N-Vinylformamide – Syntheses and Chemistry of a Multifunctional Monomer

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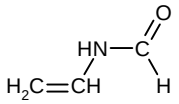
Abstract. *N*-Vinylformamide (VFA), the simplest member of the enamide group, is the key compound in the synthesis of linear cationic polymers with primary amino groups. In recent decades VFA has been the object of intensive research activity in industry and in universities with the aim of developing an economic method of synthesis. The various principles underlying the synthesis are described and the possibilities for their industrial realisation are discussed. From the large number of methods two variants have now been established as industrial production procedures at BASF and Mitsubishi Kasei Corp. (MKC). VFA is now available in tonne quantities in high purity. An overview of the versatile reaction possibilities of this multifunctional monomer and an extensive list of references are also given. The radical polymerisation to polyvinylformamides and their further reaction to polyvinylamines are not covered in this review.

Contents

I Introduction

N-Vinylformamide (VFA) **1** [1])



1

is the simplest member of the enamide group and is also the synthetic equivalent of N-vinylamine which does not exist in the free state. VFA has a molecular weight of M = 71 g/mol (*N*-vinylamine equivalent 43 g/mol) and a high boiling point of 10 mbar 80 °C. It is a clear, colourless liquid and can be stored without decomposition for several months under suitable conditions.

VFA is the key compound in the synthesis of linear cationic polymers with reactive primary amino groups. For decades efforts were made all over the world to work out an economically attractive and ecological route to these polymers, which were expected to display a large number of interesting technical properties. These include the following:

· the very high possible charge density of maximum 23 meq/g, because of the low molar mass of vinylamine of 43 g/mol, more than 50% of which is still retained even at pH 7 [1],

[1]) abbreviations used (in alphabetical order): ACA acetaldehyde; AF ammonium formate; AIBN azobisisobutyronitrile; APC Air Products and Chemicals; BIS ethylidenebisformamide; DIN α,α′-iminodipropionitrile; FA formamide; FAC formic acid; FAN *N*-formylalaninenitrile; MKC Mitsubishi Kasei Corporation; LAN lactonitrile PVAm polyvinylamine; VFA *N*-vinylformamide

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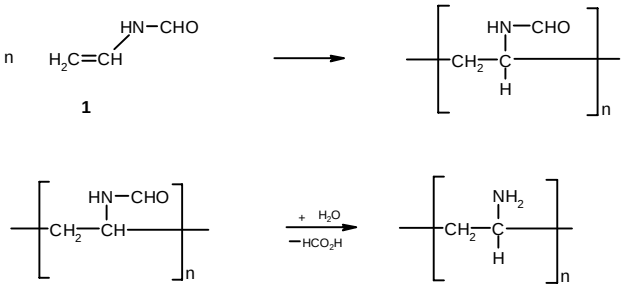
· the high availability of H-atoms in the primary amino groups, which, according to F. Linhart and W. Auhorn[2] are available for hydrogen bonding to suitable substrates, and

· favourable environmental aspects because the polymer solutions are completely free of residual monomer after hydrolysis to polyvinylamines (*cf.* Section IV 1.2).

Earlier attempts to gain access to such polymers mostly failed because of the insufficient purity of the monomer. However, after a commercial process for the production of high purity VFA was developed, development work on VFA was undertaken all over the world.

High purity VFA can undergo radical polymerisation very easily and can copolymerise with a large number of other monomers to form products of various molar masses. The formyl protecting group can then be completely or partially cleaved by hydrolysis from the mostly water-soluble polymers leading to the strongly basic polyvinylamines (PVAm) [3–4].

Scheme 1 shows the homopolymerisation and hydrolysis processes.



Scheme 1 Homopolymerisation of VFA **1** and hydrolysis to yield PVAm

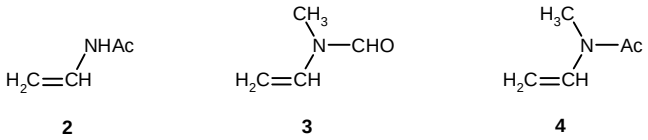
By the use of suitable comonomers and by varying the hydrolysis conditions, the basicity (charge density), hydrophilicity, solubility or reactivity can be controlled within wide limits during the polymerisation reactions.

The polyelectrolytes thus obtained have outstanding property profiles as additives in paper manufacture (dry and wet strength, retention, dewatering, starch modification) [5–6] and in domestic sewage sludge processing. There are also interesting possibilities for applications in other areas, among them dye fixation, ion exchangers, UV-curable coatings and oilfield chemicals.

Details of the copolymerisation of VFA and the possible uses of the copolymers are outside the scope of this review and will be the subject of a later publication.

Until well into the 1980s the companies Dynapol, Showa Denko, Celanese and Hoechst were manufacturing the more highly substituted enamides **2**, **3** or **4** because they seemed to be more accessible, although it had been possible to prepare in good yield and characterise the simplest molecule, VFA, since 1965 [7].

Because VFA **1** had the following advantages compared with its higher homologues, interest in **2**, **3** and **4** finally decreased in favour of *N*-vinylformamide itself.



· After polymerisation the amino protecting groups must be readily hydrolysable by acids or bases in order to prevent cleavage of the polymer chains. There are significant differences here which favour the use of polyvinylformamide (PVFA) [8–11]. Summerville and Stackman [12] attribute the difficulty of achieving 100% acidic hydrolysis of a polymer based on **2** (*e.g.* MW 34 000: 27 h/100 °C) to the density and frequency of occurrence of the positive charges. In the hydrolysis of PVFA this obviously plays only an insignificant role (MW ca. 300 000: 4 h/75 °C).

· The polymerisation and hydrolysis of the monomers **3** and **4** do not give the polymers preferred for technical applications which have reactive *primary* amino groups. The *N*-methyl-polyvinylamines formed also have a ca. 33% higher molar mass per cationic centre, which leads to environmental problems on use.

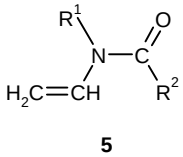
· Only with VFA can molar masses in the million region, comparable with that of polyacrylamide, be achieved. This is attributed to the fact that, for example, unlike **2** [13], VFA can be obtained in particularly high purity [14].

· VFA can copolymerise readily with, for example, vinyl acetate, acrylamide, sodium acrylate, acrylic esters or maleic anhydride [15].

· Protection of resources: the use of VFA allows simple recycling of the formic acid (FAC) liberated on hydrolysis of the polymer as methyl formate. The latter can be converted into formamide with ammonia and recycled to the monomer synthesis.

II *N*-Vinylformamide Syntheses

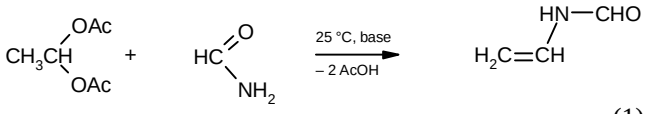
N-Vinylformamide is a secondary enamide. While tertiary enamides of type **5**



are relatively accessible by various routes, *e.g.* by vinylation of secondary amides with acetylene [16–18]

or HX-elimination from β-substituted *N*-ethylamides [19–20], secondary enamides have not yet been obtained in this way. A base-catalysed direct vinylation of formamide with acetylene would be problematic, particularly because of the thermal instability of the starting material and product, the sensitivity of VFA towards bases, and the presence of two reactive NH-bonded functional groups in the formamide.

More recent work describes a synthesis of VFA starting from ethylidene acetate **6** [21] (1). **6** is readily synthesised from acetic anhydride and acetaldehyde (ACA).

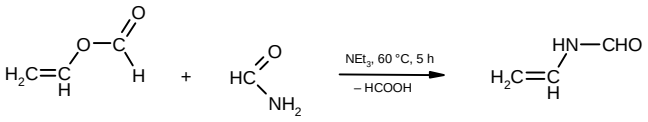


(1)

6 **1**

The reaction takes place at room temperature, but requires 2 mol of base per mol of diacetate **6** to bind the acetic acid liberated. The selectivities (yields based on diacetate converted) are only 23%.

The work of Ruehl *et al*. [22] is of greater industrial interest. The authors describe the vinylation of formamide (FA) with vinyl formate **7** at 60 °C in the presence of base (2).



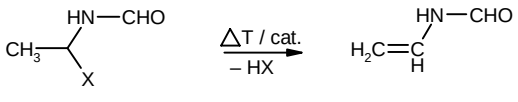
(2)

7 **1**

Selectivities of up to 92% are found (yields based on vinyl formate converted). The use of stoichiometric quantities of base, however, makes the work-up of the product mixtures obtained more difficult.

1. Industrial Precursors

All industrially interesting syntheses of *N*-vinylformamide **1** start from α-substituted *N*-ethylformamides **8**. VFA is always formed in very good yields of over 90% through the thermal or catalytic elimination of HX (3).



(3)

8 **1**

Depending on the nature of the substituent X, very different synthetic processes have been developed by some companies on an industrial scale (Table 1).

Table 1 Industrial procedures for preparing *N*-vinylformamide according to (3)

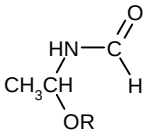
Starting material	X	Selectivity [a])	Reference
9	-OR	94	[46]
11	–NHC(=O)H	98	[41a]
12	-OAc	89	[41b]
13	-CN	93	[51]

[a]) Yield in % based on converted starting material

The syntheses of the starting materials for procedures used according to equation (3) first need to be described.

1.1 N-(α-Alkoxyethyl)formamides

N-(α-Alkoxyethyl)formamides are *O,N*-acetals of type **9**.

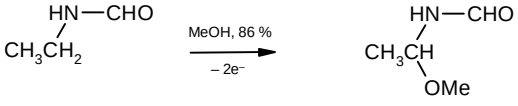


	R
a	Me
b	Et
c	*i*-C_3H_7

9 a - c

There have been numerous publications concerning their synthesis and purification [23–31]. Various synthetic principles have been followed:

· In the 1970s Mitzlaff[23] described the electrochemical methoxylation of *N*-ethylamides (4).

