexation to large anions such as polyphenols, anionic dyes, and surfactants. In addition to the ability to complex, PVP and its analogues along with a large assortment of copolymers are excellent film formers. They exhibit the ability to interact with a variety of surfaces by hydrogen or electrostatic bonding, resulting in protective coatings and adhesive applications of commercial significance such as hair-spray fixatives, tablet binders, disintegrants, iodophors, antidye redeposition agents in detergents, protective colloids, dispersants, and solubilizers, among many others.

## Monomers

*N*-Vinylamides and *N*-vinylimides can be prepared by reaction of amides and imides with acetylene (3), by dehydration of hydroxyethyl derivatives (4), by pyrolysis of ethylidenebisamides (5), or by vinyl exchange (6), among other methods; the monomers are stable when properly stored.



Poly *N*-vinyl-2-pyrrolidinone (VP) [88-12-0] is of significant commercial importance and hence is the principal focus of this article. Vinylcaprolactam is available (BASF) and is growing in importance, and vinyl formamide is available as a developmental monomer (Air Products). Some physical properties are given in Table 1.

***N*-Vinyl-2-Pyrrolidinone.** Commonly called vinylpyrrolidinone or VP, *N*-vinyl-2-pyrrolidinone was developed in Germany at the beginning of World War II. It is a clear, colorless liquid that is miscible in all proportions with water and most organic solvents. It can polymerize slowly by itself but can be easily inhibited by small amounts of ammonia, sodium hydroxide (caustic pellets), or

**Table 1. Physical Properties of Selected Vinylamides and Vinylimides**

| Compound | CAS Registry Number | Bp, °C$_{kPa}$[a] | Mp, °C |
|---|---|---|---|
| *N*-Vinylacetamide | [5202-78-8] | 107–109 | |
| *N*,*N*-Methylvinylacetamide | [3195-78-6] | $70_{3.3}$ | |
| *N*-Vinylacetanilide | [4091-14-9] | $102–105_{0.13}$ | 52 |
| *N*-Vinyl-2-piperidinone | [4370-23-4] | $125–126_{3.3}$ | 45 |
| *N*-Vinylcaprolactam | [2235-00-9] | $129–130_{2.7}$ | 34.5 |
| *N*-Vinylphthalimide | [3485-84-5] | $128–130_{3.3}$ | 86.5 |
| *N*-Vinyl-2-oxazolidinone | [4271-26-5] | $77–78_{0.067}$ | |
| *N*-Vinyl-5-methyl-2-oxazolidinone | [3395-98-0] | $105–108_{0.33}$ | |

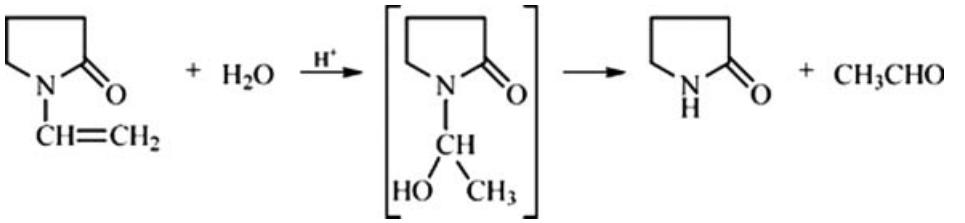
[a] To convert kPa to mmHg, multiply by 7.5. Pressure = 101.3 kPa (760 mmHg) if not shown.

**Table 2. Properties of *N*-Vinyl-2-Pyrrolidinone (Commercial Production)**

| Property | Value |
|---|---|
| Molecular wt. | 111 |
| Assay, % | 98.5[a] |
| Moisture content, % | 0.2[b] |
| Color (APHA) | 100[b] |
| Vapor pressure, Pa[c] at | |
| 17°C | 6.7 |
| 24°C | 13.3 |
| 45°C | 67 |
| 54°C | 133 |
| 64°C | 266 |
| 77°C | 667 |
| Boiling point at 400 mmHg | 193 |
| Freezing point | 13.5 |
| Flash point (open cup) | 98.4 |
| Fire point | 100.5 |
| Viscosity at 25°C, mPa·s (=cP) | 2.07 |
| Specific gravity (25/4°C) | 1.04 |
| Refractive index, $n^{25}{}_{D}$ | 1.511 |
| Solubility | Completely miscible in water and most organic solvents, including methanol, ethyl acetate, methylene chloride, ethyl ether, and hydro-carbons in general |
| Ultraviolet spectrum | No significant absorption at wavelengths longer than 220 nm |

[a]Value is minimum.
[b]Value is maximum.
[c]To convert Pa to mmHg, multiply by 0.0075.

antioxidants such as *N,N′*-di-*sec*-butyl-*p*-phenylenediamine. It is stable in neutral or basic aqueous solution but readily hydrolyzed in the presence of acid to form 2-pyrrolidinone and acetaldehyde. Properties are given in Table 2.




Commercially available VP is usually over 99% pure but does contain several methyl-substituted homologues and 2-pyrrolidinone. Even at this high level of purity, further purification is required if reliable kinetic data concerning rates of polymerization are desired. This can be accomplished only by recrystallization, because distillation will not separate methyl-substituted isomers (7).

*Manufacture.* The principal manufacturers of *N*-vinyl-2-pyrrolidinone are ISP and BASF. Both consume most of their production captively as a monomer for the manufacture of PVP and copolymers. The vinylation of 2-pyrrolidinone is carried out under alkaline catalysis analogous to the vinylation of alcohols. 2-Pyrrolidinone is treated with ca 5% potassium hydroxide, then water and some pyrrolidinone are distilled at reduced pressure. A ca 1:1 mixture (by vol) of acetylene and nitrogen is heated at 150–160°C and ca 2 MPa (22 atm). Fresh 2-pyrrolidinone and catalyst are added continuously while product is withdrawn. Conversion is limited to ca 60% to avoid excessive formation of by-products. The *N*-vinyl-2-pyrrolidinone is distilled at 70–85°C at 670 Pa (5 mmHg) and the yield is 70–80% (8).

*Shipment and Storage; Specifications.* *N*-Vinyl-2-pyrrolidinone is available in tank cars and tank trailers and in drums of various sizes. Shipping containers are normally steel or stainless steel. Tank cars are provided with heating coils to facilitate unloading in cold weather. Rubber, epoxy, and epoxy–phenolic coatings are attacked and must be avoided. Carbon steel has been successfully used for storage tanks, but stainless steel preserves product quality better. Aluminum and certain phenolic coatings are also satisfactory.

*Toxicity Data on N-Vinyl-2-Pyrrolidinone.* Results of a chronic inhalation study in rats warrant a review of industrial hygiene practices to assure that VP vapor concentrations are maintained at a safe level. One of the manufacturers, ISP, recommends that an appropriate workplace exposure limit be set at 0.1 ppm (vapor) (9). Additionally, normal hygienic practices and precautions are recommended, such as prompt removal from skin and avoidance of ingestion. In case of accidental eye contact, immediately flush with water for at least 15 min and seek medical attention. Refer to the manufacturers' Material Safety Data Sheets for more detailed information. Table 3 provides some toxicity data.

**Table 3. Summary of Toxicity Data for *N*-Vinyl-2-Pyrrolidinone**

| Test | Result |
|---|---|
| Acute oral $LD_{50}$ | 1.5 mL/kg (rats) |
| Acute dermal $LD_{50}$ | 0.56 g/kg (rabbits) |
| Acute inhalation $LC_{50}$ | $700 \pm 100$ ppm(rats) |
| Eye irritation | Severe (rabbits) |
| Primary irritation index (PII) | 0.38 (rabbits) |
| Skin Repeated Insult Patch Test | Not a primary irritant or sensitizer (humans) |
| Subacute inhalation | No gross or clinical abnormal effects; subacute/chronic inflammation of respiratory tract at 16.5 and 66 ppm (rats) |
| Subchronic inhalation | Evidence of liver damage at 15, 45, and 120 ppm; no evidence of toxicity at 1 ppm (rats) |
| Chronic inhalation | Benign and malignant tumors of the nasal mucosa at the 10 and 20 ppm levels; liver tumors noted at 20 ppm |
| Mutagenicity | Negative in a battery of five assays |

## Homopolymerization of *N*-Vinyl-2-Pyrrolidinone

VP was originally polymerized in bulk by heating in the presence of small amounts of hydrogen peroxide. This neat polymerization was a difficult process to work-up, requiring crushing of the solidified polymer mass and extraction with ether to remove unreacted monomer and by-products. However, it was important to the original application as a blood substitute because it afforded low molecular weight (10,11). Low molecular weight is necessary for excretion from the kidneys (12). Bulk polymerization favors the tendency of VP to undergo chain transfer to monomer. Neat VP polymerized with di-*tert*-butyl peroxalate in the presence of a nitroxide scavenger that exclusively traps carbon centered radicals generates considerable nonvinyl radicals by chain transfer (13,14). VP (and presumably PVP) can, under the right circumstances, undergo chain transfer, and this route is more prevalent as the concentration of monomer is increased.

