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N-VINYLFORMAMIDE — BUILDING BLOCK FOR NOVEL POLYMER STRUCTURES

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ABSTRACT

N-Vinylformamide (NVF, N-ethenylformamide) is a precursor to amide and amine functional polymers and to other monomers, oligomers, and functional polymers. NVF shows attractive physical and toxicological properties and high reactivity, both in polymerization and in subsequent hydrolysis to cationic and reactive amine functional polymers or oligomers. NVF radical polymerization readily yields water soluble homopolymers with molecular weights from 10^4 to $>10^6$. Copolymerizability is similar to other vinyl amides. Unexpectedly, NVF will also undergo cationic oligomerization. Hydrolysis of polymers and copolymers with base or acid is facile, although reactions with neighboring groups (e.g., with coacrylate ester groups to give lactams) complicate copolymer hydrolysis.

Reaction of NVF at the unusually acidic NH group allows reaction with isocyanates to give vinylacylureas or Michael addition to acrylates to give a family of new N-vinylformamidopropionate esters. These esters in turn react with functional amines to generate new families of divinyl, vinyl/alcohol functional, or vinyl/amino functional comonomers. Applications for NVF and its derived monomers and polymers appear numerous, in particular in radiation cure coatings, based on their good physical and toxicological properties.

INTRODUCTION

N-Vinylformamide (13162-05-5) is the lowest member of the N-vinyl amide family. It offers a unique mix of physical and chemical properties which make it highly attractive, from both scientific and commercial perspectives, as a precursor to amide and amine functional polymers [1, 2] and as a precursor to other monomers, oligomers, and their derived polymers. Key factors in the utility of NVF include attractive physical and toxicological properties [1] (Table 1) and high reactivity. Earlier work [1, 3, 4] has focused on the high reactivity in polymerization and convenient subsequent hydrolysis to cationic and reactive amine functional polymers or oligomers. This paper will also discuss options arising from the high ionic reactivity of NVF monomer.

EXPERIMENTAL

Hydrolysis of PNVF at Elevated Temperatures [8]

Dry, powdered PNVF or PNVF copolymer was added to a 100 mL SS Parr reactor, dissolved in deionizedwater (typically to give a 20% solution) and 1% on reaction volume of 5% Pd/C was added. The reactor was sealed, stirring was init-iated, and the reaction was heated 2-6 hours at 165-180°C (180-480 psig). The reactor was cooled to ambient and vented to release hydrogen and carbon dioxide. Product samples were analyzed by NMR after sparging with nitrogen. Formyl-hydrolysis and conversions were 60-80%, giving products with 11-28%PNVF, 54 -71% PVAm, and 16-37% amidine.

General Procedure for Preparation of Michael Adducts

To a 1000 mL three-neck round bottom flask equipped with a cold water condenser was added acrylate (2.5 mol), NVF (2.75 mol) and benzoquinone (0.1 g), with or without solvent (150 mL of THF). The mixture was stirred at ambient temperature for 2 minutes, base (1.5 g of NaOMe unless otherwise indicated) was added dropwise. The mixture was stirred and allowed to stand overnight. Solvent was removed at reduced pressure using a rotary evaporator. The residual was distilled at ~1 torr to give a colorless liquid. Specific synthesis conditions and properties of these adducts are shown below and in Tables 2 and 3.

Preparation of Methyl 3-(N-Vinylformamido)propionate (MANVF)

To a 1000 mL four-neck glass jacketed reactor, equipped with cold water

TABLE 1. Physical and Toxicological Properties of NVF Monomer (Modified from Reference 1).

Formula Weight	71.02
Purity, %	98-99+
Appearance	Clear Liquid
Color	<300(APHA)
Odor	Mild Characteristic
Boiling Point, @ 13.3 mbar (10 torr)	84°C
	[theor: 210°C @ 760 torr]
Melting Point, °C	~-16
Density, g/ml @ 25°C	1.014
Vapor Pressure, mbar @ 25°C	<0.013
Flash Point, °C (ASTM D-3828)	102
Viscosity, cps @ 25°C	4
Surface Tension, dynes/cm @ 21°C	36.2
DH Polymerization, kJ/mole	~80
kcal/mole	~19
Miscibility	All common solvents (limited with alkanes)
Mutagenicity testing	negative
Acute oral LD_{50}(rat), mg/kg	1,444
Dermal LD_{50}, mg/kg	>2000
Regulatory status	"Listed" on TSCA, EINCS

condenser, thermal couple, and mechanical stirrer, was added 501.7 g of methyl acrylate (5.83 mol, Aldrich), 424.3 g of NVF (5.98 mol) and 0.425 g of benzoquinone. The reactor was kept at ~40°C with circulated water. With stirring, 7.5mL of sodium methoxide (25% in methanol, Aldrich) was added to the reaction mixture in one portion. Exothermic reaction took off in about 10 to 30 minutes. The mixture was stirred at ambient temperature for two hours. GC analysis indi-cated that there were about 2.2% methyl acrylate and 2.2% NVF left. The mixture was stirred and allowed to stand overnight. The resultant mixture was purified by distillation. Fractions at 72-74°C/0.3 torr (128-132°C/10 torr) were collected to give a colorless liquid, 809.8 g (87.9%). ^{1}H NMR (Brucker 300 MHz, $CDCl_3$) for major rotamer: δ8.17 (1H, s), 6.47 (1H, d,d, J = 15 Hz, J = 9 Hz), 4.51 (1H, d,d, J = 15 Hz, J = 2 Hz), 4.35 (1H, d,d, J = 9 Hz, J = 2 Hz), 3.76 (2H, t, J = 7 Hz), 3.56 (3H, s), 2.46 (2H, t, J = 7 Hz); and for minor rotamer: δ 8.12 (1H, s), 7.04 (1H, d,d, J = 16 Hz, J = 9 Hz), 4.44 (1H, t, J = 1.5 Hz), 4.41 (1H, t, J = 1.5 Hz), 3.69 (2H, t, J = 7 Hz), 3.57 (3H, s), 2.56 (2H, t, J = 7 Hz). Major rotamer: minor rotamer = 74:26. Acute toxicity measurements showed Oral LD-50 > 5000 mg/kg