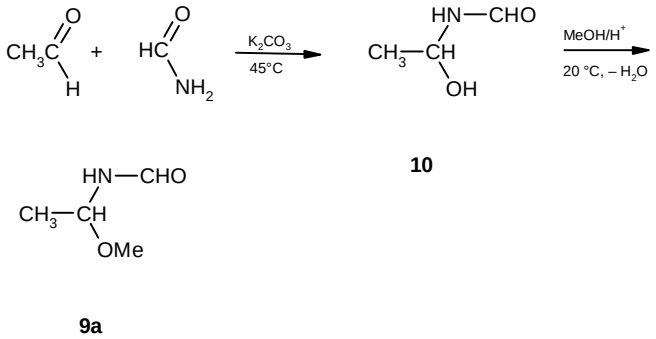


(4)

9a

The reaction proceeds particularly well with *N*-ethylacetamide as the starting material and gives *N*-vinylacetamide **2** in 92% yield [24].

· Higher selectivities (yields based on acetaldehyde converted) of at least 95% can be achieved by treatment of the acetaldehyde with formamide under base catalysis and subsequent reaction with methanol according to Scheme 2 [25].



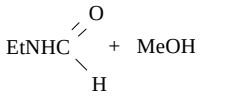
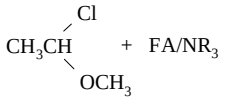
10

9a

Scheme 2 Two step synthesis of α-methoxyethylformamide **9a**

The process involves the formation of *N*-(α-hydroxyethyl)formamide **10**, a crystalline compound with a melting point of 53 °C, the isolation of which can, however, be avoided [26]. Other possible synthesis routes are shown in Table 2.

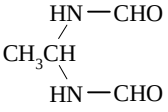
Table 2 Syntheses of *O,N*-acetals **9**

Starting materials	Catalyst	Yield (%)	Ref.
	Supporting electrolytes	86	[23–24]
ACA + FA/ROH	Bases	95	[25–26]
ACA + FA/ROH	Acids	58 [a]	[27]
11 (BIS) + ROH	Acids	60 [b]	[28]
ACA-acetal + FA	Acids	82 [c]	[29]
	–	23	[30]
Vinyl ether + FA	Acids	63	[31]

[a]) Selectivity: 88% (yield based on ACA converted)
[b]) Selectivity: 92% (yield based on **11** (BIS) converted)
[c]) Yield based on FA

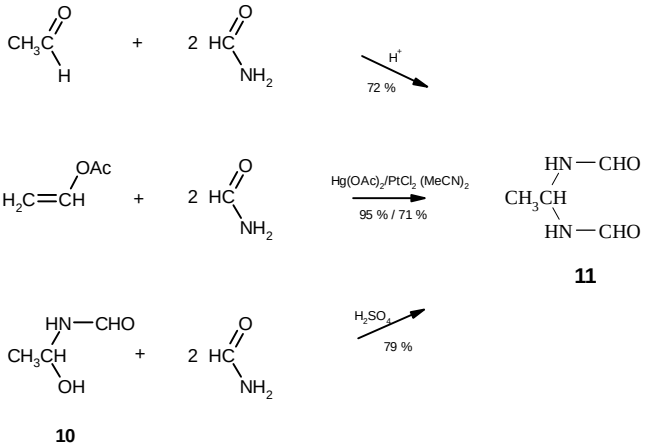
1.2 N-(α-N'-Formamidoethyl)formamide

N-(α-*N'*-Formamidoethyl)formamide is an ethylidenebisformamide BIS with formula **11**.



11

It can be synthesised particularly well by the method of Dawson and Otteson [32–33] from acetaldehyde and formamide under acidic catalysis in yields of 72% (Scheme 3). Vinyl acetate can also be used as an acetaldehyde equivalent [34–35] and gives the bis-formamide in 95% and 71% yields on Hg and Pt catalysts respectively. Another possible starting material is the hydroxyethylformamide **10** [36]. The etherification of this compound with methanol to give *N*-(α-methoxyethyl)formamide **9a** has already been discussed. An overview is shown in Scheme 3.



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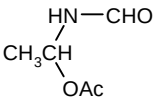
Scheme 3 Three synthetic routes to *N*-(α-*N'*-formamidoethyl)formamide **11**

1.3 N-(α-Acetoxyethyl)formamide

N-(α-Acetoxyethyl)formamide (AEF) **12**

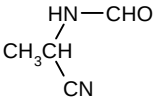


12

was prepared by Parris and Armor in 82% yield, characterised spectroscopically, and pyrolysed [41b]. The precise details were not given.

1.4 N-(α-Cyanoethyl)formamide

Formylated alaninenitrile **13** is an outstanding precursor for VFA.

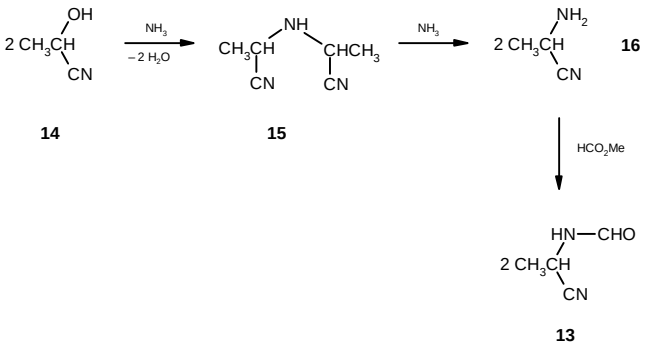


13

Kurtz and Disselnkötter reported their work in this area in Liebigs Annalen in 1972 [7]. They first succeeded

in preparing and characterising VFA as the simplest member of the enamide group in 84% yield in 1965 [37a–c] (3, X = CN).

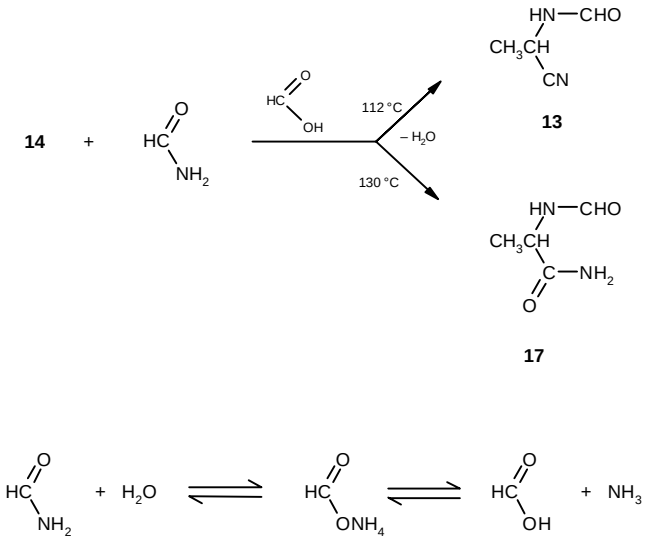
N-Formylalaninenitrile **13** (FAN) required for the pyrolysis to give VFA was synthesised according to Scheme 4 [37d–e].



Scheme 4 3 step synthesis of *N*-formylalaninenitrile FAN **13** from LAN **14**

Lactonitrile (LAN) **14** is converted almost quantitatively with ammonia into α,α'-iminodipropionitrile (DIN) **15** in 4 h at 70 °C and the water of reaction removed. After drying, the dinitrile is converted with excess ammonia into alaninenitrile **16**. The latter is formylated with a 5 molar excess of methyl formate in the presence of 15 mol % formic acid (FAC) in 95 % yield.

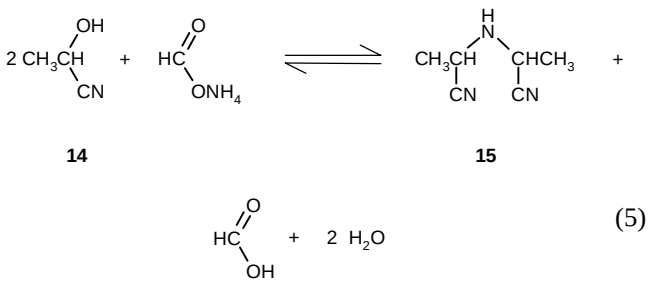
In 1969 Becke and Pässler [38–39] succeeded in synthesising FAN **13** by a direct route, shown in Scheme 5, involving lactonitrile **14** and formamide in the presence of acid, *e.g.* formic acid.



Scheme 5 Direct synthesis of FAN **13** from LAN **14** and formamide and equilibria between FA and water

However, we considered the yields of 82% based on acetaldehyde and 75% based on formamide to be unsatisfactory for an industrial process. Among the reaction products we found not only *N*-formylalanineamide **17** anticipated by the authors from hydrolysis of the nitrile group, which at higher temperatures and acid concentrations became the main product, but also large quantities of ammonium formate (AF) formed by hydrolysis of formamide. Furthermore gases formed by decomposition of formic acid, essentially CO and CO_2, which removed 2–3 mol% free HCN from the reaction system, were also formed.

Kinetic measurements on the FAN synthesis and the determination of by-products showed that an equilibrium between lactonitrile (LAN) and ammonium formate on the one side, and DIN and formic acid on the other is set up before the actual FAN synthesis (5).



(5)

The first priority was to make this equilibrium independent of the ammonium formate, which was only formed gradually by hydrolysis of the formamide (FA) (Scheme 5) by adding AF as a cocatalyst at the beginning.

Figures 1 and 2 show the AF and FAC kinetics with and without AF cocatalysis.

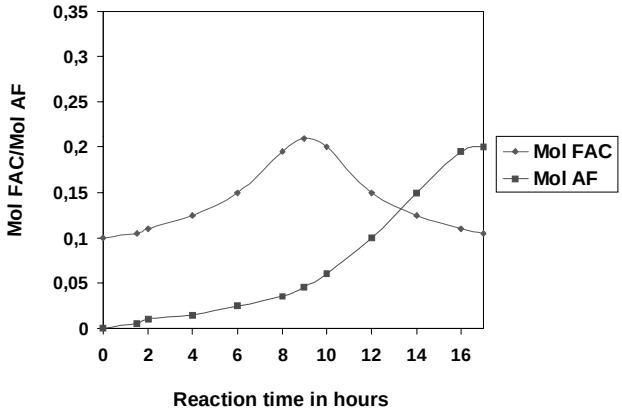


Fig. 1 *N*-Formylalaninenitrile synthesis at 90 °C without ammonium formate cocatalysis, molar ratio LAN : FA : FAC = 1: 1,5 : 0,10

Without AF cocatalysis the AF concentration increases continuously during the reaction to a value of ca. 0.20 mol in a 1 mol reaction mixture; *i.e.* initially all the AF produced by FA hydrolysis is consumed in dinitrile formation. Formic acid (FAC) is thus formed, which reaches a maximum concentration after 9 h, as in the further reaction of DIN to FAN FAC is consumed again, so that at the end of the reaction after ca. 17 h the original FAC concentration is reached. The formation of the dinitrile **15** is analogous to the liberation of FAC from AF and occurs simultaneously.