Because VP and PVP are soluble in water, early workers realized that polymerization could be more easily controlled in such a high heat capacity solvent. In the presence of acid, VP readily hydrolyzes, and when initiated with hydrogen peroxide, the pH drops quickly into the acidic range. The problem this presents was solved by buffering with bases. Of all of the bases tried by the early German chemists, ammonia not only prevented hydrolysis by neutralizing acidic by-products, it accelerated the polymerization. The early workers found that with an optimized concentration of monomer and ammonia level, the molecular weight was reproducibly controlled by the hydrogen peroxide level. Even relatively high molecular weight could be achieved by small amounts of hydrogen peroxide, but such levels might easily be compromised by unproductive side reactions. High molecular weight homopolymers are more reliably produced by initiation with organic peroxides and azo initiators.

**Ammonia $H_2O_2$ Initiation.** The lower molecular weight grades (K-15 and K-30) of PVP are prepared industrially with an ammonia/$H_2O_2$ initiation system. Such products are the standards for the pharmaceutical industry and conform to the various national pharmacopeias. Several papers have appeared concerning the mechanism of this polymerization (15).

The proposed rate expression for the ammonia/$H_2O_2$ process is as follows:

$$R_p = k[H_2O_2]^{1/2}[NH_3]^{1/4}[VP]^{3/2} \tag{1}$$

Comparing this to the theoretical expression based on the steady state approximation suggests that the mechanism is not straightforward:

$$R_p = k_p[M]\ \frac{(fkd[I])^{1/2}}{kt} \tag{2}$$

Higher than first order for monomer, such as the 3/2 power suggests that VP is involved in initiation (16). If the efficiency of initiation is a function of the monomer concentration, then $f = f^1[M]$, and substituting in equation 2 gives

$$R_p = k_p[M]^{3/2}\ \frac{(f^1kd[I])^{1/2}}{k_t} \tag{3}$$

The $[I]^{1/2}$ is reflected in $[H_2O_2]^{1/2}$ but $[NH_3]^{1/4}$ can be explained by the finding (17) that the rate of polymerization is proportional to $[NH_4^+]^{1/2}$. If the equilibrium expression for $NH_3/[NH_4^+]$ is solved for $[NH_4^+]$ and this expression substituted, the quarter power for ammonia is apparent.

Several papers (6,18) have appeared that attempt to reconcile the ability of $H_2O_2$ to act as a rather strong transfer agent (hydrogen donor), generating the weakly initiating species $HOO^\bullet$, with its ability to act as a source of $HO^\bullet$ hydroxy radicals that are known to be active vinyl initiators. Such studies demonstrate that $HO^\bullet$ generated by photolysis behaves classically as an initiator for PVP (the rate is, as expected, first order in VP and half order in $H_2O_2$). Polymerization with 2,2′-azobisisobutyronitrile (AIBN) in the presence of $H_2O_2$ demonstrates that $H_2O_2$ in this case acts as a proton donor, reducing molecular weight, suggesting it also functions similarly during $NH_3/H_2O_2$ initiation. Even with other water-soluble initiators, VP behaves classically, with the rate expression being first order in monomer and half order in initiator (19,20). This would indicate that VP is a vinyl monomer with normal behavior and hence the $H_2O_2/NH_3$ initiation system is unusual. The evidence clearly demonstrates that it is a redox initiator system requiring trace amounts of cuprous or ferrous salt (21). Other bases such as NaOH or KOH can be employed to replace $NH_3$ if precautions are taken to sequester these metal ions, preventing them from being deactivated in the redox complex (22).

In one of the few published studies of $H_2O_2$ initiation, it is shown that in the case of methacrylamide, the monomer participates in its own initiation by reacting with $H_2O_2$, forming an intermediate hydroperoxide (23). Subsequently, this hydroperoxide generates hydroxyl radicals capable of initiation. Like that of methacrylamide, VP polymerization is very sensitive to molecular oxygen reacting faster with it than propagation to polymer (18), and a similar reaction might be at work with VP that would be expected to generate an intermediate hydroperoxide capable of entering into a redox initiation system. The proposed mechanism would also explain the formation of 2-pyrrolidinone as a consequence of redox polymerization, dispelling the previous belief that 2-pyrrolidinone was a result of primary radical termination caused by reaction of hydroxyl radicals with the growing chain, followed by hydrolysis of the hemiacetal (24,25) subsequently formed. Hydroxyl radicals afford PVP with one hydroxyl per chain, correlating well with a mechanism that relies on hydroxyl radical initiation and strong $H_2O_2$ chain transfer (26). In this case, one end of the polymer is not an aldehyde but rather a hydroxyl group, and no evidence for other than proton termination could be found, producing a methylene terminus at the other end of the polymer chain. Figure 1 illustrates the proposed mechanism and explains the formation of acidic by-products responsible for the acidic pH drift during polymerization.

## Organic Peroxides and Azo Initiation

The $H_2O_2$/ammonia initiation system is not employed commercially in the manufacture of higher molecular weight homologues; they are prepared with organic initiators. Such polymerizations follow simple chain theory and are usually performed in water commercially. The rate of polymerization is at a maximum in aqueous media at pH 8–10 and at 75 wt% monomer (27,28). Polymerization rates

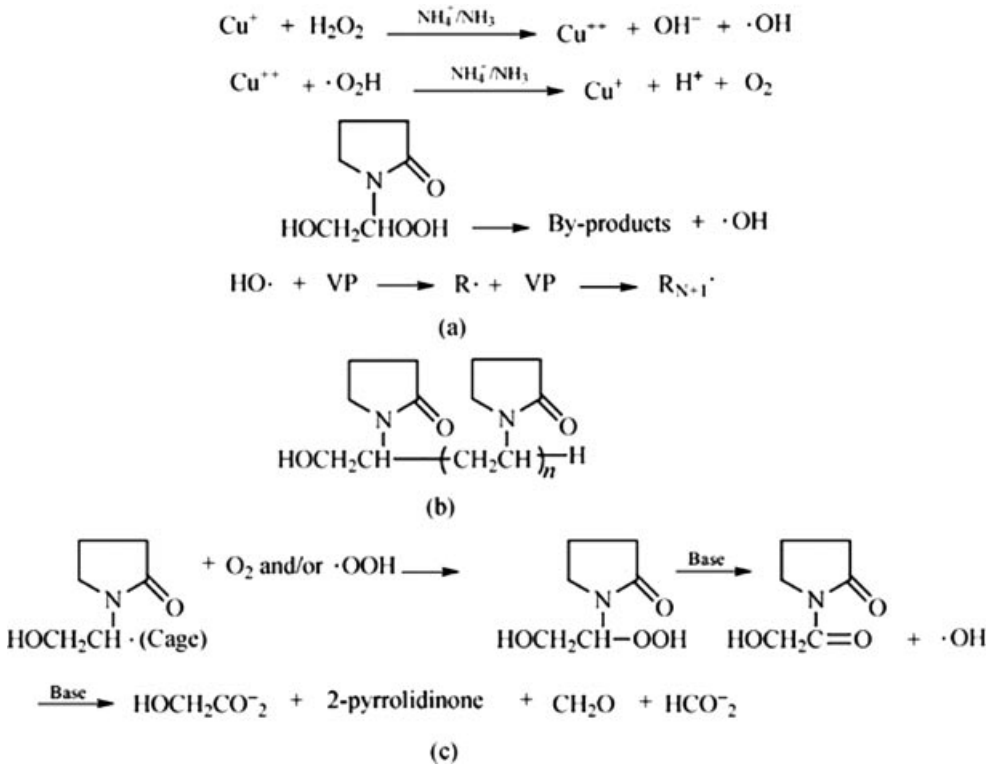



**Fig. 1.** Mechanism of $NH_3/H_2O_2$ polymerization of VP: (**a**) initiation; (**b**) end groups; (**c**) 2-pyrrolidinone generation.

follow the polarity and hydrogen bonding capability of the solvent (29). One possible explanation for this fact is that water is most capable of reducing the apparent negative charge on the beta carbon VP's vinyl group by hydrogen bonding to the pyrrolidinone carbonyl and polar interactions. Such a reduction permits the electron-rich radical terminus to more easily approach another VP and hence allows the acceleration (29). Alternatively, PVP may be somewhat more hydrophobic than VP forming associates ("micelles") capable of enhancing the rate of polymerization by concentrating monomer close to the reacting polymer terminus. This is the reason why even in relatively dilute aqueous solutions the rate can be substantial. The hydrophobic effect accounts for a higher VP concentration at the reactive polymer terminus (30).