TABLE 2. Synthesis of Michael Adducts Using NaOMe Catalyst

Michael Adduct	Michael Acceptor	Yld(%)	Comments
Methyl 3-N-vinylformamidopropionate	Methyl acrylate	88	v.exothermic,~2 h
Ethyl 3-N-vinylformamidopropionate	Ethyl acrylate	88	exothermic, ~3 h
Butyl 3-N-vinylformamidopropionate	Butyl acrylate	84	less exothermic, ~4 h
t-Butyl 3-N-vinylformamidopropionate	*t*-Butyl acrylate	45	72 h
2-Ethylhexyl 3-N-vinylformamido-propionate	2-Ethylhexyl acrylate	65	92 h
1-N-Vinylformamidobutan-3-one	Methyl vinyl ketone	74	very exothermic,~3 h
3-N-Vinylformamidopropionitrile	Acrylonitrile	72	exothermic, ~3 h

TABLE 3. Properties of Michael Adducts

Michael Adduct	Boiling point	Flash point
Methyl 3-*N*-vinylformamidopropionate	75°C/0.8 torr	124
Ethyl 3-*N*-vinylformamidopropionate	88°C/1 torr	124
Butyl 3-*N*-vinylformamidopropionate	96°C/0.5 torr	98
t-Butyl 3-*N*-vinylformamidopropionate	80°C/0.5 torr	---
2-Ethylhexyl 3-*N*-vinylformamido-propionate	122°C/0.8 torr	---
1-*N*-Vinylformamidobutan-3-one	70°C/0.8 torr	---
3-*N*-Vinylformamidopropionitrile	99°C/1.5 torr	~150

and Dermal LD50 >2000 mg/kg. The compound was Ames negative with and without activation and was not sensitizing. It did show some eye irritation.

Ethyl 3-(N-Vinylformamido)propionate (EANVF)

^{1}H NMR ($CDCl_3$) Major rotamer: 8.15 (1H, s), 6.45 (1H, d,d, J = 15 Hz, J = 9 Hz), 4.49 (1H, d,d, J = 15 Hz, J = 2 Hz), 4.32 (1H, d,d, J = 9 Hz, J = 2 Hz), 4.00 (2H, m), 3.72 (2H, t, J = 7 Hz), 2.42 (2H, t, J = 7 Hz), 1.11 (3H, s). Minor rotamer: 8.09 (1H, s), 7.00 (1H, d,d, J = 16 Hz, J = 9 Hz), 4.42 (1H, m), 4.40 (1H, t, J = 1.5 Hz), 4.00 (2H, m), 3.66 (2H, t, J = 6 Hz), 2.52 (2H, t, J = 6 Hz), 1.11 (3H, s). Major rotamer: minor rotamer = 70:30.

Butyl 3-(N-Vinylformamido)propionate (BANVF)

^{1}H NMR ($CDCl_3$) Major rotamer: 8.21 (1H, s), 6.49 (1H, d,d, J = 16 Hz, J = 9 Hz), 4.56 (1H, d,d, J = 15 Hz, J = 2 Hz), 4.38 (1H, d,d, J = 9 Hz, J = 2 Hz),

4.00 (2H, t, J = 7 Hz), 3.79 (2H, t, J = 7 Hz), 2.49 (2H, t, J = 7 Hz), 1.52 (2H, m), 1.28 (2H, m), 0.85 (3H, t, J= 7 Hz). Minor rotamer: 8.15 (1H, s), 7.10 (1H, d,d, J = 16 Hz, J = 9 Hz), 4.48 (2H, m), 4.00 (2H, t, J = 7 Hz), 3.72 (2H, t, J = 6 Hz), 2.58 (2H, t, J = 6 Hz), 1.52 (2H, m), 1.28 (2H, m), 0.85 (3H, t, J= 7 Hz). Major rotamer: minor rotamer = 70:30.

Preparation of 1,4-butanediol Di-(3-(N-vinylformamido)propionate)

To a 500 mL three-neck round bottom flask equipped with a condenser and a stirrer was added 1.6 g of 60% sodium hydride in mineral oil. The sodium hydride was washed with hexane twice and the solvent was decanted. Under nitrogen, 50 g of methyl-*t*-butyl ether were added in one portion. With vigorous stirring, a mixture of 104.2 g of butanediol diacrylate and 74.7 g of NVF was added in 10 min. After the addition, the mixture was stirred at room temperature for 24 hours. The mixture was then neutralized with acetic acid and filtered through a silica gel layer (~0.5 cm). The filtrate was placed on a rotary evaporator. Solvent was removed at 45°C to give 141 g (78.8%) of pale yellow liquid.

Preparation of Methyl 2-Methyl-3-N-vinylformamidopropionate

To a 100 mL three-neck round bottom flask, equipped with cold water condenser, was added methyl methacrylate (33.2 g), NVF (23.6 g) and benzoquinone (20 mg). The mixture was stirred at ambient temperature for 2 minutes, butyl lithium (80 mg, 2.5 *M* in hexane, Aldrich) was added in one portion. The mixture was stirred at 65°C for 8 hours. The mixture was distilled to give a colorless liquid (29.5 g, 52%) at ~75-77°C/0.5 torr.

Preparation of N-2-Hydroxyethyl 3-(N-Vinylformamido)propionamide

Into a 250 mL three-neck round bottom flask equipped with a cold water condenser and stirrer was added 28.0 g (0.459 mol) of ethanolamine, 72.5 g (0.456 mol) of methyl 3-(N-vinylformamido)propionate, and 0.3 g of 25% sodium methoxide methanol solution (Aldrich). The mixture was stirred at 90°C for 20 minutes, and then cooled to ambient temperature. The mixture was next placed on a rotary evaporator to remove the generated methanol, yielding 85.0 g of product as a colorless viscous liquid. Proton NMR analyses indicated a near complete conversion of the starting materials to the desired 2-hydroxyethyl 3-(N-vinylformamido)propionamide. ^{1}H NMR ($CDCl_3$) δ, major rotamer: 2.19 (t, 2H, J = 7.5 Hz), 3.04 (br s, 2H), 3.35 (t, 2H, J = 5.2 Hz), 3.57 (t, 2H, J = 7.8 Hz), 4.04 (br s, 1H), 4.21 (d, 1H, J = 9.1 Hz), 4.44 (d, 1H, J = 15.7 Hz), 6.35 (d,d, 2H, J = 9.2

Hz, J = 15.6 Hz), 7.33 (br s, 1H), 8.01 (s, 1H); minor rotamer: most peaks overlapped with peaks of the major rotamer, except, 2.28 (t, 2H, J = 6.4 Hz), 4.28 (d, 1H, J = 9.5), 4.40 (d, 1H, J = 16.2 Hz), 6.82 (d, d, 1H, J = 9.4 Hz, J = 16.2 Hz), 7.90 (s, 1H). Major/minor rotamer ratio: 70:30.