If AF is added at the beginning (*e.g.* 0.26 mol per mol of LAN) and the reaction allowed to proceed at 90 °C, the reaction time is reduced from 17 to 6 h [40a].

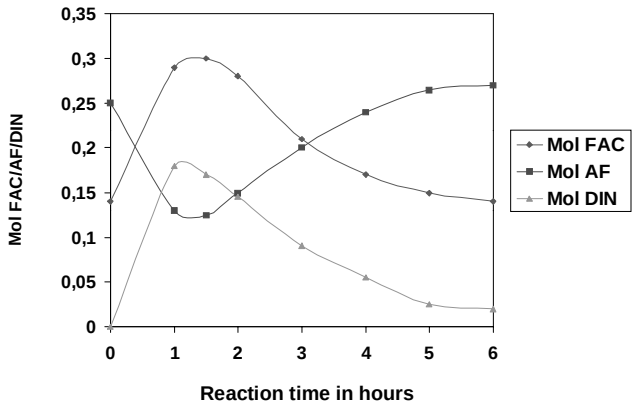
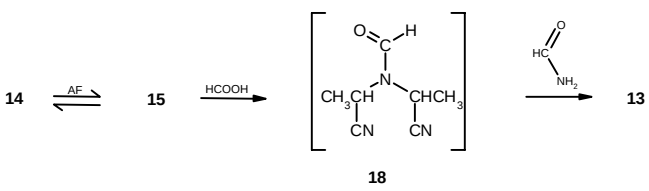


Fig. 2 *N*-Formylalaninenitrile synthesis at 90 °C with ammonium formate cocatalysis, molar ratio LAN : FA : FAC : AF = 1 : 1,5 : 0,14 : 0,26

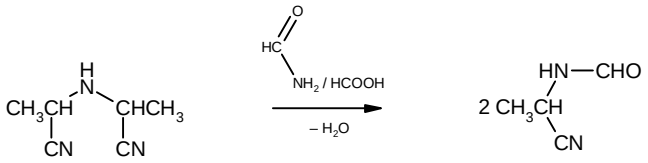
The FAC and DIN concentrations reach a maximum after ca. 1.5 h, and at this point the AF concentration reaches a minimum. The final concentration of AF is only slightly above the initial concentration; *i.e.* higher FA losses are thus avoided. With even higher AF concentrations in the reaction mixture, *e.g.* 0.5 mol per mol of LAN, the reaction is finished after 3 h and the FA hydrolysis completely suppressed (Scheme 5). AF is readily distilled *in vacuo* and can thus easily be recycled.

Scheme 6 shows the possible reaction path. The α,α'-iminodipropionitrile **15** is formed initially in an equilibrium reaction and is then formylated by FAC on nitrogen giving **18**. FA subsequently effects the cleavage giving 2 mol of *N*-formylalaninenitrile **13**. At the same time AF is formed again by the hydrolysis of FA.



Scheme 6 Proposed reaction mechanism for the direct synthesis of FAN **13**

In agreement with this is the observation that FAN can easily be obtained from previously isolated pure dinitrile, FA and FAC. The reaction takes place at 90 °C in 4 h and gives FAN in 87% yield [40b], (6).



(6)

15 **13**

18 could not be detected but is known from the literature [40c].

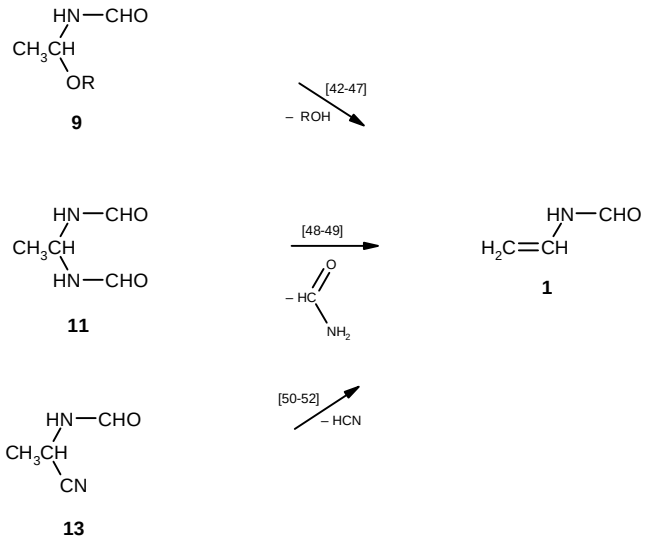
The AF cocatalysis brings considerable advantages to the synthesis of *N*-formylalaninenitrile from LAN and FA, in particular an increase in yield to 95% based on ACA and FA, and at the same time a lowering of the reaction temperature and thus a significant reduction in waste gas production. The cocatalyst can easily be recycled by distillation and this makes the reaction more economical.

2. Pyrolysis Procedures

The pyrolysis of the starting materials **9**, **11** and **13** (3) with the α-substituents discussed in Section II. 1 is a highly endothermic process which takes place optimally in the gas phase at temperatures of 400–600 °C and residence times of a few seconds down to around a tenth of a second. If the gases are passed over a solid bed catalyst, *e.g.* $CaCO_3$ or MgO [37c, 49], the pyrolysis temperatures can often be drastically lowered, *e.g.* to 275 °C at the beginning of the pyrolysis campaign with the bis-starting materials [41a]. The vacuum to be applied depends on the boiling point of the precursor and is generally between 10 and 150 mbar. If the HX species cleaved is a high-boiling compound, such as formamide, the partial pressure can be lowered by an inert stripping gas, such as nitrogen, at normal pressure. However more energy is thus used.

With optimised processes selectivities (yields based on the starting materials converted) of up to 98% are described. However, work-up losses of up to 20% can occur. The *N*-vinylformamide obtained is thermally and chemically labile (*cf.* sections III and IV) and requires particularly careful work-up, according to Scheme 7.

In choosing the best procedure, besides the chemical selectivities, the most economic purification operations, mostly involving distillation, and the ease of recycling of the liberated gases are important.



Scheme 7 Industrial syntheses of VFA **1** *via* precursors **9** (MKC), **11** (APC) and **13** (BASF)

The procedure shown in (3, X = CN) with FAN as the starting material is particularly favourable as already in the quench, *i.e*. in the first condensation stage after the pyrolysis reactor, the HCN liberated can be separated almost quantitatively from the VFA without a separate distillation step. At the same time, *i.e*. still *in vacuo* of *e.g*. 10 mbar, it can be reconverted into lactonitrile with acetaldehyde. This chemisorption [52] takes place almost quantitatively using a circulation loop, which is fed with lactonitrile and formamide at, for example, 10 °C. The lactonitrile thus obtained can be fed back directly into the FAN synthesis. This results in an economically and ecologically attractive procedure.

In [41b] Parris and Armor discuss the various known pyrolysis procedures and mention *N*-(α-acetoxyethyl) formamide (AEF) **12**. Enthalpies of reactions of different precursors to give VFA are compared with each other and with those of possible competing reactions. The authors take the view that these enthalpies represent the activation energies for the thermal cleavage in the gas phase (see Table 3).

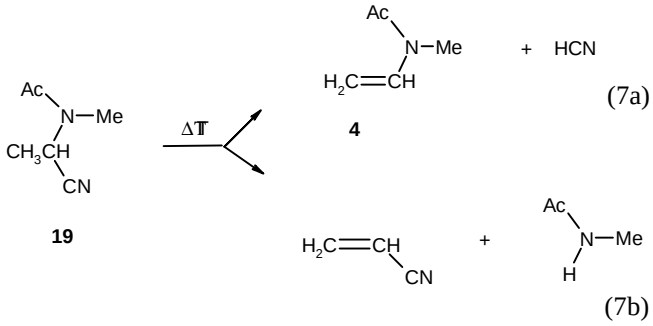
The authors consider that the reaction shown in (3, X = CN) is particularly favourable as no by-product formation is possible and the relatively low reaction enthalpy of 7.6 kcal/mol allows lower and therefore less drastic pyrolysis temperatures.

However, we found outstanding selectivities of over 95% on basic catalysts even for the reaction (3, X = CN). Acrylonitrile was not detected, although the significantly lower reaction enthalpy would make its formation likely. Kurtz and Disselnkötter [7] showed as early as 1972 how strongly the solid bed catalysts and the chemical structure of the starting material affect the direction of the reaction.

- On silica gel catalysts FAN is converted into acrylonitrile in 45% yield. This may be the result of a secondary reaction: nitrile formation from *N*-alkylformamides on silica gel.
- *N*-Methyl-*N*-acetylalaninenitrile **19** gives acrylonitrile (7b) and *N*-methylacetamide as by-products of thermal cleavage as well as the expected enamide **4** (7a).

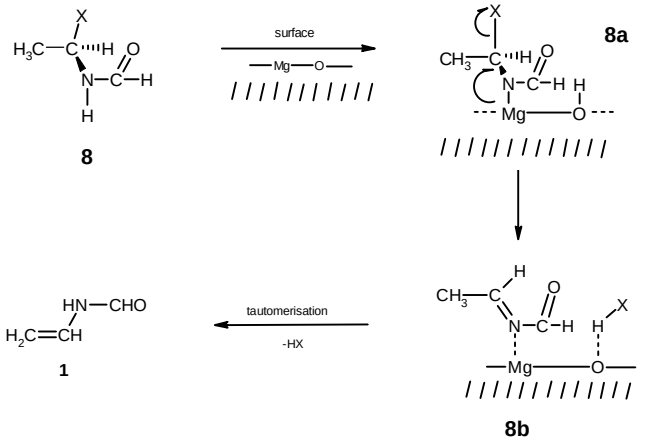
Table 3 Enthalpies of various reactions of **9 b**, **11**, **12** and **13** to give VFA and possible competing reactions

Pyrolysis reaction		Equation	ΔH_R (kcal/mol)
HN—CHO, CH3CH, OEt (**9b**)	– EtOH → **1**	(3, X = OEt)	16,7
	– FA → CH_2=CH(OEt)		16,0
HN—CHO, CH3CH, HN—CHO (**11**)	– FA → **1**	(3, X = NHCHO)	7,6
HN—CHO, CH3CH, OAc (**12**)	- AcOH → **1**	(3, X = OAc)	– 0,8
	– FA → CH_2=CH(OAc)		10,4
HN—CHO, CH3CH, CN (**13**)	– HCN → **1**	(3, X = CN)	20,9
	– FA → CH_2=CH(CN)		9,0



Parris and Armor [41b] also discuss a possible reaction mechanism for the pyrolysis of secondary amides. The authors found that a tertiary amide, *e.g.* *N*-methyl-*N*-(α-ethoxyethyl)acetamide, does not form *any* *N*-methyl-*N*-vinylacetamide **4** on MgO solid bed catalysts under standard conditions at 275 °C. This finding supports the suggestion for the reaction mechanism of the catalytic pyrolysis of secondary amides of type **8**.