**Cationic Polymerization.** VP polymerizes to low molecular weight (oligomers) with typical cationic initiators, such as boron trifloride etherate (31). This reaction requires high concentrations, if not neat, of monomer and scrupulously anhydrous conditions for high yields; VP will readily hydrolyze to 2-pyrrolidinone and acetaldehyde even in the presence of trace moisture when catalyzed by strongly acidic reagents. Pyrrolidinone derivatives apparently complex and deactivate cationic polymerization catalysts and generally present an unfavorable environment for polymerization (32). Thus, initiating species are relatively

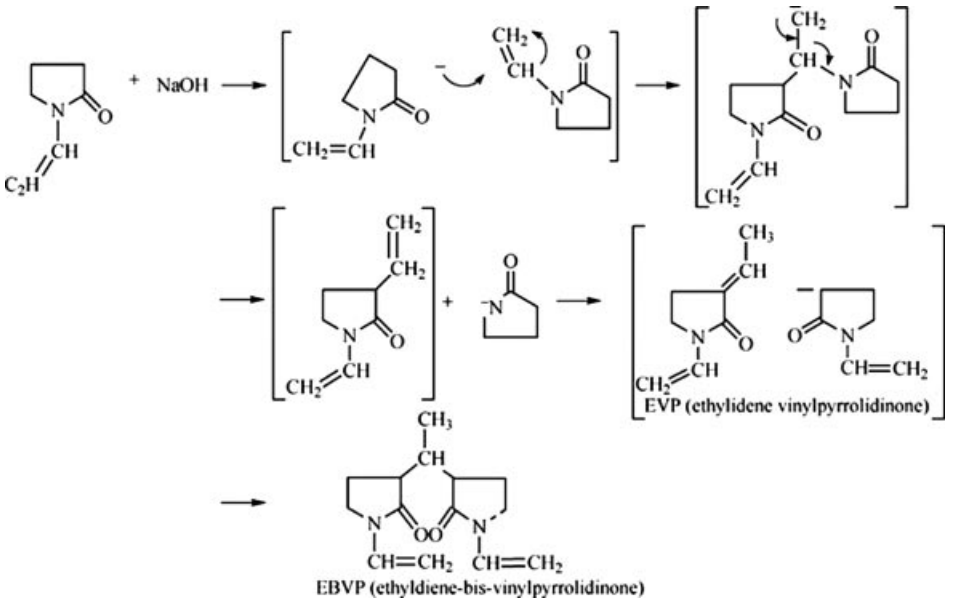
short-lived and readily deactivated, or undergo chain transfer; hence, more than catalytic amounts of initiator are required for high yields.

Interest has been rekindled in cationic polymerization by the discovery that carboxylic acid groups trapped in insoluble matrices like activated carbon or poly(glutamic acid) can generate higher mol wt. polymers (33–35). Additionally, oxoaminium salts (36) derived from 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or anodic polymerization (37) on platinum electrode surfaces will also afford higher molecular weight polymers. Such cationically generated polymers would be expected to afford microstructure and greater tacticity because of the higher activation energy for inversion associated with a growing cationic terminus vs a growing free-radical terminus. Unfortunately, none of the above references present detailed polymer structural characterizations.

**Microstructure.** Interest in PVP microstructure and the potential for tacticity has been reviewed (38,39). PVP generated by free radicals has been shown to be atactic except when polymerization is conducted in water. In this case, some syndiotacticity is observed (39). In the presence of syndiotactic templates of poly(methacrylic acid) (or poly(MAA)), VP will apparently polymerize with syndiotactic microstructure, although proof is lacking (40–44). The reverse, polymerization of MAA in the presence of PVP, affords, as expected, atactic poly(MAA) (45,46).

Advances in VP cationic polymerization hold out the possibility of tacticity, and the study of this route to crystalline homologues continues to be of interest.

**Proliferous Polymerization.** Early attempts to polymerize VP anionically resulted in proliferous or "popcorn" polymerization (47). This was found to be a special form of free-radical addition polymerization, and not an example of anionic polymerization, as originally thought. VP contains a relatively acidic proton alpha to the pyrrolidinone carbonyl. In the presence of strong base such as sodium hydroxide, VP forms crosslinkers *in situ*, probably by the following mechanism:



Both ethylidene vinyl pyrrolidinone (EVP) and ethylidene-bis-vinylpyrrolidinone (EBVP) are generated in about a 10:1 ratio, respectively (24). At the temperature required to generate these cross-linkers and when their concentration reaches some minimum level, usually a few percent, proliferous polymerization begins (48). The same situation can be reached by the addition of a suitable cross-linker (49). Although no initiator is required, the polymerization can be prevented in the presence of typical free-radical inhibitors or initiated by very small amounts of AIBN. Reviews indicate that the rate of polymerization accelerates because the initially formed cross-linked seeds swell to generate active sites by bond homolysis and that growing chains resist termination because of the rigid cross-linked structure. Very high conversions can be achieved and the resulting product, a granular "popcorn" mass, can be freed of residual monomer/soluble polymer by careful washing. Drying results in a free-flowing white powder (50).

Crospovidones are produced commercially by these two processes, ie, *in situ* generation of cross-linker or addition of divinylimidazoline, and they are indistinguishable by ir. Both types exhibit a $T_g$ of 190–195°C, which is not that much above the 175°C of high molecular weight, soluble PVP (24). Proliferous polymers prepared with easily hydrolyzed cross-linker containing an imine linkage do not further swell even when the cross-links are hydrolyzed (49). In order to reach the low swell volume typical of these resins with a typical VP/cross-linker polymerized with free-radical initiator, sizeable amounts of cross-linker are actually required, resulting in much higher (240°C) $T_g$s. The crospovidones are therefore unusually high molecular weight, highly chain-entangled polymers having covalent cross-links that most likely retard the termination reaction during polymerization and are not entirely responsible for the resulting mechanical properties, such as swell ratio. Even hydrolyzing such cross-links is not sufficient to cause dissolution.

The crospovidones are easily compressed when anhydrous but readily regain their form upon exposure to moisture. This is an ideal situation for use in pharmaceutical tablet disintegration and they have found commercial application in this technology. PVP strongly interacts with polyphenols, the crospovidones can readily remove them from beer, preventing subsequent interaction with beer proteins and the resulting formation of haze. The resin can be recovered and regenerated with dilute caustic.

## PVP Hydrogels

Cross-linked versions of Water-Soluble Polymers (qv) swollen in aqueous media are broadly referred to as Hydrogels (qv) and have a growing commercial utility in such applications as oxygen-permeable soft contact lenses (Table 4) and controlled-release pharmaceutical drug delivery devices (51). Cross-linked PVP and selected copolymers fit this definition and are of interest because of the following structure/performance characteristics:

| Structure | Performance | Benefit |
|---|---|---|
| Nonionic | Compatibility with other ingredients | Stable formulation |
| Pyrrolidinone | Low toxicity | Nonirritating/nonthrombogenic |
| | Complexation actives/$O_2$ | Controlled release transport |
| | High $T_g$ | Mechanical stability |
| | Hydrolytic stability | Storage stable |
| Ethylene backbone | Nonbiodegradable, hydrolytic stability | Resists biocontamination storage-stable |
| Cross-links | Swell volume/viscosity | Mechanical stability/diffusion control |

Cross-linked PVP can be prepared by several routes other than proliferous polymerization PPVP (crospovidones). Although a hydrogel, the swell volume of this type of polymer cannot be controlled over a large increment because the granular particles cannot be formed into larger uniform assemblies. These limitations can be overcome by the polymerization of VP in the presence of a few percent of suitable cross-linker utilizing standard free-radical initiation by, for example, AIBN (52–54) or actinic radiation (gamma rays) (55,56). This results in a lightly cross-linked PVP. If the polymerization is carried out incorrectly, significant amounts of uncross-linked soluble polymer may be present that must be removed before a meaningful physical analysis such as swell ratio can be accomplished. The solution to this problem is to balance the reactivity ratios of the cross-linker and other comonomers with those of VP to obtain uniform copolymerization and cross-linking (57,58). Not only does this reduce the level of soluble uncross-linked polymer but affords crystal-clear hydrogels so important for use in contact lenses. Allyl-substituted sugars used to generate cross-linked polyacrylic acid gels,

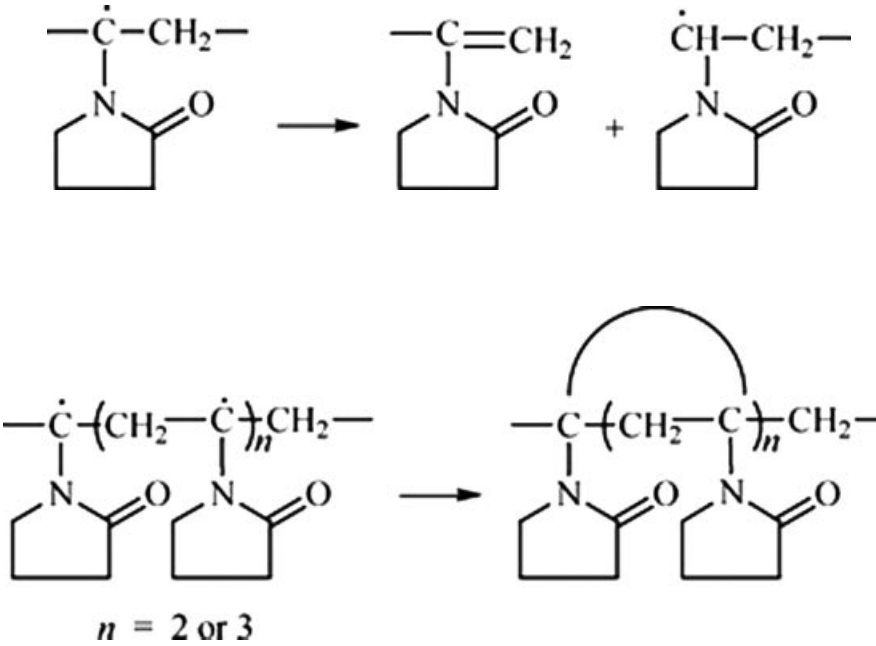
**Table 4. Generic Names of Polymeric Compositions Used in Soft Contact Lenses**

| USAN Generic Name | Polymer composition[a] | Water, % | Trademarks | Manufacturer |
|---|---|---|---|---|
| Droxifilcon-A | Copolymer of HEMA and MA modified with poly(2-vinyl-pyrrolidone) | 47 | Accugel | Strieter Labs |
| Lidofilcon-B | Copolymer of MMA and 2-vinylpyrro-lidone (VP) | 79 | Sauflon PW | American Medical Optics |
| Surfilcon-A | Copolymer of MMA, VP, and other methacrylates | 74 | Permaflex | Cooper Vision, Inc. |
| Tetrafilcon-A | Terpolymer of HEMA, MMA, and VP cross-linked with divinylbenzene | 42.5 | Aosoft Aquaflex | American Optical Corp., Cooper Vision, Inc. |
| Vifilcon-A | Copolymer of HEMA and MA with PVP cross-linked with EGDM | 55 | Softcon | American Optical Corp. |

[a] HEMA, hydroxyethylmethacrylate; EGDM, ethyleneglycoldimethacrylate.

carbomers, employed as thickeners in pharmaceutical formulations, have been shown to work well with VP (59).