Preparation of N,N-Di-(2-hydroxyethyl)-3-(N-vinylformamido)propionamide

A 50 mL single-neck round bottom flask equipped with a distillation head was charged with 15.1 g (0.096 mol) of methyl 3-(N-vinylformamido)propionate, 9.95 g (0.09 mol) of diethanolamine and 0.15 g of 25% sodium methoxide in methanol solution. The mixture was stirred at 90°C for 2 hours, and the generated methanol was removed by distillation at reduced pressure. Both proton NMR and GC analyses indicated approximately a 90% conversion to the title product.

Preparation of 1,2-Di-[3-(N-vinylformamido)propionamido]ethane

The apparatus above was charged with 17.1 g (0.1 mol) of ethyl 3-(N-vinylformamido)propionate, 3.0 g (0.05 mol) of ethylenediamine and 0.12 g of 25% sodium methoxide in methanol solution. The mixture was stirred at 90°C for 3 hours, after which the ethanol coproduct was removed by distillation at reduced pressure. The mixture was then allowed to cool to room temperature yielding the crude product as a yellow solid. NMR analysis of the reaction mixture indicated nearly complete conversion of the ethylenediamine. The solid was recrystallized from toluene/acetone to give pale yellow crystals of 1,2-di-[3-(N-vinylformamido)-propionamido]ethane. ^{1}H NMR ($CDCl_3$) δ, major rotamer: 2.46 (t, 4H, J = 6.2 Hz), 3.30 (br s, 4H), 3.86 (t, 4H, J = 7.3 Hz), 4.48 (d, 2H, J = 8.7 Hz), 4.70 (d, 2H, J = 15.8 Hz), 6.54 (d,d, 2H, J = 9.1 Hz, J = 15.6 Hz), 6.90 (br s, 2H), 8.25 (d, 2H, J = 5.6 Hz); minor rotamer: most peaks overlapped with peaks of the major rotamer, except, 6.68 (br s, 2H), 7.13 (d,d, 2H, J = 9.3 Hz, J = 16.3 Hz), 8.14 (d, 2H, J = 5.3 Hz). Major/minor rotamer ratio: 76:24.

Copolymerization of Methyl 3-(N-Vinylformamido)propionate with Butyl Acrylate

A three-neck round bottom flask, equipped with a mechanical stirrer, a water condenser, nitrogen inlet/outlet tube and an additional funnel, was charged with 11.5 g of MANVF, 0.1 g of Trigonox 23, and 20.4 g of methanol. The mixture was heated to 60°C, and the mixture was stirred at that temperature for 30 minutes. A mixture of 9.4 g of butyl acrylate, 0.1 g of Triginox 23 in 20.1 g of methanol was added through the addition funnel over about 3 hours. The mixture was heated continuously at 60°C for 2 hours. A sample withdrawn from the

reaction solution and analyzed by GC showed that 77% of the MANVF and 100% of the butyl acrylate were converted to polymer. The molecular weight of this polymer, determined by GPC (polystyrene standard), were: $\overline{M}_w$ = 105,485 and $\overline{M}_n$ = 33,616.

Synthesis of N-Vinyl-N-acylurea Resins

A 1:1 molar ratio of NVF (28.5 g, 0.4 mol) and isophoronediisocyanate (88.8 g) were reacted neat in a 500 mL flask at 80°C for 210 minutes using 0.38 mol% zinc ethylhexanoate as catalyst. To 0.378 mol of this adduct were added 113.5 g (0.189 mol) of polyethylene glycol MW 600. The reaction self-heated to 62°C over 1 hour. The product was dissolved in toluene, separated from insolubles and concentrated to give 177 g of viscous oil which analyzed as a mixture of the desired product, contaminated with NVF and other polyol/isocyanate condensates.

RADIATION CURE EXPERIMENTS

General Procedure

A mixture comprising epoxy acrylate, photoinitiator, triacrylate and NVF/-acrylate Michael adduct was prepared and mixed well. Wet films were cast on pre-cleaned (methylene chloride) aluminum panels with a #10 drawing bar. Panels were exposed to UV light at a conveyor speed of 105 fpm. The approximate UV dose per pass was 150-180 mJ/cm^2 as measured with a UV Process Supply Company compact radiometer. Film water and solvent resistance experiments were performed by double rub test. Film hardness was evaluated by measuring pendulum hardness [BYK Gardner Pendulum Hardness Tester, calibrated on glass (412 second)]. The degree of cure of the films was estimated and compared by both depth of cure (DOC, mil) and one pass vs. four passes pendulum hardness ratio (%), where four passes of UV irradiation are assumed to completely cure the film.

DISCUSSION

Although NVF has been known for over 30 years, [5] the monomer is only now coming into prominence with the development of commercially practical synthetic processes and the emergence of significant markets for the derived polymers and copolymers.

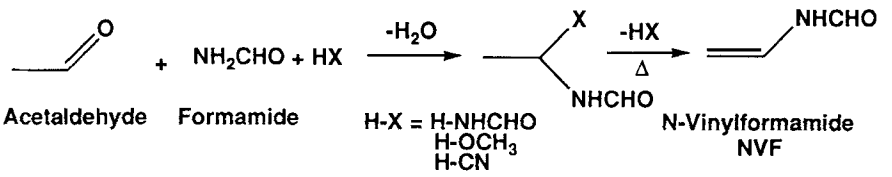

Figure 1. N-Vinylformamide Synthesis.

A large number of synthetic routes have been reported for NVF [2], but the most commercially attractive approaches at present are essentially acid and/or base catalyzed condensations of acetaldehyde and formamide, optionally with an additional active hydrogen component, to give a relatively stable hemiamidal, bisamidal, or cyanoamide (Figure 1). This is then cracked at elevated temperature and low partial pressure to give NVF and coproduct (alcohol, formamide, or HCN). Synthesis of NVF under low partial pressure conditions is an important consideration in suppressing the facile bimolecular reactions of NVF with itself under acid, base, or free radical conditions.