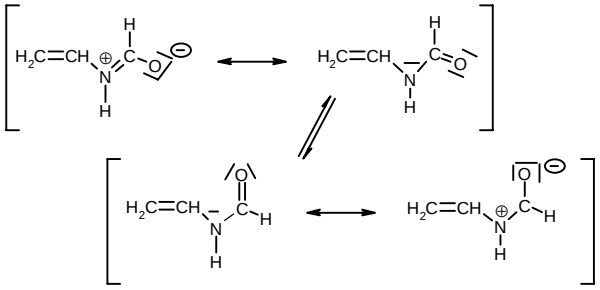
The N–H bonds are activated on the MgO surface and transition complexes **8a** and **8b** are formed with subsequent tautomerisation of the formylimine to VFA according to Scheme 8.



Scheme 8 Proposed reaction mechanism for the catalytic pyrolysis of α-substituted *N*-Ethyl-formamide **8**

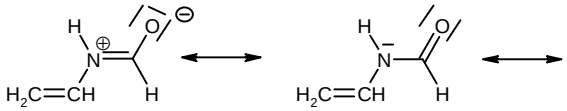
III Physical Properties, Storage and Toxicological Data for *N*-Vinylformamide

N-Vinylformamide **1** is a multifunctional molecule

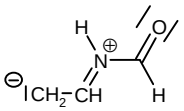


with the partial double bond character between the carbonyl-C and N typical of an amide. The ^{1}H- and ^{13}C-NMR spectra in CD_3CN gave an isomer ratio of *Z* : *E* of 77:23. Lankes [53] obtained a similar result of 75% *Z* conformer in CD_3OD. These results were obtained by comparing the integration of the formyl proton signal (δ = 8.3/8.28 and 8.01/8.03 ppm) in the respective solvents.

Further investigations of Gehring *et al.* [54], Ajo *et al.* [55] (ab initio and PEM calculations) and Yoder and Gardner [56] show that the barriers to rotation of the partial C=N double bond are lowered by the vinyl group compared with saturated alkyl groups. This indicates that the vinyl group competes with the electronegative oxygen for the lone pair on the nitrogen and thus reduces the double bond character of the C=N bond.



1a **1**



1b

The C=C double bond of the vinyl group is consequently more electron rich than those of simple olefins, but less than those in simple enamines because of the neighbouring carbonyl group.

VFA is miscible with water in all proportions and readily soluble in most organic solvents, though less than 1% in aliphatic and alicyclic hydrocarbons.

Other important physical data are shown below:

Molecular weight:	71 g/mol
Boiling point at 10 mbar:	80 °C
Melting point:	ca. –16 °C
Vapour pressure at 25 °C:	0.27 mbar
Heat of molar polymerisation:	82 kJ/mol
Density at 20 °C:	1.017 g/ml
Surface tension (at 20 °C):	37.1 mN/m
Flashpoint (DIN 71 758):	105 °C
pH (50% in water):	6.0 to 7.0

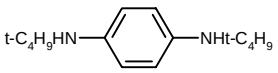
Molar extinction coefficient ε in MeOH (λ_{max}: 225 nm): 16 000 l/mole × cm

These data roughly correspond to those in the literature [57–58].

The stability of VFA to storage at room temperature depends mainly on its purity [59]. Acidic or basic impurities are not critical provided that the pH of a 50% aqueous VFA solution is in the range of 6–7. On either

side of these limits an exothermic cationically or anionically initiated polymerisation can occur. In order to avoid this, storage at ≤ 10 °C is recommended, particularly when the material is required for high molecular weight polymers.

The addition of, for example, di-*tert*-butyl-*p*-phenylenediamine **20** is recommended for preventing radical-initiated slow polymerisation on storage.



20

Stabilisers based on, for example, hydroquinone [60], fullerene [61a] or *N*-oxyl compounds [61b] have also been described. A further means of stabilisation is achieved by diluting the pure VFA with a comonomer planned for copolymerisation, *e.g*. vinyl acetate [62].

When handling VFA its toxicological properties should be taken into account:

Acute oral toxicity (rat):	LD_{50} 1150 mg/kg
Acute dermal toxicity (rabbit):	LD_{50} > 2000 mg/kg
Skin irritation:	nonirritant
Mucus membrane irritation:	danger of severe damage to the eyes
Gene toxicity:	
Ames test	negative
HPRT test *)	negative
Micronucleus test *)	negative

*) These mutagenicity tests were sponsored by APC and performed by Microbiological Associates, Inc.

Subchronic inhalation toxicity (rat 90 days, 6 h/d): 350 mg/m^3 (= 86 ppm) toxic to the kidneys and liver but no neurotoxic effects, at <= 50 mg/m^3 (= 17 ppm) no substance-related effects observed **).

**) This test was sponsored by APC, MKC and BASF. It was performed at the toxicology labs of BASF Aktiengesellschaft, Luwigshafen.

Deviations from already published data can be attributed to various impurities in the tenth of a percent region [15, 57].

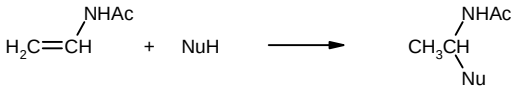
IV Chemical properties of *N*-Vinylformamide

1. General

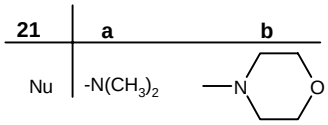
VFA is a multifunctional molecule: on the one hand the C=C double bond is available for addition and polymerisation reactions, and on the other hand there is the weakly acidic proton on the nitrogen flanked by the formyl and vinyl groups, so that with base catalysis VFA can react as a nucleophile.

1.1 Addition of N-Nucleophiles

The first C=C addition compounds were obtained by Kurtz and Disselnkötter [7] through the action of secondary amines on *N*-vinylacetamide **2** (8).

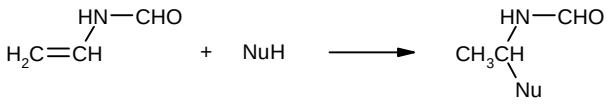


2 **21** (8)



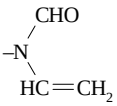
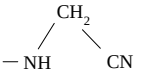
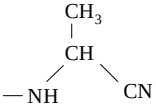
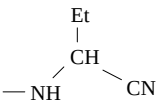
With dimethylamine at 50 °C in 12 h the aminal **21a** and with morpholine at 20 °C in 14 d the aminal **21b** are formed by attack of the nucleophile at the α-C-atom.

During our attempts to react VFA with *N*-nucleophiles we carried out the reactions (9) with the starting materials shown in Table 4. Because of the polarisation of the double bond analogous to that found in enamines, in our examples also only the Markovnikov adducts **22** were formed.



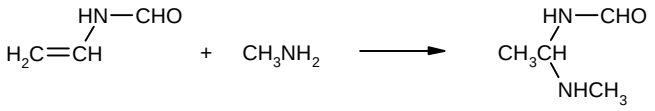
1 **22** (9)

Table 4 Addition of *N*-nucleophiles to VFA (mol per mol VFA)

-Nu	Catalyst/ mol %	Aminal	Reaction conditions (T/t)	Yield (%)
–$NHCH_3$	–	**23**	40 °C/8 h	93 [a])
	NMe_3/7	**25**	25 °C/42 h	93 [b])
	HCl/25	**28a**	25 °C/20 d	65 [c])
	–	**28b**	25 °C/34 d	62 [c])
	–	**28c**	25 °C/34 d	63 [c])

[a]) spectroscopic determination; [b]) isolated by multistep thin film distillation; [c]) isolated by column chromatography

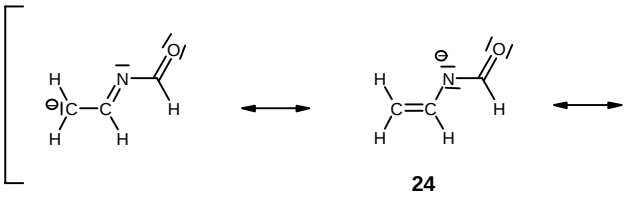
When stoichiometric quantities of methylamine are allowed to react with VFA without a solvent in an autoclave at 40 °C the aminal **23** was obtained, which was identified spectroscopically (10).



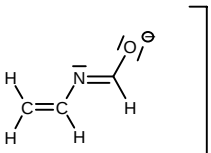
1 **23** (10)

During distillative work-up *in vacuo* at a maximum of 80 °C oligomeric aminals were formed, which could be fractionated by GPC.

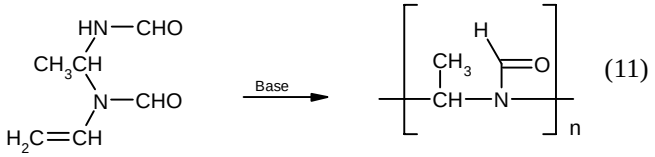
VFA itself can act as a nucleophile. In the presence of bases, *e.g.* alkali alcoholates or tertiary amines, the resonance-stabilised anion **24** is formed in an equilibrium reaction.



24



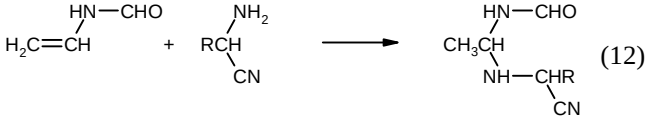
In the absence of protic solvents it adds to VFA and forms *N*-(α-*N*'-vinyl-*N*'-formamidoethyl)formamide **25** (dimeric VFA) (Table 4). Particularly at temperatures above room temperature this reacts further giving oligo-*N*-formylaminals **26** (11):



25 **26** (11)

The dimer is cleaved thermally but can be obtained in 99% purity by distillative work-up in a thin film evaporator (single pass) (*b.p.* $\rho_{0.2\ mbar}$ = 127 °C, *m.p.* 34–36 °C). The ^{1}H- and ^{13}C-NMR spectra indicate that there are three isomers in the ratio 61:11:28. Their presence is attributed to the existence of two amide groups with C=N double bond character corresponding to different conformer combinations [63].