Cross-linked PVP can also be obtained by cross-linking the preformed polymer chemically (with persulfates, hydrazine, or peroxides) or with actinic radiation (60). This approach requires a source of free radicals capable of hydrogen abstraction from one or another of the labile hydrogens attached alpha to the pyrrolidone carbonyl or lactam nitrogen. The subsequently formed PVP radical can combine with another such radical to form a cross-link or undergo side reactions such as scission or cyclization (61,62), thus:



$n = 2$ or 3

If the starting PVP homopolymer is too low in molecular weight or too dilute, cyclization or cleavage is preferred (62,63). However, because of the high $T_g$ of PVP, the backbone is sufficiently rigid to avoid reorientation during bond homolysis so that the same bond has a good chance of reforming; hence, PVP yields cross-linked structures in preference to cleavage (64) and PVP hydrogels formed by e-beam have become commercially important for use as conductive electrodes for medical applications (65).

## Poly(*N*-Vinyl-2-Pyrrolidinone)

Poly(*N*-vinyl-2-pyrrolidinone) (PVP) is undoubtedly the best characterized and most widely studied *N*-vinyl polymer. It derives its commercial success from its biological compatibility, low toxicity, film-forming and adhesive characteristics, unusual complexing ability, relatively inert behavior toward salts and acids, and thermal and hydrolytic stability.

First developed in Germany by I. G. Farben (W. Reppe) during the 1930s, PVP was subsequently widely used in Germany as a blood–plasma substitute and extender during World War II (66). In the United States, it has been manufactured since 1956 by ISP, and more recently by BASF.

**Molecular Weight and *K* Value.** Poly(*N*-vinyl-2-pyrrolidinone) is described in the *United States Pharmacopeia* (67) as consisting of linear *N*-vinyl-2-pyrrolidinone groups of varying degrees of polymerization. The molecular weights of PVP samples are determined by size-exclusion chromatography (sec), osmometry, ultracentrifugation, light scattering, and solution viscosity techniques. The most frequently employed method of determining and reporting the molecular weight of PVP samples utilizes the sec/low angle light-scattering (lalls) technique (68,69).

A frequently used and commonly recognized method of distinguishing between different molecular weight grades of PVP is the $K$ value. Its nomenclature is accepted by the USP, FDA, and other authoritative bodies worldwide. The *Pharmacopeia* (USP) specifies that for very low molecular weight, a 5% solution whereas for very high molecular weight, a 0.1% solution be measured. All other molecular weights employ a 1% solution. The relative viscosity is obtained with an Ostwald–Fenske or Cannon–Fenske capillary viscometer, and the $K$ value is derived from Fikentscher's equation (70).

$$\log \frac{\eta_{\text{rel}}}{c} = \frac{75K_{\text{o}}^2}{1 + 1.5K_{\text{o}}c} + K_{\text{o}}$$

where $K = 1000K_{\text{o}}\eta_{\text{rel}}$ = relative viscosity, and $c$ = concentration of the solution in g/100 mL. Solving directly for $K$, the Fikentscher equation is converted to

$$K = [300c \log Z + (c + 1.5c \log Z)^2 + 1.5c \log Z - c]/(0.15c + 0.0003c^2)$$

where $Z = \eta_{\text{rel}}$. Table 5 illustrates a correlation chart where the $K$ value is simply read off from a knowledge of $\eta_{\text{rel}}$.

The intrinsic viscosity $[\eta]$ may be approximated from the Fikentscher equation by

$$[\eta] = 2.303\ (0.001K + 0.000075K^2)$$

where $[\eta]$ = intrinsic viscosity and $K = K$ value of sample.

**Table 5. $K_{\text{o}}$ Value vs Relative Viscosity at 1% Concentration (wt/vol)[a]**

| $K$ value | Relative viscosity | $K$ value | Relative viscosity |
|---|---|---|---|
| 20 | 1.120 | 60 | 2.031 |
| 25 | 1.175 | 65 | 2.258 |
| 30 | 1.243 | 70 | 2.527 |
| 35 | 1.325 | 75 | 2.846 |
| 40 | 1.423 | 80 | 3.225 |
| 45 | 1.539 | 85 | 3.678 |
| 50 | 1.677 | 90 | 4.219 |
| 55 | 1.839 | 95 | 4.870 |

[a] Ref. 68.

**Table 6. *K* Value vs Weight-Average Molecular Weight for PVP[a]**

| *K* value | $\overline{M}_w$, amu | *K* value | $\overline{M}_w$, amu |
|---|---|---|---|
| 10 | 2,600 | 70 | 626,900 |
| 15 | 8,100 | 75 | 761,500 |
| 20 | 18,300 | 80 | 913,500 |
| 25 | 34,400 | 85 | 1,084,000 |
| 30 | 57,500 | 90 | 1,273,000 |
| 35 | 88,800 | 95 | 1,483,000 |
| 40 | 129,300 | 100 | 1,714,000 |
| 45 | 180,300 | 105 | 1,967,000 |
| 50 | 242,700 | 110 | 2,242,000 |
| 55 | 317,600 | 115 | 2,542,000 |
| 60 | 405,900 | 120 | 2,866,000 |
| 65 | 508,600 | | |

[a]Ref. 68.

Utilizing the Mark–Houwink equation (71)

$$[\eta] = K\bar{M}_v^a$$

it is possible to relate the viscosity-average molecular weight ($\bar{M}_v$) to the *K* value.

For commercial grades of unfractionated PVP prepared by similar means (presumed to exhibit similar molecular weight distribution (MWD) and degree of branching), the following regression formula can be employed (68):

$$\log \text{mol wt.} = 2.82 \log K + 0.594$$

Table 6 indicates mol wt. vs *K* value obtained by this technique. Table 7 lists $M_n$ obtained by osmometry methods. The specifications for Technical and Pharmaceutical grades are given in Tables 8 and 9.

**Glass-Transition Temperature.** The $T_g$ of PVP is sensitive to residual moisture (72) and unreacted monomer. It is even sensitive to how the polymer was prepared, suggesting that MWD, branching, and cross-linking may play a part (73). Polymers presumably with the same molecular weight prepared by bulk polymerization exhibit lower $T_g$s compared to samples prepared by aqueous solution polymerization, lending credence to an example, in this case, of branching caused by chain transfer to monomer.

**Table 7. Osmometry Molecular Weights for PVP[a]**

| Sample | Technique | $\overline{M}_n$ |
|---|---|---|
| K-90 | Membrane osmometry | 37,4000 |
| K-60 | Membrane osmometry | 67,500 |
| K-30 | Vapor pressure osmometry | 8,430 |
| K-15 | Vapor pressure osmometry | 5,170 |

[a]Ref. 69.

**Table 8. Specifications of Technical PVP Grades**

| Designation | Form | $K$ range | Water, %max | Ash, %max | $M_v(\times 10^{-3})^a$ |
|---|---|---|---|---|---|
| K-15 | Powder | 13–19 | 5 | 0.02 | 10 |
| K-15 | Aqueous solution | 13–19 | 72 | | 10 |
| K-30 | Powder | 26–34 | 5 | 0.02 | 40 |
| K-60 | Aqueous solution | 50–62 | 55 | 0.02 | 220 |
| K-90 | Aqueous solution | 80–100 | 80 | 0.02 | 630 |
| K-90 | Powder | 88–100 | 5 | 0.02 | 630 |
| K-120 | Powder | 115–125 | 5 | 0.02 | 1450 |

[a]Performed at 25°C, in $H_2O$, using Mark–Houwink constants of $K = 1.4 \times 10^{-4}$ and $a = 0.7$.

**Table 9. Specifications of Pharmaceutical PVP Grades (Povidone)**

| Assay | Value[a] |
|---|---|
| $K$ value | |
| 10–15 | 85–115% of stated supplier's value |
| 16–90 | 90–107% of stated supplier's value |
| Moisture, % | 5 |
| pH[b] | 3.0–7.0 |
| Residue on ignition, % | 0.02 |
| Aldehydes, %[c] | 0.02 |
| *N*-Vinyl-2-pyrrolidinone, % | 0.20 |
| Lead, ppm | 10 |
| Arsenic, ppm | 1 |
| Nitrogen, % | 11.5–12.8 |

[a]All single values are maximum.
[b]Of a 5% solution in distilled water.
[c]Calculated as acetaldehyde.