NVF Polymerization and Oligomerization

NVF radical polymerization readily yields homopolymers with molecular weights from 10^4 to $>10^6$ [1]. Although NVF monomer is soluble in water and in all common organic solvents except saturated hydrocarbons, poly-N-vinylformamide (PNVF) is very soluble in water, but insoluble in most other common solvents except formamide, ethylene glycol and dimethylsulfoxide (at elevated temperatures) (Figure 2). Radical polymerization by solution, precipitation, suspension, or inverse emulsion techniques is facile using most common initiators: redox, thermal, or radiation triggered. Persulfate, for poorly understood reasons, is unreliable and should be avoided as an initiator with NVF. Copolymerizability is similar to that of other vinyl amides (Table 8). Random copolymers with vinyl esters and ethylene form readily, while largely alternating copolymers are observed with acrylates, acrylamide, maleates, or acrylonitrile. NVF will copolymerize more or less uniformly with methacrylates if the latter are added slowly in a delay feed to batch NVF, but copolymerizability is notably poor with styrene, butadiene, and alpha-olefins. NVF is similar to vinyl acetate in this regard. Terpolymers of styrene, NVF, and acrylates are also possible, presumably with styryl radical adding to acrylate, adding in turn to NVF [4].

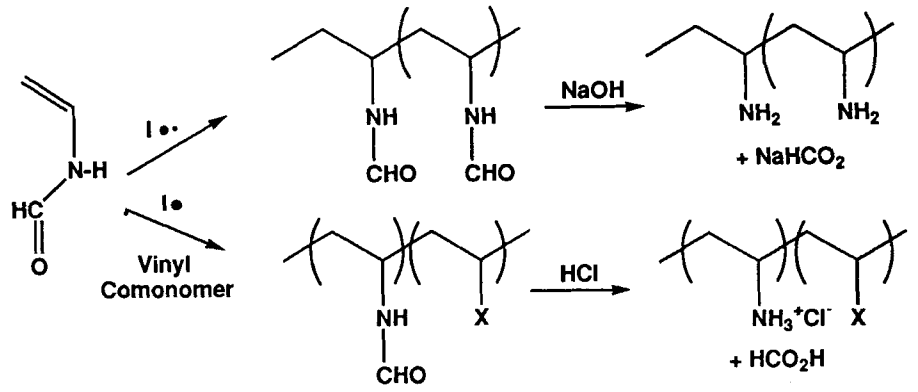

Figure 2. NVF (co-)Polymerization and Hydrolysis.

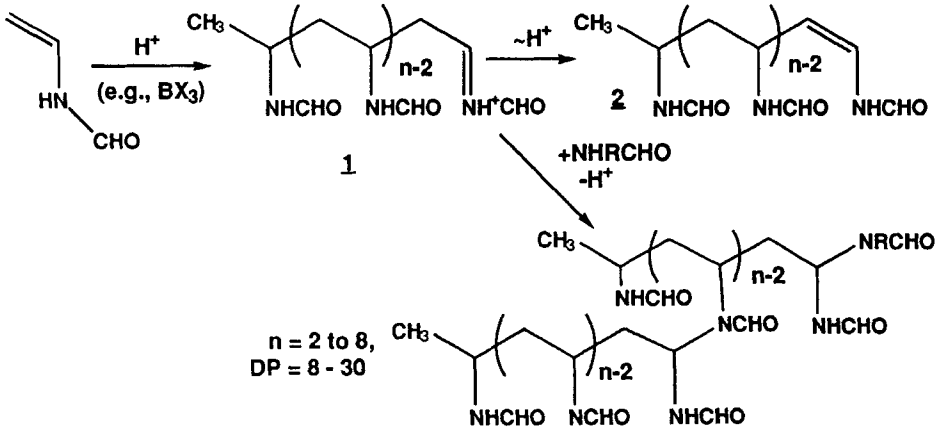

Figure 3. Cationic Oligomerization of NVF.

Unexpectedly, NVF will undergo cationic oligomerization [4] (Figure 3). Although NVF radical polymerization with vinyl ethers is sluggish, it also cooligomerizes with vinyl ethers under cationic conditions. The products show low molecular weights even when reacted neat at low temperatures and with low levels of catalyst. High levels of CH_3- by NMR in the products indicate rapid proton transfer, i.e., DP's of 3-7 between chain transfer events. Since typical oligomers have molecular weights between 600 and 1500 (DP 9 to 20), a mechanism involving chain transfer by reaction with NVF or oligoamide NH and generating high branching is indicated.

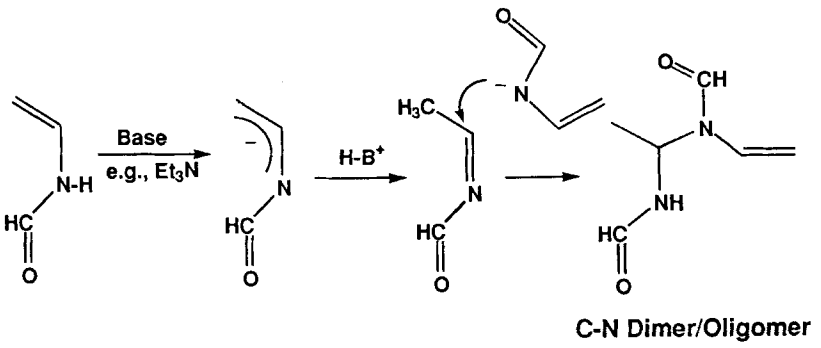

Figure 4. Base Catalyzed Dimerization.

Dimerization and low oligomer synthesis from NVF under base conditions has also been reported [6]). This product, which forms readily under catalysis from weak base amines such as Et_3N, has a different backbone structure, as shown in Figure 4.