Aminonitriles of type **27a**–**c** only react slowly with VFA at room temperature. They also add at the α-position and give the homologous CN-substituted aminals **28a**–**c** (12).



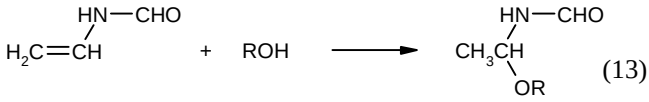
1 **27 a - c** **28 a - c** (12)

	R
a	H
b	Me
c	Et

While **28a** is formed as a crystalline racemate (*m.p.* 69–70 °C), **28b** and **28c** are always isolated as a mixture of diastereoisomers because of the presence of two asymmetric centres in the molecule. These can be separated by column chromatography to give two pairs of enantiomers.

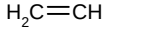
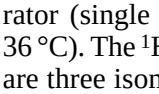
1.2 Addition of O-Nucleophiles

The addition of *O*-nucleophiles, unlike that of *N*-nucleophiles, takes place only under acid or base catalysis. We investigated the systems shown in Table 5 corresponding to (13).

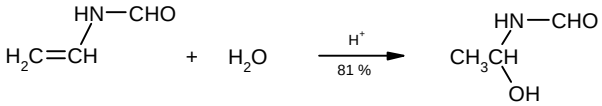


1 **9** (13)

Table 5 Addition of OH–acidic compounds to VFA

–OR	Molar equiv. ROH	Catalyst/ mol%	*O,N*-Acetal	Reaction conditions	Yield (%)
– OH	1	HCOOH/50	**10**	25 °C/8 h	81
	1	–	**31**	25 °C/1 h	95
– OMe	7.4	NaOMe/5	**9a**	25 °C/18 h	93
–O–*i*–C_3H_7	3.4	HCl/2	**9c**	0 °C/2 h	92
	1.5	BF_3/0,5	**32**	0 °C/18 h	91

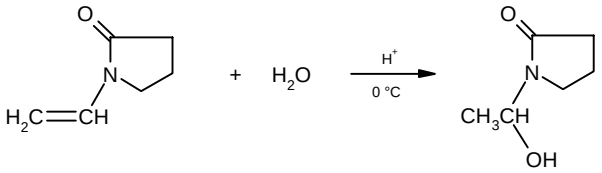
Addition of water can be effected using, for example, 50 mol% formic acid (14) and gives *N*-(α-hydroxyethyl)formamide **10**:



(14)

1 **10**

The careful addition of water to *N*-vinylpyrrolidone **29** at 0 °C proceeds similarly. Senogles and Thomas [64] obtained *N*-(α-hydroxyethyl)pyrrolidone **30** analogous to **10** (15).

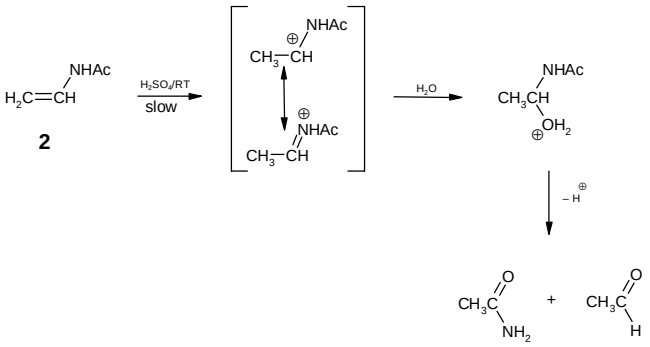


(15)

29 **30**

The hydrolysis proceeds further in aqueous mineral acid. In the VFA hydrolysis with 2N HCl at room temperature Kurtz and Disselnkötter [7] were only able to isolate 57% acetaldehyde and 63% formamide.

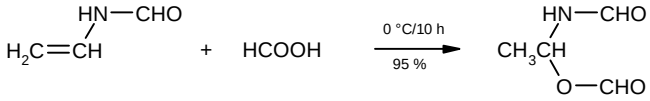
The hydrolysis of *N*-vinylacetamide **2** in aqueous sulfuric acid at 25 °C was investigated by Csizmadia *et al*. [65]. The kinetic data show that the protonation of the β-C-atom can be considered to be the rate determining step. As expected only acetamide and acetaldehyde are obtained as hydrolysis products (Scheme 9).



2

Scheme 9 Hydrolysis of *N*-vinylacetamide **2** to give acetamide and acetaldehyde

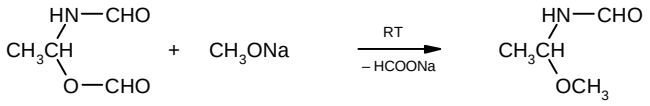
In an anhydrous medium formic acid itself adds to VFA. This takes place at 0 °C within 10 h and at room temperature within an hour (16) and gives *N*-(α-formoxyethyl)formamide **31**.



(16)

1 **31**

The ^{1}H-and ^{13}C-NMR spectra confirmed the identity of **31**. The latter was also treated with $NaOCH_3$ (17).

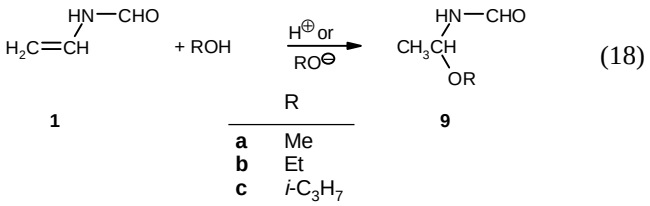


(17)

31 **9 a**

We thus obtained *N*-(α-methoxyethyl)formamide **9a** in 48% yield and sodium formate in 93% yield.

Alcohols also add directly to VFA under acid or base catalysis and give *N*-(α-alkoxyethyl)formamides **9** (18).

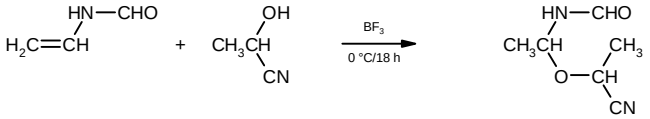


(18)

1 **9**

R	
a	Me
b	Et
c	*i*-C_3H_7

The cyanohydrin, lactonitrile **14** adds to VFA like a simple aliphatic alcohol and gives *N*-[α-(α'-cyanoethoxy)ethyl]formamide **32** (19).

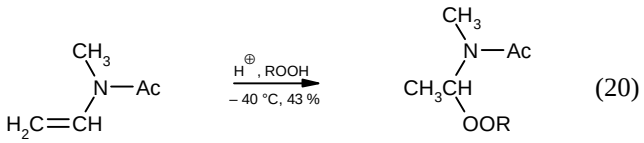


(19)

1 **14** **32**

Because of the tendency of VFA to undergo anionic polymerisation and because of the cleavage of cyanohydrins in alkaline solution, the addition is best carried out with BF_3 as a catalyst and with an excess of lactonitrile, which suppresses cationic polymerisation. In this way yields of over 90% of the addition product are obtained. Because of the two asymmetric centres in the molecule, two fractions consisting of the two pairs of enantiomers are obtained when the product is worked up by column chromatography.

The addition of peroxides to tertiary enamides described in 1972, which is analogous to the addition of alcohols, is interesting [66]. Under acid catalysis the peroxide **33** is obtained by addition at the α-position (20).

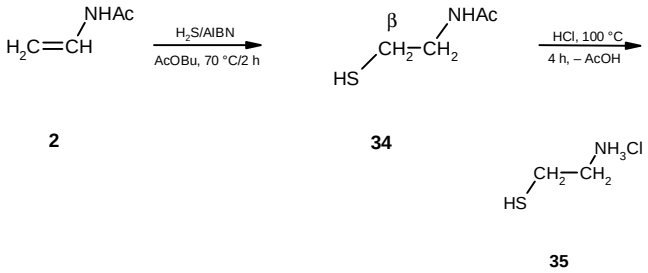


(20)

4 **33**

1.3 Addition of S-Nucleophiles

As a supplement to the addition of OH-acidic compounds to the C=C double bond of VFA, we also investigated the sulfur analogues. We were particularly interested in the radical addition of H_2S to VFA in the β-position. There had already been a patent application by Sugita *et al*. [67] for the synthesis of *N*-(β-mercaptoethyl)acetamide **34** in which *N*-vinylacetamide **2** was treated with excess H_2S in butyl acetate at 70 °C in the presence of azobisisobutyronitrile (AIBN). The selectivity (yield based on **2** converted) is 93%. Subsequent hydrolysis with HCl gives cysteamine hydrochloride **35** in high yields (Scheme 10).



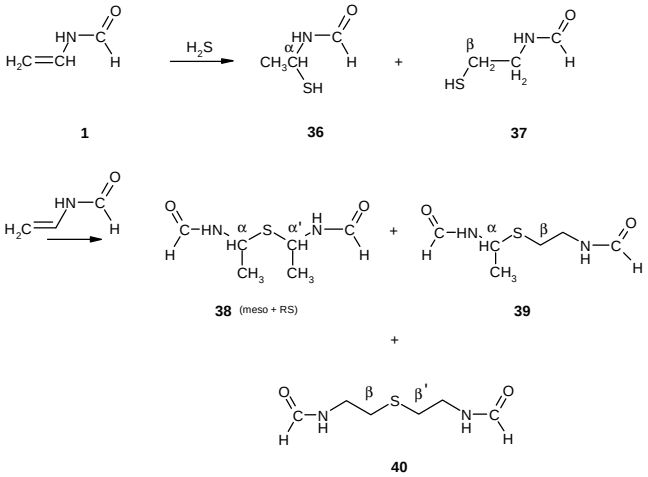
2 **34** **35**

Scheme 10 Addition reaction of H_2S to *N*-Vinylacetamide **2**

The possible products of a reaction of VFA with H_2S are shown in Scheme 11. In our own investigations we isolated the products **36**–**39**, but not the bis-β,β'-(*N*-formamidoethyl)sulfide **40**.

The exact reaction conditions and product ratios can be found in Table 6.