Molecular weight also plays a significant role in $T_g$, which increases to a limiting value of 180°C for high purity samples above K-90 in molecular weight. The following equation applies:

$$T_g(^\circ\mathrm{C}) = 175 - \frac{9685}{K^2}$$

and Table 10 illustrates this relationship with commercially available samples.

**Table 10. Glass-Transition Temperatures of PVP**

| Sample[a] | Measured $K$ value | $T_g$, °C |
|---|---|---|
| Plasdone K-15 | 14.0 | 126 |
| PVP K-15 | 14.9 | 130 |
| Plasdone K-25 | 22.5 | 160 |
| PVP K-30 | 27.5 | 163 |
| Plasdone K-29/32 | 28.7 | 164 |
| PVP K-60 | 55.5 | 170 |
| PVP K-90 | 89.6 | 174 |

[a]Courtesy of ISP Corp.

**Solubility.** One of PVP's more outstanding attributes is its solubility in both water and a variety of organic solvents. PVP is soluble in alcohols, acids, ethyl lactate, chlorinated hydrocarbons, amines, glycols, lactams, and nitroparaffins. Solubility means a minimum of 10 wt% PVP dissolves at room temperature (moisture content of PVP can influence solubility). PVP is insoluble in hydrocarbons, ethers, ethyl acetate, *sec*-butyl-4-acetate, 2-butanone, acetone, cyclohexanone, and chlorobenzene. Both solvent polarity and Hbonding strongly influence solubility (74).

*Swelling Behavior.* One way to visualize the interaction of solvents with PVP is to examine the effect the former have on lightly cross-linked PVP, as a model for the linear polymer (75).

Such gels can be prepared from a minimum of diallyl cross-linker and VP to afford products that are mechanically stable and easy to handle as hydrogels. Such samples must be extracted because soluble polymer competes for solvent, affording lower swell volumes than those expected. The extracted and dried samples are swollen to equilibrium in a variety of solvents (Table 11). Three groups of solvents can be distinguished: the first includes those in which the cross-linked polymer swells 15–25 times. VP, $H_2O$, $CH_3OH$, $C_2H_5OH$, benzylamine, and chloroform are examples. Swelling drops off with longer chain-length alcohols. Aromatic derivatives like benzyl alcohol and aniline afford similar swelling ratios to each other and to aliphatic analogues. This indicates that simple aromatic groups do not interact. When comparing volume instead of weight, water actually causes a 0.36% shrinkage of the gel. Water can therefore cross-link by hydrogen bonding to a limited but measurable extent. The second group consists of acetone, MEK, and dioxane solvents that not only increase the swell ratio (to a much lesser extent) but also increase the swell volume by 60–100%. The third group consists of hydrocarbons, benzene, carbon tetrachloride, isopropyl ether, and triethyl amine. In this case, they have little or no effect on swelling. The hallmark of this group is lack of hydrogen-bonding capability.

In water, the swell ratio actually decreases with temperature at a constant rate of $-0.12\%/^{\circ}C$. PVP gels therefore swell exothermically in water, and, as expected, heat reverses the process. Cooling back to a lower temperature results in the expected higher swell ratio being reestablished. Alcohols and other

**Table 11. Swelling of Cross-linked Polyvinylpyrrolidone in Various Liquids at 20°C[a]**

| Liquid | Degree of swelling | Liquid | Degree of swelling |
|---|---|---|---|
| 1-Propanol | 25.6 | Chloroform | 16.7 |
| Ethanol | 24.8 | Ethylenediamine | 15.6 |
| Isoamyl alcohol | 24.8 | Acetone | 2.1 |
| Methanol | 24.0 | Methyl ethyl ketone | 2.0 |
| Water | 19.7 | Cyclohexanone | 1.9 |
| Benzyl alcohol | 19.5 | Dioxane | 1.6 |
| *n*-Octanol | 19.1 | Trimethylamine | 1.07 |
| Benzylamine | 17.1 | Carbon tetrachloride | 1.03 |
| Prim-phenyl ethyl alcohol | 16.9 | Benzene | 1.02 |
| | | Isopropyl ether | 1.0 |

[a]Ref. 75.

hydrogen bonding solvents cause the same effect but to a lesser extent. Nonhydrogen-bonding solvents actually cause an increase in swelling with temperature (Table 12).

*Rheology.* PVP solubility in water is limited only by the viscosity of the resulting solution. The heat of solution is −16.61kJ/mol (−3.97 kcal/mol) (76); aqueous solutions are slightly acidic (pH 4–5). Figure 2 illustrates the kinematic

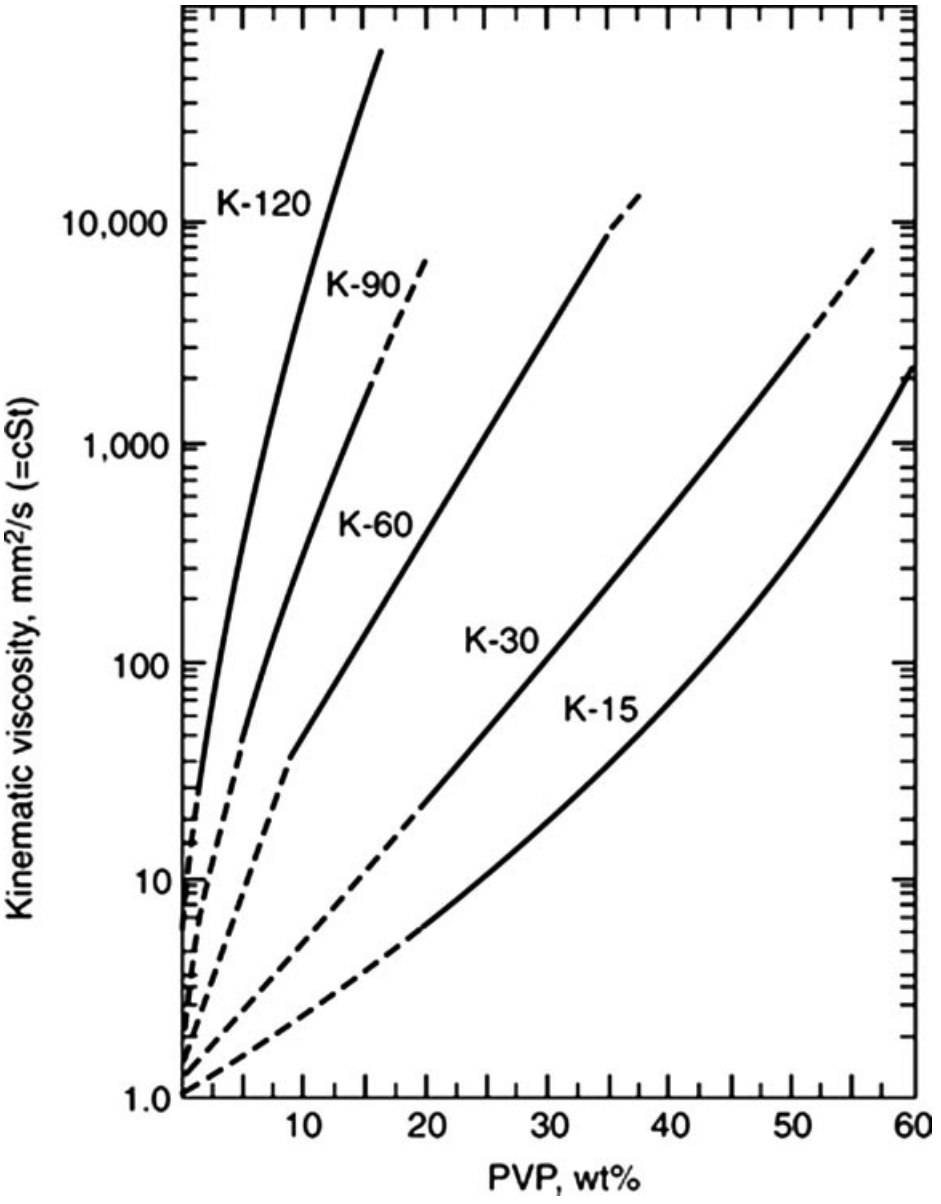



**Fig. 2.** Kinematic viscosity of PVP in aqueous solutions.

**Table 12. Temperature-Dependence of Degree of Swelling in Four Liquids[a]**

| Liquid | Temperature, °C | Degree of swelling |
|---|---|---|
| Dioxane | 20 | 1.57 |
| | 50 | 2.34 |
| Methyl ethyl ketone | 20 | 1.69 |
| | 50 | 2.86 |
| Ethanol | 20 | 18.3 |
| | 50 | 17.3 |
| Chloroform | 20 | 24.6 |
| | 50 | 24.0 |

[a]Ref. 75.

viscosity of PVP in aqueous solution. The kinematic viscosity of PVP K-30 in various organic solvents is given in Table 13.