Hydrolysis

Hydrolysis of NVF polymers and copolymers to the free amine with base or to the cationic ammonium salt with acid is rapid, especially compared to polymers of higher homologs of NVF or other polyvinylamine (PVAm) precursors [2] (Figure 5). PNVF hydrolysis under stoichiometric acid conditions is 60-70% under typical conditions of 60°C/6h. Conversion above this level is slower due to charge repulsion effects, but can be increased using additional acid under harsher conditions. Stoichiometric base hydrolysis is usually a more efficient approach for taking PNVF to poly(vinylamine). Kinetic measurements of the hydrolysis reaction gave ca. 95% formamide group hydrolysis within 3 hours using stoichiometric base at 60-80°C. After 6-8 hours, no formamide groups were detected by NMR [1]. Although not a problem in many applications, one issue with PNVF hydrolysis is the removal of hydrolysis byproducts. Acid hydrolysis with a strong acid gives the salt of PVAm plus formic acid, although the latter can be removed as alcohol formate by performing the hydrolysis in the presence of an alcohol. Base hydrolysis with, for example, sodium hydroxide, generates an equivalent of sodium formate. Careful solvent selection offers some options for precipitating the product from soluble salt solutions, or one may use ion exchange or ultrafiltration to prepare salt free polymer [1].

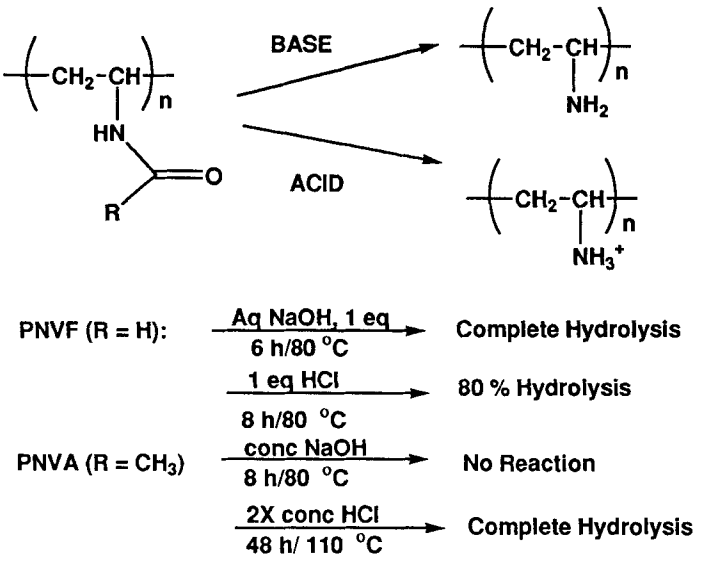

Figure 5. Polyvinylformamide and Polyvinylacetamide Hydrolysis Compared.

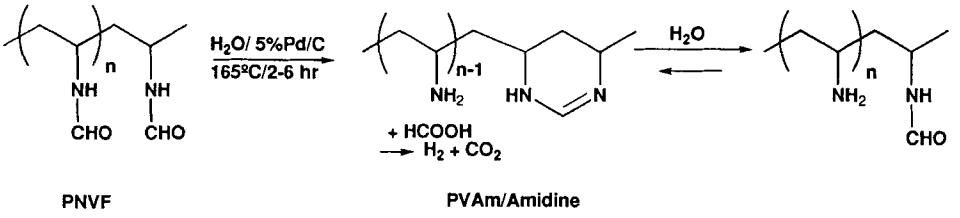

Figure 6. Catalytic PNVF Hydrolysis - Amidine Formation (Modified from Reference 4).

An alternative approach is to hydrolyze PNVF at elevated temperature in water alone [7] or with added ammonia as a volatile base (Figure 6). PVAm•HCOOH salts form and can be decomposed *in situ* if a small amount of palladium catalyst is present via the reaction:

$$PVAm{\bullet}HCOOH \text{ ---> } PVAm + H_2 + CO_2 \quad [8]$$

Hydrolysis levels of 30-70% are readily obtained in this way and the removal of byproduct salts is avoided.

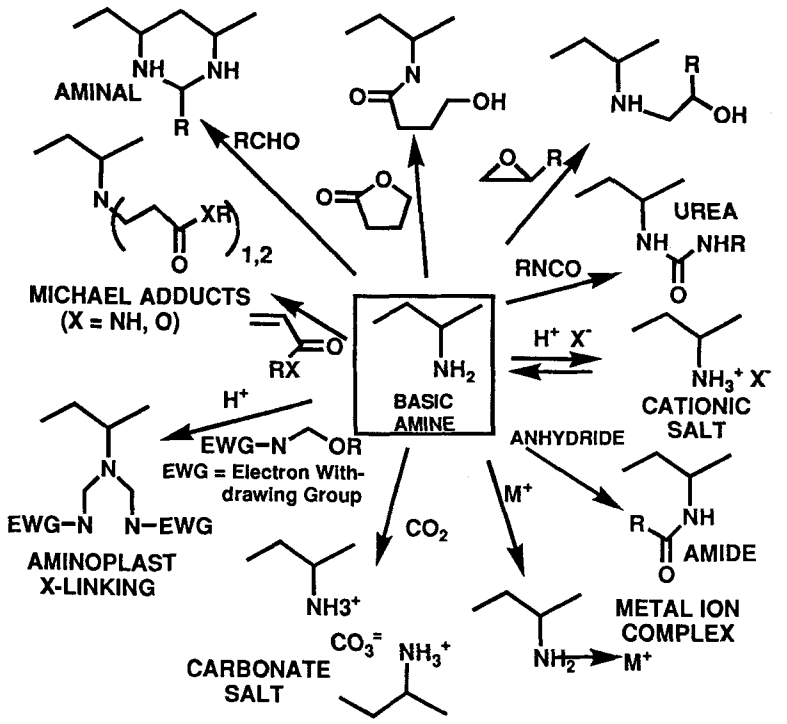

Figure 7. PVAm Chemistry (From Reference 1).

Water Soluble Polymer Applications

Water soluble NVF and vinylamine polymers and copolymers appear useful in a wide variety of applications, including water treatment, papermaking, and personal care [2]. The cationic forms in particular show superior adhesion or substantivity to anionically charged biological surfaces, such as cellulosics, skin, and hair, in addition to metal surfaces and glass. The wide chemistry of PVAm with its highly reactive primary amine functionality has been reviewed [2]. Some of the demonstrated reactions are shown in Figure 7. The high concentration of reactive, cationic primary amine groups covalently bonded to an all-carbon backbone and available in both very high and low molecular weights also provide a starting point for demanding applications in enhanced oil recovery, ion exchange resins, mining chemicals, surfactants and emulsifiers, adhesives, and biotechnology.