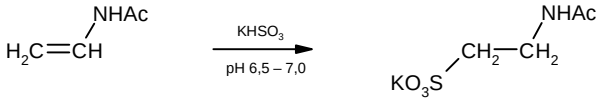
As expected, with a large excess of H_2S the primary addition products *N*-(α-mercaptoethyl)formamide **36** and *N*-(β-mercaptoethyl)formamide **37** are increasingly formed. Radical-initiated additions did not lead to the desired β-selectivity. As nucleophiles, the primary



Scheme 11 Simple and multiple addition reactions of H_2S to **1**

adducts **36** and **37** tend to react further with VFA. Bis-α,α'-(*N*-formamidoethyl)sulfide **38** and also the α,β-isomer **39** are formed preferentially.

We also investigated the addition of $NaHSO_3$ to VFA. In a patent application Sugita *et al*. [68] describe the addition of $KHSO_3$ to *N*-vinylacetamide **2** (21). They obtained potassium 2-(*N*-acetamido)ethanesulfonate which could be hydrolysed to taurine.



(21)

2 **41**

By addition of $NaHSO_3$ to *N*-vinylformamide **1** and catalysis with 2,2'-azobis(2-methylpropionamidine) dihydrochloride (5 mol%) we obtained after distillative work-up *N*-formyltaurine **42** and the α-addition product sodium 1-(*N*-formamido)ethanesulfonate **43** in a ratio of ca. 1:1 in 95% yield (22).

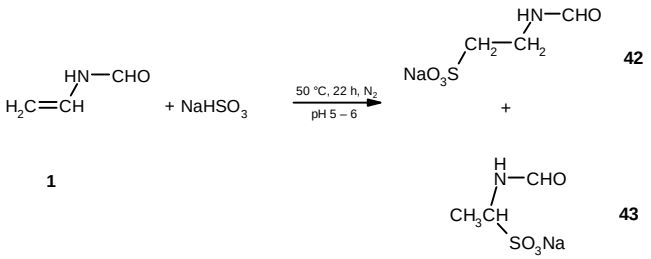
1.4 Addition of Carbanions

Unlike the additions of NH-, OH- or SH-compounds to the C=C double bonds in VFA, the addition of carbanions should involve a C–C bond-forming reaction.

Table 6 Addition of H_2S to *N*–vinylformamide

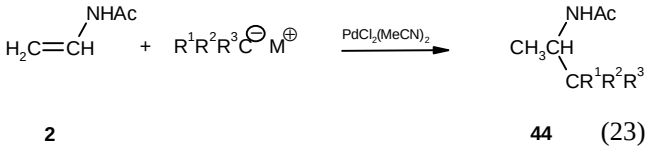
VFA conc. mol/l solvent	Solvent	Initiator/ mol%	Molar equiv. H_2S	Reaction conditions °C/h/bar [a])	Conversion VFA [%]	Selectivities **36**	**37**	**38**	**39**
2	THF	NaSH/5	1,2	50/6/3	91	–	–	78	–
2	Toluene	V65/1 [b])	1,1	60/6/5	96	–	–	91	–
2	Acetonitrile	V60/3 [c])	2,4	80/5/10	86	4	2	46	45
2	THF	V60/3	5,4	75/8/11	96	32	16	22	23

[a]) Self-generated pressure; [b]) ® V65 (Wako Chemicals USA) = 2,2'–Azobis(2,4–dimethylvaleronitrile)
[c]) ® V60 (Wako Chemicals USA) = 2,2'–Azobisisobutyronitrile (AIBN)



(22)

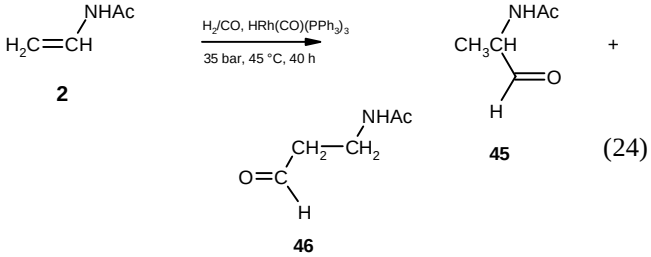
From 1977–1982 Hedegus *et al*. [69–71] published their work on the addition reactions of resonance-stabilised carbanions to *N*-vinylacetamide **2** in the presence of $PdCl_2$-complexes (23).



(23)

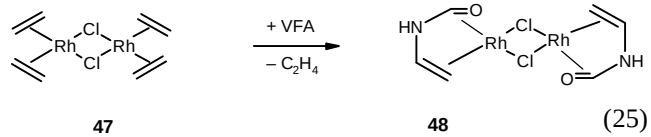
Reactions with benzyl-Grignard, or the sodium and lithium enolates of (methyl)malonic ester were described. Nucleophilic attack always takes place at the α-C-atom of the VFA. The yields of the addition products **44** were between 52 and 88%.

In 1980 Stille *et al*. [72] reported the hydroformylation of *N*-vinylacetamide **2** in the presence of optically active rhodium catalyst systems. They obtained a 1:1 mixture of the α- and β-substituted aldehydes **45** and **46** in 75% yield (24).



(24)

Building on these results, Lankes [53] then investigated complex formation between VFA and rhodium compounds. VFA reacted smoothly with $[RhCl(C_2H_4)_2]_2$ **47** to give the complex $[RhCl(VFA)]_2$ **48** (25).

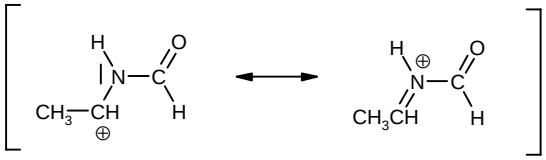


(25)

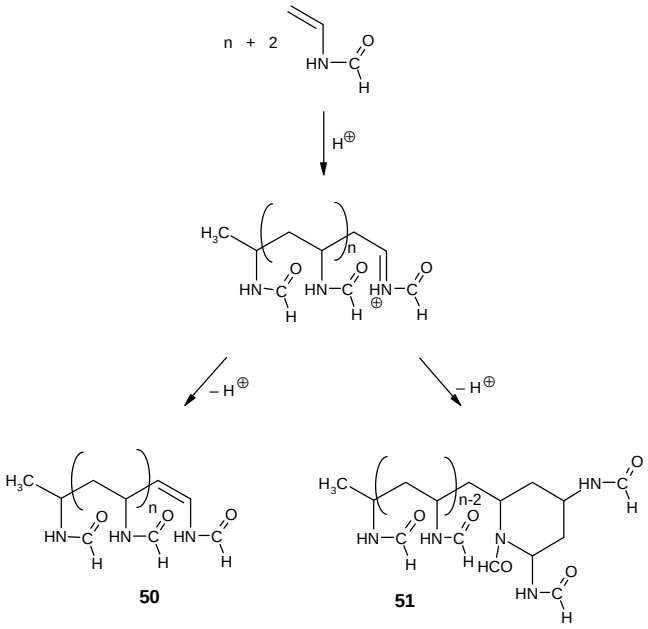
Attempts to homo-oligomerise VFA in the presence of $[CpRh(C_2H_4)_2$-π–H$]BF_4$ and to telomerise it with butadiene on $Pd(dba)_2/PPh_3$ (dba = dibenzylideneacetone) only gave mixtures of nonuniform, branched products.

1.5 Cationic Polymerisation

While VFA is in equilibrium with the resonance-stabilised anion **24** in the presence of base undergoes anionic polymerisation in the absence of a protic solvent or other reaction partners, the presence of catalytic quantities of protic acids leads to formation of the resonance-stabilised cations **49a**/**49b**. With Lewis acids the corresponding addition product is formed.



As a result cationic oligomerisation of the VFA occurs. Pinschmidt *et al*. [15, 73] describe the cationic oligomerisation of the neat material, as a two-phase system with pentane or in solution with initiators, such as $SnCl_4$ or $BF_3 \cdot Et_2O$. The oligomers obtained show broad MW peaks in GPC analysis in water at 975–2 500. NMR analysis indicated that C–C bond formation had taken place. The authors formulate chain termination as shown in Scheme 12.



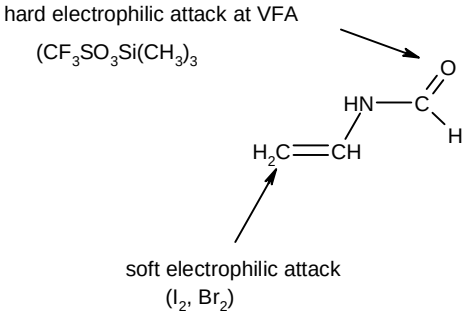
Scheme 12 Cationic oligomerisation of **1** and possible chain termination reactions

The terminal groups of molecules of the type **50** and **51** are enamides and cyclic amidals respectively, which can be regarded as aldehyde equivalents. Correspondingly, alkaline hydrolysis in methanol (5 h reflux) leads to crosslinking and coloration.

Our own work (1991/92) on cationic oligomerisation of VFA with Lewis acids, such as BF_3, $FeCl_3$ or $CuBr_2$, in aprotic solvents gave similar results. However, we drew other conclusions from the results of the hydrolysis of the oligomers obtained. With the neat material or as a two-phase system in aliphatic or alicyclic solvents we obtained oligomers in the molecular weight range of 1 000 – 2 000 (GPC in DMF against a poly(ethylene glycol) standard). In other solvents, *e.g.* CH_2Cl_2, DMF, THF or MeCN, oligomerisation always begins in homogeneous solution. In the course of the reaction the oligomer separates as an oily, sticky mass or is dissolved in both phases. After distillative work-up, hygroscopic, brittle oligomers remain which can be ground up without further purification to give colourless powders. These types of solution oligomers usually have MW values of < 500, *i.e.* degrees of oligomerisation of 3 – 6. We hydrolysed the oligomers thus obtained with molar quantities of HCl in aqueous solution (50 °C/5 h). Besides the oligo-amine hydrochlorides and formic acid, NH_4Cl was formed in yields of between 23 mol% (MW 1 000 – 2 000) and 45 mol% (MW < 500). From this it must be concluded that during oligomerisation not only C–C bond formation takes place, but also bonding at the nitrogen, which leads to oligomers with *N*-formylaminal structures comparable to the anionically initiated oligomers. For oligomers of type **50** or **51** with, for example, n = 8 a maximum of 10 mol% NH_4Cl should be formed on hydrolysis.

Our results of preparative HPLC in DMF agree with this. The higher molecular weight oligomers can be separated from the lower molecular weight ones and analysed spectroscopically by NMR.