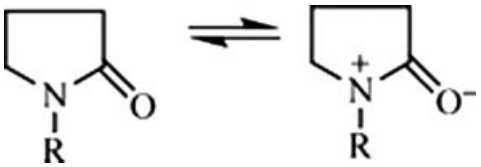
*Aqueous Solutions of PVP.* Although it is soluble in a variety of polar solvents, PVP has generated significant interest because of its aqueous solubility. Water can readily hydrogen bond to the polar, negatively charged pyrrolidinone carbonyl oxygen because pyrrolidinone, a five-membered planar lactam, affords maximum $\pi, \pi$-orbital overlap. The canonical resonance forms highlight the

**Table 13. Kinematic Viscosity of PVP K-30 in Organic Solvents**

| | Kinematic viscosity,[a] $mm^2/s$ (=cSt) | |
|---|---|---|
| Solvent | 2% PVP | 10% PVP |
| Acetic acid (glacial) | 2 | 12 |
| 1,4-Butanediol | 101 | 425 |
| Butyrolactone | 2 | 8 |
| Cyclohexanol | 80 | 376 |
| Diacetone alcohol | 5 | 22 |
| Diethylene glycol | 39 | 165 |
| Ethanol (absolute) | 2 | 6 |
| Ethyl lactate | 4 | 18 |
| Ethylene glycol | 24 | 95 |
| Ethylene glycol monoethyl ether | 3 | 12 |
| Glycerol | 1480 | 2046 |
| 2-Propanol | 4 | 12 |
| Methyl cyclohexanone | 3 | 10 |
| *N*-Methyl-2-pyrrolidone | 2 | 8 |
| Methylene dichloride | 1 | 3 |
| Monoethanolamine | 27 | 83 |
| Nitroethane | 1 | 3 |
| Nonylphenol | 3300 | |
| Propylene glycol | 66 | 261 |
| Triethanolamine | 156 | 666 |

[a]Kinematic viscosity = absolute viscosity/density.

potential for a partial negative charge to form on oxygen:



The partial charge on nitrogen is sterically shielded by the polymer backbone and the surrounding pyrrolidinone methylenes. Because of high dipole moment and polarity, PVP has a noticeable effect on water structure and various methods have been proposed to measure bound water (77). One study even illustrates the different categories of water generated by freezing aqueous PVP solutions (78). The results are summarized in Figure 3, and, as can be seen, PVP is hydrated with

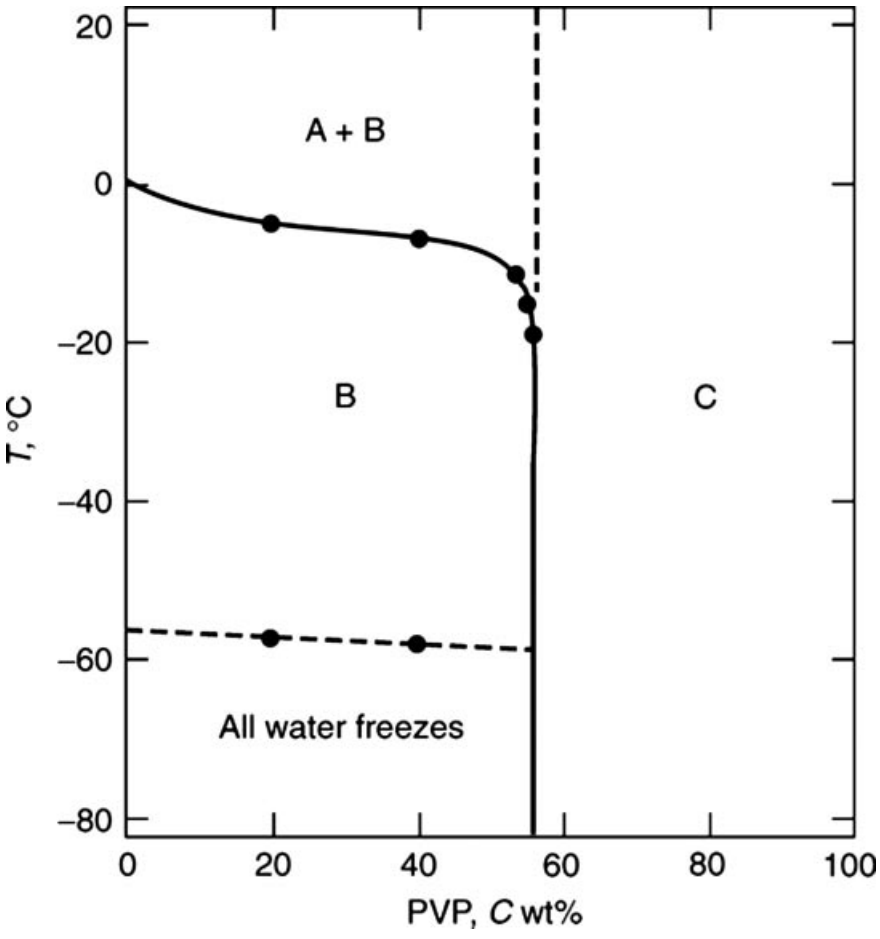



**Fig. 3.** Phase diagram for the three kinds of water in PVP aqueous solutions (78). A, freezable water; B, bound, nonfreezable water (six per repeat unit); C, nonfreezable water.

bound water that will not freeze (concentrated solutions >57% will not freeze). PVP is therefore used as a protectorate in cryobiology (79).

The actual amount and structure of this "bound" water have been the subject of debate (80), but the key factor is that in water, PVP and related polymers are water structure organizers, which is a lower entropy situation (81). Therefore, it is not unexpected that water would play a significant role in the homopolymerization of VP, because the polymer and its reactive terminus are more rigidly constrained in this solvent and termination $k_t$ is reduced (82).

## Complexation

The combination of electrostatic interaction (induced dipole–dipole interaction) with an increase in entropy resulting from the discharge of bound water is fundamental to PVP's ability to complex with a variety of large anions.

Other factors that can stabilize such a forming complex are hydrophobic bonding by a variety of mechanisms (van der Waals, Debye, ion dipole, charge transfer, etc). Such forces complement the stronger hydrogen bonding and electrostatic interactions.

Approximately a minimum $\bar{M}_n$ of 1–5000 is required before complexation is no longer dependent on molecular weight for small anions such as $KI_3$ and 1-anilinonaphthaline-8-sulfonate (ANS) (83,84). The latter anion is a fluorescent probe that, when bound in hydrophobic environments, will display increased fluorescence and, as expected, shows this effect in the presence of aqueous PVP. PVP, when complexed with $HI_3$, shrinks in size as it loses hydrodynamic volume, possibly because of interchain complexation. ANS, on the other hand, causes the polymer to swell by charge repulsion because it behaves like a typical polyelectrolyte (85).

**Adsorption Isotherms.** Equilibrium dialysis studies indicate around 10 repeat VP units (base moles) are required to form favorable complexes (86,87). This figure can rise to several hundred for methyl orange and other anions depending on structure (88,89).

Although hydrophobic bonding is well established as a significant force stabilizing such complexes, some work suggests that such generalizations do not apply to every case (89). However, a study of the complexes of PVP with tetraanionic porphyrins has shown that the reaction of porphyrin with cupric ion is slowed dramatically in the presence of PVP. This is interpreted as demonstrating the existence of hydrophobic pockets preventing a reaction that is clearly favored if both species are in aqueous environments (90). Hydrophobic bonding has been illustrated by comparing competitive binding of butyl orange (BO) with 1-amino-4-methylamino anthraquinone-2-sulfonate (AQ) (91). The thermodynamic data for BO show that the binding process is athermal and stabilized entirely by the entropy term. On the other hand, AQ exhibits a large enthalpy and small entropy value and its binding is by the stronger and energetic interaction caused by hydrogen bonding (NH groups of AQ) and hydrophobic interaction of the polynuclear aromatic AQ; both structural features are missing from BO (91).

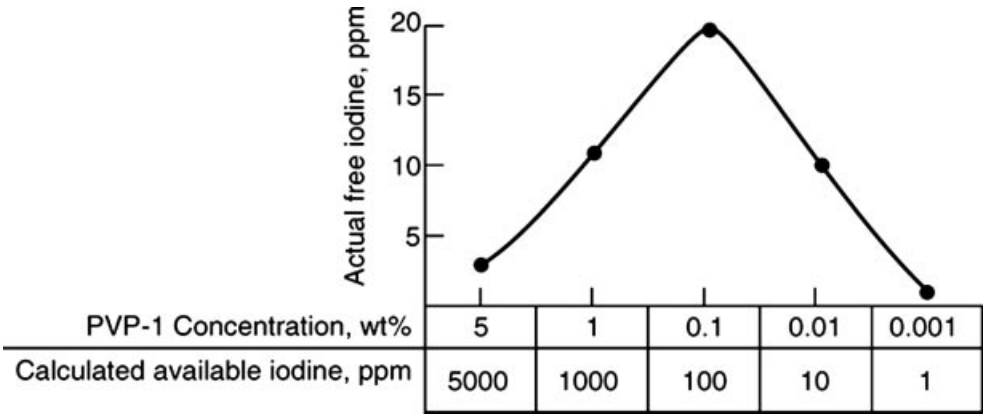
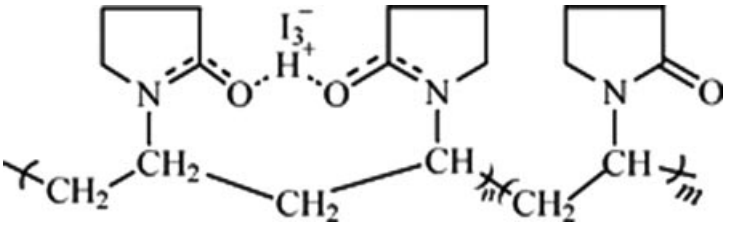