Copolymer Synthesis and Hydrolysis

Copolymers of vinyl acetate and NVF are readily hydrolyzed with base in a two step process to poly-(vinyl alcohol)-co-vinylamine (PVOH/VAm, Figure 8).

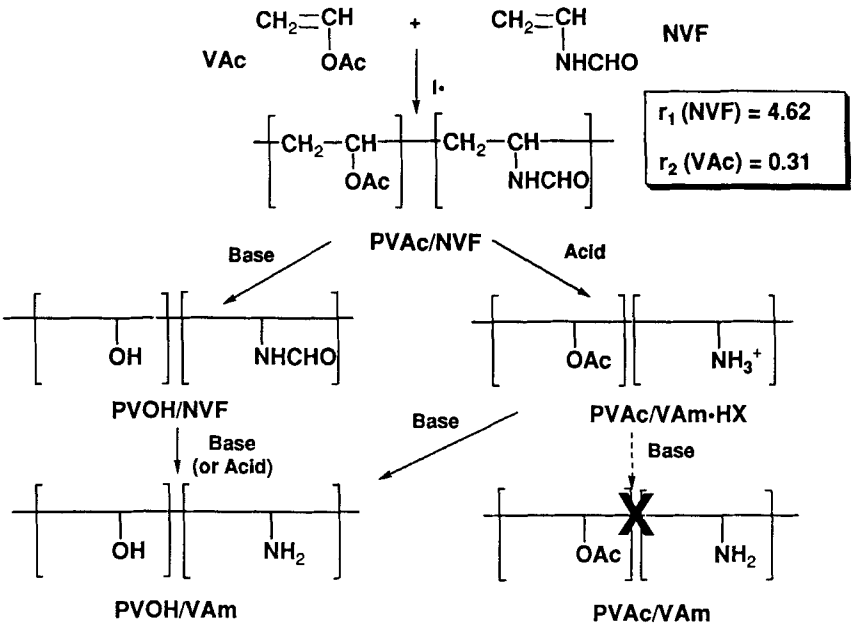

Figure 8. Vinyl acetate/NVF Copolymers and Their Hydrolysis Products.

This product, even with low levels of vinylamine (or co-PNVF) shows differentiated properties vs PVOH itself. In particular, the copolymers show much better low temperature hydrolysis in water and dramatically different reactivity, adhesion, and substantivity (partitioning onto surfaces from water) to cellulosics (wood, paper), skin, and hair.

Unlike water soluble PVOH/VAm, preparation of moderately priced hydrophobic copolymers with stable, but reactive free base amine functionality has proved difficult. Copolymerization with comonomers such as styrene which are chemically inert to PNVF hydrolysis conditions or to primary amines is at best difficult. NVF copolymerization with (meth)acrylates or acrylonitrile is convenient, and the resulting polymers can be readily hydrolyzed under acid conditions in high conversion because of the lack of strong charge repulsion between vinylamine groups in these strongly alternating copolymers. Unfortunately, an initially unexpected, but rapid side reaction occurs on attempted neutralization (or direct base hydrolysis). The amine groups very rapidly form lactams with neighboring ester (or nitrile) groups, as shown in Figure 9 [4].

Vinyl ester/VAm copolymers should in theory avoid this problem Vinyl acetate is too hydrolytically unstable and PVAc/NVF copolymers rapidly generate

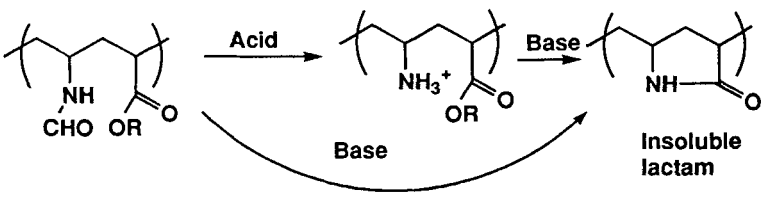

Figure 9. Hydrolysis of NVF/Acrylate Copolymers Yields Lactams.

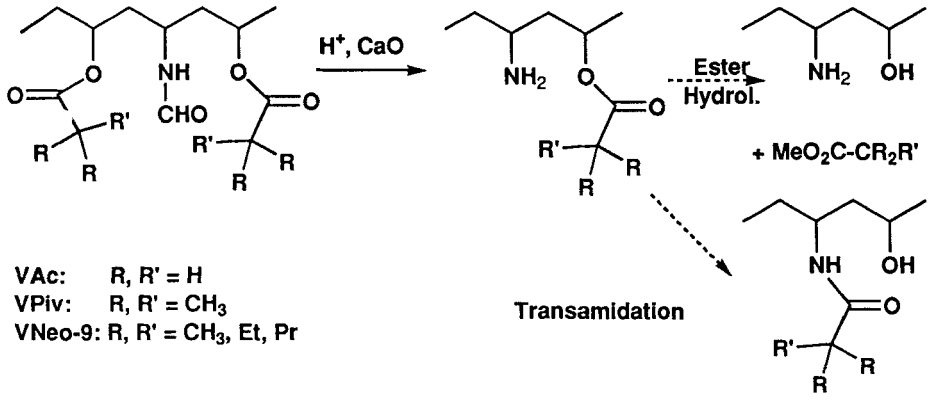

Figure 10. Vinyl Ester/VAm Copolymers - Steric Bulk Improves Stability (Modified from Reference 4).

high levels of vinyl alcohol (Figure 8) and (under acid) some vinylacetamide functionality on attempted formamide hydrolysis. Higher vinyl esters, such as those of neoacids, can be coaxed to generate free base amine functional hydrophobic copolymers, but preferred comonomer availability, processing, and stability issues remain (Figure 10) [4].

NVF Derivatives

Although normally considered as a raw material for polymers by radical (and oligomers by ionic) reaction, derivatives can be made from NVF by reaction at the unusually acidic NH group. As reported briefly in a landmark Bayer paper [5b], reaction with isocyanates and addition to Michael acceptors are both possible, leading to new families of vinyl functional and hydrolysis resistant resins and comonomers.