More recent and more extensive work by Spange *et al.* [74] involved the investigation of cationic polymerisation of VFA with other initiators, *e.g.* iodine, triphenylmethyl chloride/silica gel, trimethylsilyl triflate and



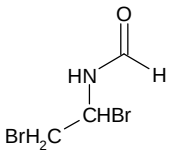
Scheme 13 Preferential attack of hard and soft electrophiles on VFA

oligomers. The polymers purified by precipitation are well characterised C–C chain oligomers with narrow molecular weight ranges.

The yields of the purified oligomers are at maximum 50%.

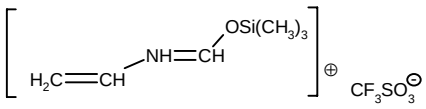
The authors differentiate between soft (I_2, Br_2) and hard (trimethylsilyl triflate) electrophilic attack on the VFA molecule (Scheme 13).

At low temperatures the 1:1 adducts 1,2-dibromoethylformamide **52**



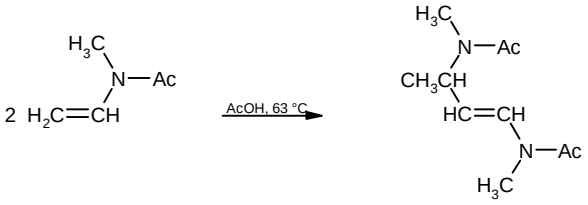
52

and the immonium salt **53** can be characterised by ^1H NMR.



53

The case of tertiary enamides appears to be simpler, *e.g.* that of *N*-methyl-*N*-vinylacetamide **4**. Here Lynn and Ash [75] isolated *N*,*N*′-diacetyl-*N*,*N*′-dimethyl-1,3-diaminobut-1-ene **54** during distillative work-up of the acetic acid solution produced in the synthesis of **4** (26).



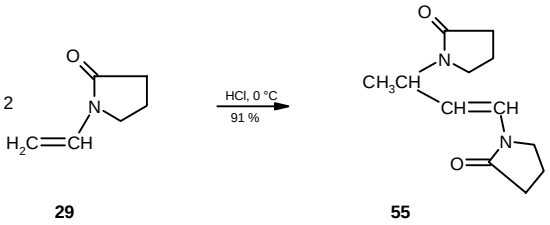
(26)

4 **54**

Compound **54** is thought to be the primary product of a cationic polymerisation with subsequent deprotonation.

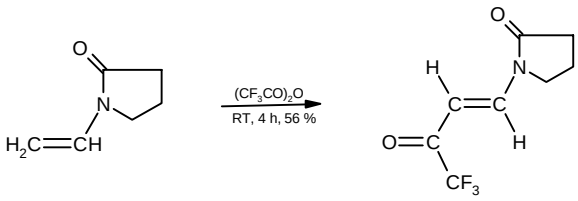
N-Vinylpyrrolidone **29** also undergoes cationic dimerisation. Breitenbach *et al.* [76] describe the formation of 1,3-bis(*N*-pyrrolidonyl)but-1-ene **55** in the reaction of dry HCl with the monomer (27).

The electrophilic addition of trifluoroacetic anhydride to *N*-vinylpyrrolidone **29** proceeds similarly [77]. Deprotonation follows the electrophilic addition of a trifluoroacetyl cation even under the reaction conditions at



29 **55** (27)

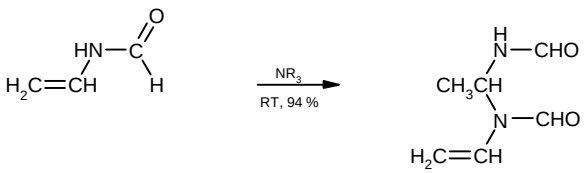
room temperature, whereby regiospecific *trans*-β-substitution takes place with formation of *N*-(β-trifluoroacetylvinyl)pyrrolidone **56** (28).



29 **56** (28)

2. N-Vinylformamide as a Nucleophile

The nucleophilic properties of VFA have already been referred to when discussing its dimerisation to *N*-(α-*N*'-vinyl-*N*'-formamidoethyl)formamide **25** (29) (*cf.* Table 4).



1 **25** (29)

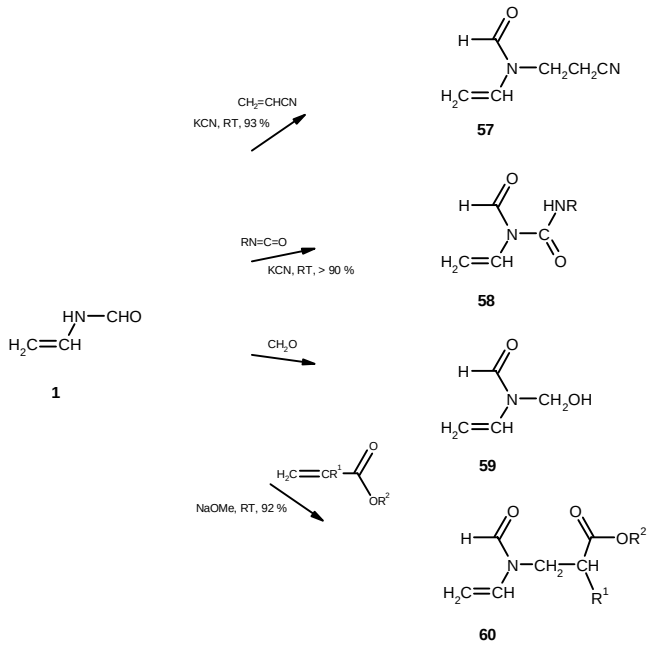
In the same way VFA adds to activated C=C, C=O or C=N double bonds with retention of the vinyl group. Base-catalysed reactions with acrylonitrile and alkyl/aryl isocyanates [7], formaldehyde [78] and (meth) acrylic acid esters [79, 80] have been described. These lead to the compounds **57**–**60**, as shown in Scheme 14.

Because of the acidic character of the NH-proton in VFA, Li and K salts can be formed which can be isolated as powders under nitrogen (Table 7).

It has not yet been possible to determine the precise structure of these metals salts. It is only known for certain that on subsequent methylation using methyl iodide *N*-methyl-*N*-vinylformamide **3** is formed in 89% yield through substitution at the nitrogen. The alkylation of VFA with methyl iodide to give **3** in the presence of 50% NaOH at room temperature in 59% yield has already been described [24] (30).

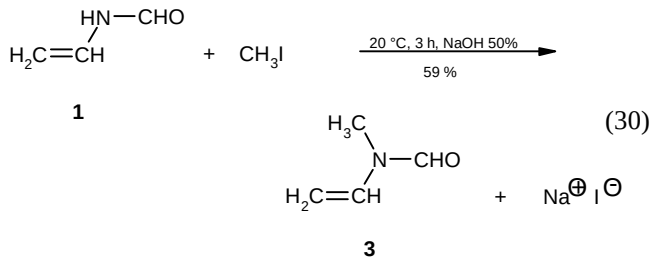
Table 7 Metalation of *N*-vinylformamide

R-Met	Temp. (°C)	Yield (%)
Bu–Li 15 % in *n*–hexane	–40 to RT	70
tert–BuO-K 13% in THF	–20 to RT	95



1 **57** **58** **59** **60**

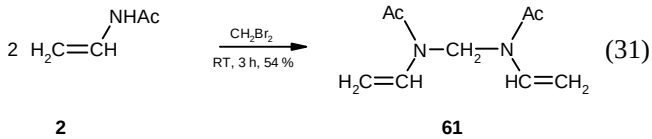
Scheme 14 Addition reactions of **1** to activated double bonds



1 **3** (30)

Our investigations showed that using *tert*-BuOK as a base in dimethylsulfoxide at 15 °C increases the yield to 96%.

In a Japanese patent application Sugita *et al.* [81] describe the twofold nucleophilic substitution of dibromomethane by *N*-vinylacetamide **2** (31).

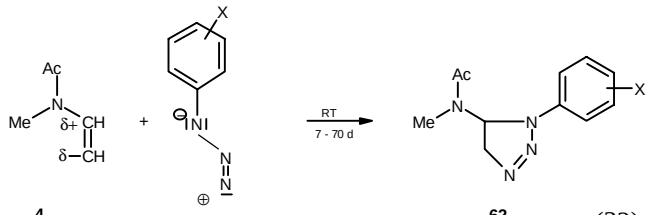


2 **61** (31)

N,*N*'-Methylenebis(*N*-vinylacetamide) **61** is formed, which can be used as a polymerisation crosslinking agent.

3. Cycloadditions

We also attempted to use VFA with its moderately electron rich C=C double bond as a partner in the inverse electron demand Diels-Alder reaction. We have not yet been successful. However, Kadaba [82] has reported the 1,3-dipolar cycloaddition of, for example, aryl azides to tertiary enamides, such as *N*-methyl-*N*-vinylacetamide **4**. Like the cycloaddition of enamines to azides, the rate determining step is the electrophilic attack of the terminal nitrogen of the azide group on the nucleophilic β-C-atom of the vinyl group. On leaving for several days at room temperature 1-aryl-5-(*N*-methyl-*N*-acetamido)-1,2,3-tiazoline **62** is formed in yields of up to 91% (32).



4 **62** (32)

V Summary and Outlook

Decades of research work aimed at finding an economical synthesis of VFA have been successful in that this multifunctional monomer is now available in tonne quantities. The synthesis and pyrolysis of *N*-formylalaninenitrile **13** provides an economic and ecological procedure. The high purities which can be achieved allow many types of radical polymerisations and copolymerisations to be carried out giving linear polymers with a wide range of molar masses. After hydrolysis in acid or neutral media, these polymers give polycationic products with primary amino groups and adjustable charge densities. This results in a wide variety of possible applications. The first large-scale experiments in sewage plants gave good results.

Paper machine trials using PVAmines for improved dewatering, retention, dry strength, fixing detrimental substances and cationic starch modification, are very promising, and often exceed the expectations of the users for this new class of substances.

The development of the chemistry of *N*-vinylformamide, which was formerly difficult to produce, is only at its beginning. The most recent work shows that it can become an interesting building block in preparative synthetic chemistry.

We thank Dr. Norbert Biedermann and Dr. Rainer Dyllick-Brenzinger for correcting the manuscript and for their advice and discussions.