**Fig. 4.** Free iodine in povidone–iodine aqueous solutions (96).

**Iodine Complexes.** The small molecule/PVP complex between iodine and PVP is probably the best-known example (92) and can be represented as follows:



It is widely employed as a disinfectant in medicine (povidone–iodine) because of its mildness, low toxicity, and water solubility. In actuality, the complex is based on $HI_3$ since HI is formed *in situ* from iodine during the manufacturing process (93). According to the *U.S. Pharmacopeia*, povidone–iodine is a free flowing, brown powder that contains from 9 to 12% available iodine. It is soluble in water and lower alcohols. When dissolved in water, the uncomplexed free-iodine level is very low (Fig. 4) (94); however, the complexed iodine acts as a reservoir and by equilibrium replenishes the free iodine to the equilibrium level. This prevents free iodine from being deactivated because the free form is continually available at effective biocidal levels from this large reservoir (95). The structure of the complex has been studied and in essence is similar to the representation above (95,96). PVP will interact with other small anions and resembles serum albumin and other proteins in this regard (97). It can be "salted in" with anions such as NaSCN or "out" with $Na_2SO_4$ much like water-soluble proteins (98).

**Phenolics.** PVP readily complexes phenolics of all types to some degree, the actual extent depending on structural features such as number and orientation of hydroxyls and electron density of the associated aromatic system. A model has been proposed (99). Complexation with phenolics can result in reduced PVP viscosity and even polymer-complex precipitation (100).

One practical result of this strong interaction is the employment of PVP to remove unwanted phenolics such as bitter tanins from beer and wine. This process is more easily carried out with insoluble crospovidone, which can be regenerated for reuse with dilute base (101). Soluble PVP has been employed to prevent photoyellowing of paper by complexing free-phenolic hydroxyl groups in lignin (102).

**Dyes.** PVP is currently (ca 1997) employed in a variety of antidye redeposition detergents as a result of its strong interaction with fugitive anionic dyes (103,104). This interaction depends on the structure of the dye. Cationic dyes complex only if they also contain hydrogen-bonding functionality. Anionic dyes complex more easily, depending on the number of anionic groups, size of the aromatic nucleolus, and number and orientation of phenolic hydroxyl groups, etc.

**Anionic Surfactants.** PVP also interacts with anionic detergents, another class of large anions (105). This interaction has generated considerable interest because addition of PVP results in the formation of micelles at lower concentration than the critical micelle concentration (CMC) of the free surfactant the mechanism is described as a "necklace" of hemimicelles along the polymer chain, the hemimicelles being surrounded to some extent with PVP (106). The effective lowering of the CMC increases the surfactant's apparent activity at interfaces. PVP will increase foaming of anionic surfactants for this reason.

Because of this interaction, PVP has found application in surfactant formulations, where it functions as a steric stabilizer for example to generate uniform particle-size polystyrene emulsions (107–109). In a variety of formulations, a surfactant's ability to emulsify is augmented by PVP's ability to stabilize colloids sterically and to control rheology.

**Polymer/Polymer Complexes.** PVP complexes with other polymers capable of interacting by hydrogen bonding, ion dipole, or dispersion forces. For example mixing of PVP with poly(acrylic acid) (PAA) in aqueous solution results in immediate precipitation of an insoluble complex (110). Addition of base results in disruption of hydrogen bonding and dissolution (111–113). Complexes with a variety of polyacids (114) and polyphenols (115) have been reported. The interest in compatibility on a molecular level, an interesting phenomenon rarely found to exist between dissimilar polymers, is favored by the ability of PVP to form polymer/polymer complexes.

Practical applications have been reported for PVP/cellulosics (105,116,117) and PVP/polysulfones (118,119) in membrane separation technology, eg, in the manufacture of dialysis membranes. Electrically conductive polymers of polyaniline are rendered more soluble and hence easier to process by complexation with PVP (120). Addition of small amounts of PVP to nylon 66 and 610 causes significant morphological changes, resulting in fewer but more regular spherulites (121).

## Copolymerization

The $Q$ and $e$ values of VP are 0.088 and −1.62, respectively (122). This indicates resonance interaction of the double bond of the vinyl group with the electrons of the lactam nitrogen, whence the electronegative nature. With high $e+$ monomers such as maleic anhydride, VP forms alternating copolymers, much as expected

**Table 14. VP Copolymerization Parameters[a]**

| Comonomer ($M_2$) | $r_1$ | $r_2$ | Reference |
|---|---|---|---|
| *N*-Vinyl caprolactam | 2.80 | 1.70 | 125 |
| Maleic anhydride | −0.027 | 0.074 | 126 |
| Methyl methacrylate | 0.01 | 4.04 | 127 |
| Styrene | 0.057 | 17.2 | 128 |
| Vinyl acetate | 3.40 | 0.195 | 128 |
| Acrylic acid | 0.100 | 0.880 | 129 |
| Dimethylaminoethyl | 0.07 | 4.7 | 130 |
| Methacrylate | 0.69 | 11.16 | 131 |

[a]Ref. 124.

(123). With other monomers between these $Q$ and $e$ extremes a wide variety of possibilities exist. Table 14 lists reactivity ratios for important comonomers.

Copolymerizations can be conveniently carried out in aqueous solution or in a variety of solvents, depending on monomer/polymer solubilities. Various strategies have been employed to compensate for the divergence in reactivity ratios in order to form uniform (statistical) copolymers such as semibatch or mixed monomer feeds, the goal being to add the more reactive monomer at the rate at which it is being consumed (132). Clearly, if the difference in reactivity is too great, then the amount of more reactive monomer that can be uniformly incorporated is significantly reduced. Of the monomers listed, styrene fits this category (133).

**Poly(Vinylpyrrolidinone-co-Vinyl Acetate).** The first commercially successful class of VP copolymers, poly(vinylpyrrolidinone-*co*-vinyl acetate) is currently manufactured in sizeable quantities by both ISP and BASF. A wide variety of compositions and molecular weights are available as powders or as solutions in ethanol, isopropanol, or water (if soluble). Properties of some examples of this class of copolymers are listed in Table 15.

**Table 15. Properties of PVP/VA Copolymers[a]**

| | PVP–VA copolymer | | | | | | |
|---|---|---|---|---|---|---|---|
| | E-735 | E-635 | E-535 | E-335 | I-735 | I-535 | I-335 |
| Physical form at 25°C | Clear liquid | | | | Light yellow liquid | | |
| Solvent | SDA-40 anhydrous ethanol | | | | 2-propanol | | |
| Solids after infrared drying, % | | 50 ± 2 | 50 ± 2 | 50 ± 2 | 50 ± 2 | 50 ± 2 | 50 ± 2 |
| Vinylpyrrolidinone–vinyl Acetate ratio | 70:30 | 60:40 | 50:50 | 30:70 | 70:30 | 50:50 | 30:70 |
| *K* value of 1% ethanol solution | 30–50 | 30–50 | 30–50 | 25–35 | 30–40 | 25–35 | 20–30 |
| Moisture as is, Karl Fischer, %max | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Nitrogen, dry basis, Kjeldahl, % | 8–9 | 7–8 | 5.8–6.8 | 3.1–4.1 | 8–9 | 5.9–6.9 | 3.9–4.9 |
| Specific gravity at 25°C | 0.955 ± 0.01 | | | | | | |

[a]Ref. 134.

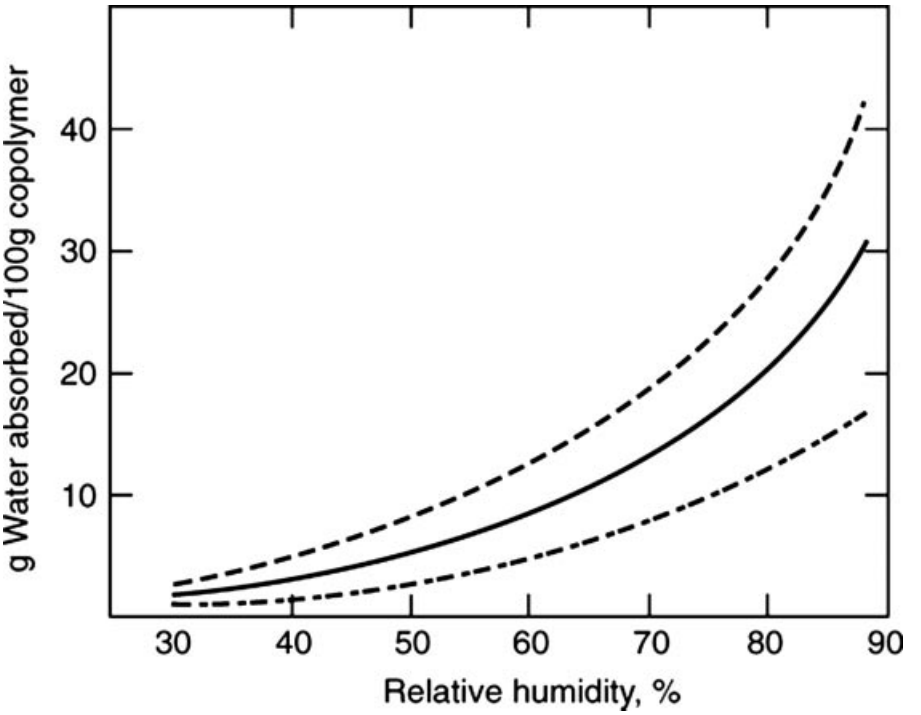



**Fig. 5.** Hydrophilicity of three wt% monomer ratios of PVP/VA: (– – –), 70/30; (—), 50/50; (—·—·), 30/70.

Although reactivity ratios indicate that VP is the more reactive monomer, reaction conditions such as solvent polarity, initiator type, percent conversion, and molecular weight of the growing radical can alter these ratios (135). Therefore, depending on polymerization conditions, copolymers produced by one manufacturer may not be identical to those of another, especially if the end use application of the resin is sensitive to monomer sequence distribution and MWD.