Reaction of NVF with aromatic isocyanates is reasonably rapid, especially using appropriate catalysts. Unfortunately, the products, acylureas in conjugation

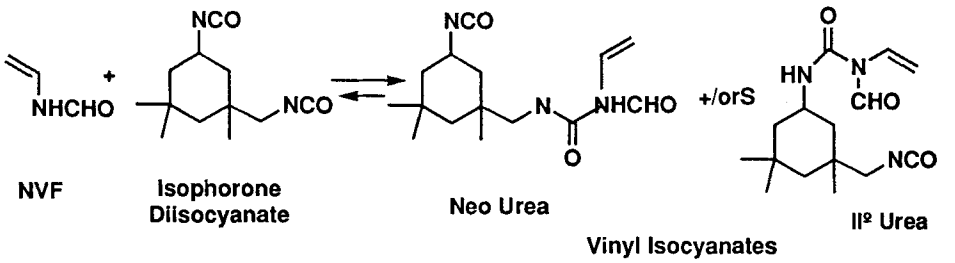

Figure 11. Synthesis of NVF/Isocyanate Adducts.

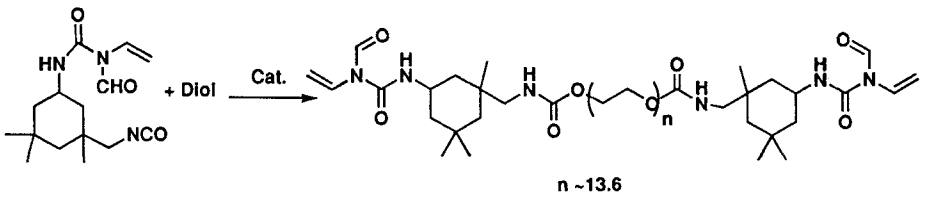

Figure 12. Divinyl Functional Resins from NVF.

with a vinyl group and an aromatic ring, are not sufficiently thermodynamically favored to allow clean or high yield conversion of the starting materials and the products have only limited stability. Better results are obtained using aliphatic isocyanates. In the presence of tin catalysts, fair to good yields of vinylacylureas can be achieved and, in the case of diisocyanate/NVF 1:1 adducts, the products have sufficient stability to be converted by reaction with diols to divinylurea functional oligomers (Figures 11 and 12). These show utility as resins in radiation curable coatings (Table 9).

NVF Michael Adducts

The products of the reaction of NVF with acrylates and methacrylates (Figure 13) are of greater current interest. Surprisingly, although NVF itself in the presence of base undergoes rapid reaction to C-N dimers and eventually oligomers, and acrylates show anionic homopolymerization, the two together rapidly and cleanly form 1:1 Michael adducts, frequently in nearly quantitative yield [9]. The alkyl 3-(N-vinylformamido)propionates are designated here by combining the component abbreviations: MANVF for methyl acrylate + N-vinylformamide, but are also trademarked generically as Vinamer™ RP, e.g., MP for the methyl acrylate adduct. They form readily from a wide variety of acrylate esters, as shown in Table

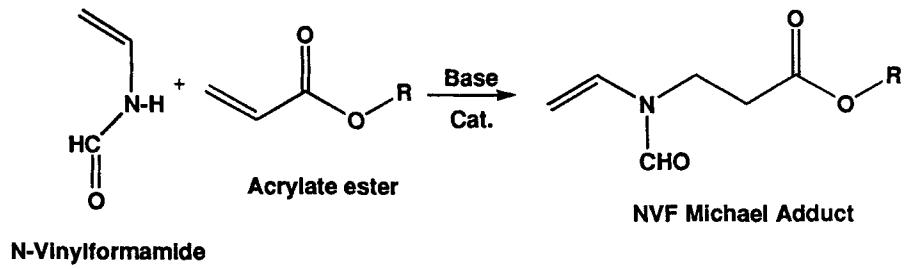

Figure 13. Synthesis of NVF/Acrylate Michael Adducts.

2. Acrylates of bulky alcohols give lower yields than simple acrylates, but they and methacrylate esters react acceptably using the right catalysts. Acrylates with active hydrogens (hydroxyethyl acrylate), acrylic acid, and acrylamides with active hydrogen fail to give the desired products.

Acceptable base catalysts include alkali metal alkoxylates, alkali and alkaline earth hydrides, and alkali hydroxides. Metal alkyls, such as butyl lithium, can also be used, but tend to produce acrylate homopolymers as a side product. Catalyst selection is broad for Michael addition to lower acrylate esters, the choice tending to be based on reaction rate (slower and more readily controlled with sodium hydroxide and calcium hydride), convenience, and cost. Reaction of NVF with diacrylates or methacrylate esters is significantly more demanding and is most successful by use of metal hydrides. The reaction can be run in solvent or, preferably, neat and is strongly exothermic (approximately 18 kcal/mole). It frequently requires either good heat removal or delay feed of the mixed monomers. An induction period after base addition is frequently observed, but ambient temperature initiation is usually acceptable. The reaction temperature is best kept under 80-100°C to minimize byproducts.

The reaction generates significant color, particularly using catalysts such as sodium methoxide and lower purity NVF, but this is readily removed by vacuum distillation of the product. Distillation becomes highly problematic with heavier products, such as the di-NVF adducts with diacrylates, and recourse is to the cleaner hydride catalyzed processes to prepare a colorless product.

The products appear to be strongly complementary to NVF. Presumably because of their greater steric bulk, they do not homopolymerize as readily and are much more difficult to hydrolyze to expose the amine functionality. On the other hand, they offer a wide range of T_g's, are much more forgiving during storage and

TABLE 4. Formulation Using Methyl 3-*N*-Vinylformamidopropionate as a Reactive Diluent

Epoxy acrylate oligomer (UCB Radcure Ebecryl 3700)	12.5 g
TMPTA[a] (UCB Radcure)	2.5 g
TRPGDA[b] (Sartomer SR 306)	2.5 g
Methyl 3-*N*-vinylformamidopropionate	16.6 g
Irgacure 184[c] (Ciba-Geigy)	0.63 g

a Trimethylolpropane triacrylate
b Tripropylene glycol diacrylate
c 1-Hydroxycyclohexyl phenyl ketone

TABLE 5. Performance of MANVF Based Radcure Formulation

Properties & Performance	
Viscosity of the mixture (cps, 25°C)	314
Pendulum hardness (1 pass)	159
Pendulum hardness (4 passes)	163
1:4 Pass hardness ratio	98
Depth of cure (DOC, mil)	78
Water Rub test (1 pass/4 passes)	>200/>200
MEK Rub test (1 pass/4 passes)	>200/>200

TABLE 6. Formulation Using Butyl 3-*N*-Vinylformamidopropionate as Reactive Diluent.