An important reason for the ongoing interest in these copolymers is that vinyl acetate reduces hydrophilicity so that applications that require less moisture-sensitive films such as those employed to set hair are less prone to plasticize and become tacky under high humidity conditions (136) (Fig. 5).

As shown in Figure 6, desirable fixative properties superior to PVP homopolymer can be specified by judicious selection of the amount of vinyl acetate. Hair sprays are limited in the molecular weight of the resin because if they are too high the resulting viscosity of the formulation will result in a poor (coarse) spray pattern. Increasing the VP/VA ratio causes properties to increase in the direction shown by the arrows.

Other applications for VP/VA copolymers are uses as water-soluble or remoistenable hot-melt adhesives (137), pharmaceutical tablet coatings, binders, and controlled-release substrates.

**Tertiary Amine-Containing Copolymers.** Copolymers based on dimethylaminoethyl methacrylate (DMAEMA) in either free-amine form or

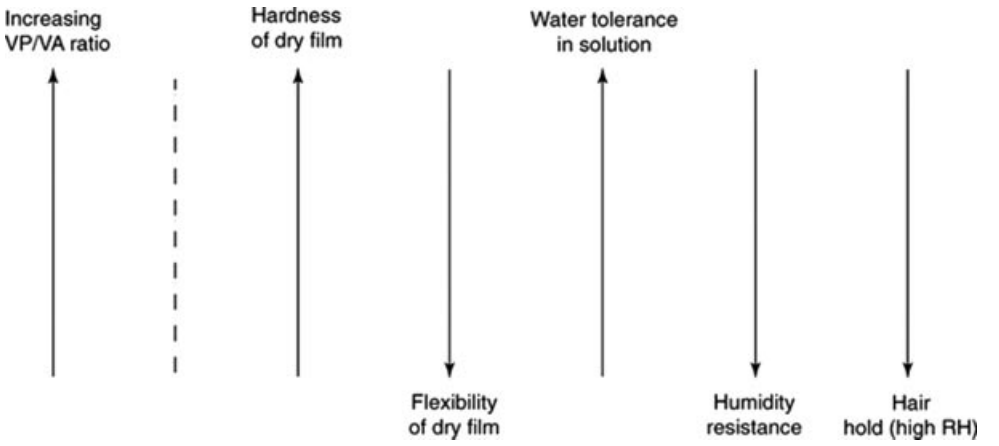



**Fig. 6.** Effect of VP/VA monomer ratio on properties of VP/VA copolymers.

quaternized with diethyl sulfate or methyl chloride have achieved commercial significance as fixatives in hair-styling formulations, especially in the well-publicized "mousses" or as hair-conditioning shampoo additives. This success has occurred because the cationic charge affords substantive resins that strongly adhere to the hair (138).

The most successful of these products contain high ratios of VP to DMAEMA and are partially quaternized with diethyl sulfate (Polyquaternium 11) (139–141). They afford very hard, clear, lustrous, nonflaking films on the hair that are easily removed by shampooing. More recently, copolymers with methylvinylimidazolium chloride (Polyquaternium 16) (142) or methacrylamidopropyltrimethyl ammonium chloride (MAPTAC) (Polyquaternium 28) have been introduced. Replacement of the ester group in DMAEMA with an amide analog as in Polyquaternium 28 results in a resin resistant to alkaline hydrolysis and hence greater utility in alkaline permanent wave and bleach formulations (see QUATERNARY AMMONIUM COMPOUNDS).

Unquaternized DMAEMA copolymers afford resins that are mildly cationic and less hydroscopic. They provide more moisture-resistant fixatives (143). Further refinements have been accomplished by adding a third comonomer such as *N*-vinylcaprolactam (VCl). In this case, replacement of VP with VCl results in a terpolymer (VP/VCl/DMAEMA) with even greater high humidity moisture resistance and curl retention.

**Copolymers Containing Carboxylic Groups.** A new line of VP/acrylic acid copolymers in powdered form prepared by precipitation polymerization (144) from heptane have been introduced commercially (145). A wide variety of compositions and molecular weights are available, from 75/25 to 25/75 wt% VP/AA and from $20 \times 10^3$ to $250 \times 10^3$ molecular weights.

The copolymers are insoluble in water unless they are neutralized to some extent with base. They are soluble, however, in various ratios of alcohol and water, suggesting applications where delivery from hydroalcoholic solutions (146) but subsequent insolubility in water is desired, such as in low volatile organic

**Table 16. Properties and Applications of Commercial PVPs**

| Polymer | Mfr/Trade name | Grades | Properties/applications |
|---|---|---|---|
| | | *Homopolymers* | |
| PVP | ISP/PVP, Plasdone BASF/Luviskol, Kollidon | K-15 to K-120 K-12 to K-90 | Film former, adhesive, binder, com-plexant, stabilizer, crystallization inhibitor, dye scavenger, detoxi-cant, viscosity modifier |
| | | *Cross-linked* | |
| Proliferous polymerization | ISP/Polyclar, Polyplasdone BASF/Divergan | Various (by particle size) various (by particle size) | Pharmaceutical tablet disintegrant, adsorbent for polyphenols (tanins), beverage clarification |
| | | *Copolymers* | |
| PVP/VA | BASF/ISP/PVP–VA copolymers | Various monomer ratios in ethanol, IPA or water in ethanol, IPA or water | Film forming adhesives for hairsprays, mousses, gels, shampoos, styling lotions, bio-adhesives, water-remoist-enable or removable adhesives |
| PVP/DMAEMA | ISP/copolymer | 845/937/958 | Mildly cationic, hair styling aids and conditioners, with strong hold; sub-stantive, lustrous film-formers |
| PVP/DMAEMA DES quaternary | ISP/Gafquat BASF/Luviquat | 755N/734PQ11 | Strongly cationic, substantive, mousse and gel hair fixative ingredients |
| PVP/imidazolinum quaternary | BASF/Luviquat FC | | |
| PVP/styrene[a] | ISP/Polectron 430 | 30% VP | Opacifier for personal care products; very stable styrene emulsion |
| PVP/alpha-olefins[a] | ISP/Ganex | Various (olefin chain length and monomer ratios) | Surface active film formers; waterproofing of sunscreens |
| | | *Terpolymers* | |
| VP/VCl/DMAEMA | ISP/Gaffix VC-713 | VC-713 | Cationic water-soluble hair styling aid hair fixatives |
| VP/tBMA/MA | BASF/Luviflex | Various | |

[a] Graft copolymers.

compound (VOC) hair-fixative formulations or tablet coatings. Unneutralized, their $T_g$s are higher than expected, indicating interchain hydrogen bonding (147).

**Miscellaneous Copolymers.** VP has been employed as a termonomer with various acrylic monomer–monomer combinations, especially to afford resins useful as hair fixatives. Because of major differences in reactivity, VP can be copolymerized with alpha-olefins, but the products are actually PVP grafted with olefin or olefin oligomers (148,149). Likewise styrene can be polymerized in the presence of PVP and the resulting dispersion is unusually stable, suggesting that this added resistance to separation is caused by some grafting of styrene onto PVP (150). The literature contains innumerable references to other copolymers but at present (ca 1997), those reviewed in this article are the only ones known to have commercial significance.

## Applications

An overview of the various product categories is given in Table 16.

The Chemical Abstracts Services Registry Number and IUPAC nomenclature for PVP are [9003-39-8] and 1-ethenyl-2-pyrrolidinone homopolymer, respectively; however, it is known by a variety of approved names by foreign and domestic regulatory authorities. For example:

| Name | Chemical name |
|---|---|
| Povidone | Poly(*N*-vinyl-2-pyrrolidinone) |
| Polyvidone | |
| Polyvidon | Poly(*N*-vinylbutyrolactam) |
| Polyvidonum | Poly(1-vinyl-2-pyrrolidinone) |
| | 1-Vinyl-2-pyrrolidinone polymer |
| | Poly{1-(2-oxo-1-pyrrolinyl)ethylene} |

Trade names for nonpharmaceutical grades are PVP, Peregal ST, Albigen A, and Luviskol; for pharmaceutical grades, Plasdone and Kollidon. The insoluble or crospovidones likewise exist as two grades: nonpharmaceutical are Polyclar and Divergan; pharmaceutical, Polyplasdone XL and Kollidon Cl.

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