Formulation:

Epoxy acrylate	12.5 g
TMPTA	2.5 g
TRPGDA	2.5 g
Butyl 3-*N*-vinylformamidopropionate	7.5 g
Irgacure 184	0.63 g

TABLE 7. Results Using BANVF

Properties & Performance	
Viscosity of the mixture (cps, 25°C)	1250
Pendulum hardness (1 pass)	160
Pendulum hardness (4 passes)	214
1:4 Pass hardness ratio	75
Depth of cure (DOC, mil)	55
Water Rub test (1 pass/4 passes)	>200/>200
MEK Rub test (1 pass/4 passes)	>200/>200

TABLE 8. NVF Monomer Reactivity Ratios (from Reference 4)

NVF Monomer, r_1	Comonomer	r_2
4.62	Vinyl acetate	0.31
0.05	Acrylamide	0.52
0.25	Sodium acrylate	0.58
0.06	n-Butyl acrylate	0.54
0.05	Maleic anhydride	0.02

TABLE 9. Divinyl Functional NVF/Urethane Resins (Unoptimized)

COMPONENT	Formula A	Formula B	Formula C
Di-NVF-Urethane Oligomer	70%		51%
Polyurethane Acrylate Oligomer (Ebecryl 230)	--	70%	---
TPGDA (Tripropylene glycol diacrylate)	20%	20%	---
N-Vinylformamide	10%	10%	10%
Diethyl maleate			39%
Darocur 1173 (photoinitiator)	5 phr	5 phr	5 phr
PENDULUM HARDNESS (24μ Films on Al Panels, 200 Watt/in, Med. Press Hg Lamp) # Passes at 105 fpm			
	4	27	35
	10		32
MEK resist.(# dbl rubs)	>200	>200	>200

handling, produce lower water sensitivity in copolymers, and show outstanding toxicological properties. A market segment for which this group of properties seems particularly appropriate is radiation cure coatings. The experimental shows several examples of the use of these materials as reactive diluents in standard radiation cure formulations (Tables 4-7, 10).

Michael Adduct Transamidation

As mentioned above, the addition of NVF to highly useful functional acrylates containing active hydrogen has not been successful. More recently, it has been observed that this deficiency can be cured by post reaction of NVF Michael

TABLE 10. NVF and EANVF in Radiation Cure Coatings

	NVP	NVF	EANVF
Water solubility (wt.%)	100	100	7
Tg (homopolymer, °C)	175	150	24
Viscosity (formulated mixture, cps, 25°C)	464	625	1080
Persoz hardness (sec.)	252	255	233
Depth of cure (mil.)	90	90	70
MEK double rub	>200	>200	>200

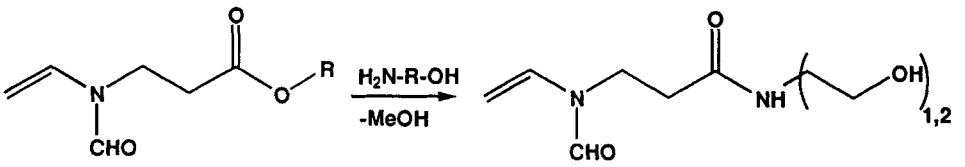

Figure 14. Synthesis of Functional NVF Derivatives.

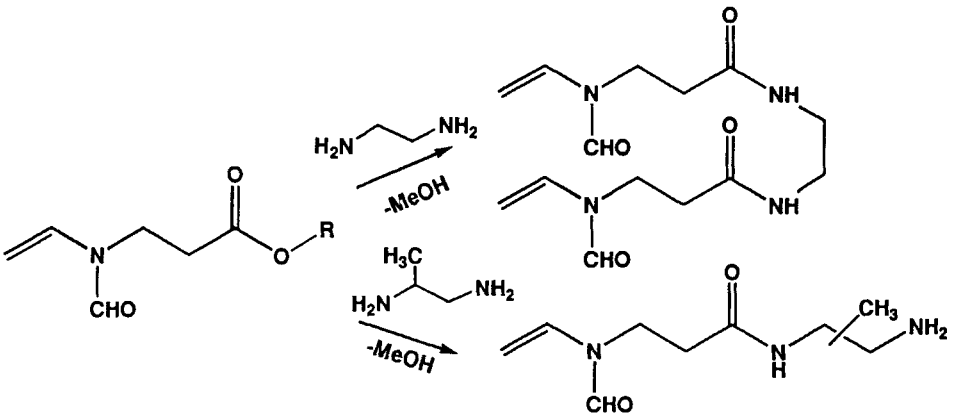

Figure 15. Synthesis of Divinyl and Amine Functional NVF Derivatives.

adducts with appropriate amines under base catalysis. Examples of this process include mono- and diethanolamine to give hydroxy functional NVF derivatives (Figure 14), ethylenediamine to give a di(vinylformamidopropionamide), and 1,2-diaminopropane to give an amine functional NVF derivative (Figure 15). More details will be forthcoming on this work as the technology develops.

CONCLUSIONS

The high reactivity of N-vinylformamide that makes it a challenging molecule to synthesize and purify, particularly on a commercial scale, makes it highly attractive for downstream application in a wide variety of forms. Water soluble polymers and copolymers are readily made by free radical reaction in the full range of molecular weights and can be easily hydrolyzed under acid or base conditions to free up cationic functionality or reactive primary amine, depending on pH. The cationic forms especially show superior adhesion or substantivity to anionically charged biological surfaces and find favor in water treatment, papermaking, personal care, and enhanced oil recovery. Poly(vinyl alcohol-co-vinylamine) is a particularly attractive example. Hydrophobic copolymers can also be selectively hydrolyzed to cationic or reactive amine functional analogs with potential application as reactive coatings.

More surprisingly, NVF can be oligomerized under cationic conditions to branched carbon-carbon oligomers or, under base conditions to low carbon-nitrogen oligomers. Under base catalysis, NVF can be reacted at the acidic amide site with isocyanates or, more usefully, with Michael acceptors, such as acrylate and methacrylate esters. These in turn can be transamidated with functional amines to prepare NVF derivatives with reactive functionality, including vinyl, allyl, hydroxy, and amine. NVF and its derived monomers and resins show particular promise in radiation cure coatings, based on their outstanding physical, chemical, and toxicological properties.

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