References

[1] D. Horn: Polyethylenimine – Physicochemical Properties and Applications – in:Polymeric Amines and Ammonium Salts, Oxford, Pergamon Press, 333 (1980), E.J. Goethals (Hrsg.)
[2] F. Linhart, W. Auhorn, Das Papier, **1992**, *46*, V38
[3] F. Brunnmüller, R. Schneider, M. Kröner, H. Müller, F. Linhart, H. Burkert, K.H. Beyer (BASF) EP 71 050 [1981]; Chem. Abstr. **1983**, *99*, 23505
[4] S. Pfohl, M. Kröner, H. Hartmann, W. Denzinger (BASF) EP 216 387 [1985]; Chem. Abstr. **1987**, *107*, 25027
[5] A. Stange, F. Linhart (BASF), Lecture at the Munich Paper Symposium, 28.03.96
[6] W. Auhorn, F. Linhart, K. Kobayashi (BASF), Kami Pa Gikyoshi 50 (2) 306 (1996); Chem. Abstr. **1996**, *124*, 205 386
[7] P. Kurtz, H. Disselnkötter, Liebigs Ann., **1972**, *69*, 764
[8] R. W. Stackman, R. H. Summerville, Ind. Eng. Chem. Prod. Res. Dev. **1985**, *24*, 242
[9] DE 1 720 737 [1967] (Hoechst); Chem. Abstr. **1968**, *68*, 24 729 q
[10] D. J. Daniel, P. J. Brock (Dynapol), US 4 393 174 [1981]; Chem. Abstr.**1983**, *99*, 123 173
[11] H. C. W. M. Buijs, A. J. Naaktgeboen, A. Van Elven (Stork Friesland), EP 219 910 [1985]; Chem. Abstr. **1987**, *107*, 154 993
[12] R. H. Summerville, R. W. Stackman, Polymer Preprints, **1983**, *24*, 12
[13] M. Akashi, E. Yashima, T. Yamashita, N. Miyauchi, S. Sugita, K. Marumo (Showa Denko), J. Pol. Sc. Part A: Polymer Chem. **1990**, *28*, 3487
[14] M. Kröner, W. Schmidt, A. Oftring, Th. Proll, H. Hartmann (BASF); EP 231 901 [1986]; Chem. Abstr. **1987**, *107*, 176 648
[15] R. K. Pinschmidt, Jr., L. A. Wasowki, G. G. Orphanides, K. Yakoub (APC), Prod.–Int. Conf. Org. Coat. Sci. Technol. 20th (1994), 437
[16] W. Reppe, H. Krzikalla, O. Dornheim, R. Sauerbier (BASF); US 2 317 804 [1943]; Chem. Abstr. **1943**, *37*, 6 057
[17] W. Reppe und Mitarbeiter, Lieb. Ann. Chem. **1956**, *601*, 134
[18] DE 1 176 124 [1962] (Hoechst); Chem. Abstr. **1964**, *61*, 4 227
[19] J. W. Lynn, B. D. Ash (Union Carbide); US 3 144 396 [1959]; Chem. Abstr. **1964**, *61*, 11 898
[20] R. Bicker (Hoechst); DE 3 030 544 [1980]; Chem. Abstr. **1982**, *96*, 180 817
[21] J. J. Rabasco, F. J. Waller (APC); Tetrahedron Lett. **1997**, *38*, 4953
[22] B. Fiechter, M. Heider, J. Henkelmann, T. Ruehl (BASF); EP 697 399 [1994]; Chem. Abstr. **1996**, *124*, 288 795
[23] M. Mitzlaff (Hoechst); DE 2 503 114 [1975]; Chem. Abstr. **1976**, *85*, 168 885
[24] J. Cramer, K. Dehmer, H. Jensen, M. Mitzlaff, H. Pietsch, R. Pistorius, E. Schmidt (Hoechst); EP 19 225 [1980]; Chem. Abstr. **1981**, *94*, 174 381
[25] Y. Murao, S. Sawayama, K. Satoh (MKC); DE 3 500 773 [1984]; Chem. Abstr. **1986**, *105*, 23 959
[26] R. Fikentscher, M. Kröner, A. Oftring (BASF); EP 251 118 [1986]; Chem. Abstr. **1988**, *108*, 151 126
[27] M. L. Listemann, R. Pierantozzi, J. N. Armor (APC); EP 330 205 [1988]; Chem. Abstr. **1990**, *112*, 55 016
[28] S. Sugita, T. Kudo, K. Marumo (Showa Denko); US 4 997 984 [1989]; Chem. Abstr. **1991**, *114*, 184 822
[29] M. L. Listemann, R. Pierantozzi, R. K. Pinschmidt (APC); EP 332 083 [1988]; Chem. Abstr. **1990**, *112*, 98 034
[30] E. Schmidt (Hoechst); US 4334 097 (1979); Chem. Abstr. **1982**, *97*, 128 260
[31] A. Oftring, E. Hahn, R. Fikentscher (BASF); DE 3 520 829

[1985]; Chem. Abstr. **1987**, *107*, 39 227
[32] D. J. Dawson, K. M. Otteson (Dynapol); US 4 490 557 [1981]; Chem. Abstr. **1985**, *102*, 132 634
[33] R. K. Pinschmidt, A. F. Nordquist (APC); US 4 906 777 [1988]; Chem. Abstr. **1990**, *112*, 237 201
[34] M. L. Listemann, R. Pierantozzi, R. K. Pinschmidt (APC) US 4 968 841 [1989]; Chem. Abstr. **1991**, *114*, 246 828
[35] M. L. Listemann (APC); US 5 023 375 [1990]; Chem. Abstr. **1991**, *115*, 158 533
[36] H. Watanabe, K. Mori, K. Ochiai (MKC); JP 03 236 360 [1990]; Chem. Abstr. **1992**, *116*, 60 187
[37] a) P. Kurtz, H. Disselnkötter (Bayer), DE 1 224 304 [1965]; Chem. Abstr. **1966**, *65*, 16 871d ; b) P. Kurtz, H. Disselnkötter (Bayer), DE 1 228 246 [1965]; Chem. Abstr. **1967**, *66*, 28 403v; c) P. Kurtz, H. Disselnkötter (Bayer), DE 1 668 038 [1967]; d) P. Kurtz, H. Disselnkötter (Bayer), DE 1 493 752 [1965]; e) P. Kurtz, H. Disselnkötter (Bayer), DE 1 543 570 [1966]
[38] F. Becke, P. Päßler (BASF); DE 1 950 280 [1969]; Chem. Abstr. **1971**, *75*, 6 346
[39] F. Becke, P. Päßler (BASF); Liebigs Ann. Chem. 1970, *735*, 27
[40] a) R. Fikentscher, M. Kröner (BASF), EP 433 883 [1989]; Chem. Abstr. **1991,** *115*, 115 102; b) R. Fikentscher, M. Kröner (BASF), EP 433 884 [1989]; Chem. Abstr. **1991**, *115*, 158 537; c) L. Zhou, G. Wang, H. Jiang, Dalian Inst. Chem. Phys., Peop. Rep. China Sepu **1985**, *2 (3)* 138; Chem. Abstr. **1985**, *103*, 171 186
[41] G. E. Parris, J. N. Armor (APC); Appl. Catal. **1991**, *78* a) S. 45, b) S. 65
[42] H. Schnabel, M. Mitzlaff (Hoechst); DE 2 336 977 [1973]; Chem. Abstr. **1975**, *83*, 11 132
[43] A. Tamaru, S. Sato, K. Mori, M. Tsuruga (MKC); JP 62 059 248 [1985]; Chem. Abstr. **1987**, *107*, 96 345
[44] S. Sato, M. Tsuruga, A. Tanaka (MKC); JP 62 195 352 [1986]; Chem. Abstr. **1988**, *108*, 38 590
[45] R. Pierantozzi, M. A. Miller, M. L. Listemann, Th. R. Gaffney, Ch. G. Coe (APC); US 4 996 322 [1989]; Chem. Abstr. **1991**, *115*, 8 105
[46] M. Tamura, S. Sato, K. Mori (MKC); JP 03 181 451 [1989]; Chem. Abstr. **1991**, *115*, 279 449
[47] S. Sato, K. Mori (MKC); JP 05 155 829 [1991]; Chem. Abstr. **1993**, *119*, 226 638
[48] G. E. Parris, J. N. Armor (APC); EP 350 666 [1988]; Chem. Abstr. **1990**, *113*, 6 987
[49] J. N. Armor, G. E. Parris (APC); US 5059 713 [1990], Chem. Abstr. **1990**, *113*, 6987
[50] F. Brunnmüller, M. Kröner, W. Götze, W. Schmidt (BASF); EP 184 074 [1984]; Chem. Abstr. **1986**, *105***,** 174 795
[51] W. Biffar, W. Hölderich, M. Kröner, P. Krötzsch (BASF); EP 208 929 [1985]; Chem. Abstr. **1987**, *106*, 87 070
[52] F. Brunnmüller, K. Stecher, M. Kröner, R. Schneider (BASF); EP 184 694 [1984]; Chem. Abstr. **1986**, *105*, 135 933
[53] A. C. Lankes, Diplomarbeit, Universität Aachen (1991)
[54] D. G. Gehring, W. A. Mosher, J. Org. Chem. **1966**, *31*, 3436
[55] D. Ajo, G. Granozzi, E. Tondello, J. of Mol. Structure **1977**, *41*, 131
[56] C. H. Yoder, R. D. Gardner, J. Org. Chem. **1981**, *46*, 64
[57] Vinamer® EF, "Technical Information" from the APC (1992)
[58] NVF®, Technisches Merkblatt der MKC
[59] S. Sawayama, K. Satoh (MKC); DE 4 328 950 [1992]; Chem. Abstr. **1994**, *121*, 84 191
[60] S. Sato, K. Kuma, T. Ionue, Y. Nishida; DOS 19 519 628 A1 [1994]; Chem. Abstr. **1996**, *124***,** 118 369
[61] a) H. Herbst, E. Hickmann, W. Hübinger, U. Jäger, R. Kropp, W. Reich, K. Harth (BASF); DE 4 414 773 [1993]; Chem. Abstr. **1986**, *105*, 291 732; b) H. Sutoris, A. Koch, A. Aumüller, J. Dupuis, M. Nießner (BASF); DOS 196 09 312 A 1 [1996]; Chem. Abstr. **1997**, *127***,** 248896
[62] M. Kröner, J. Dupuis (BASF); DE 4 218 221 [1992]; Chem. Abstr. **1994**, *120*, 246 005
[63] R. Fikentscher, M. Kröner (BASF); DE 4 030 380 [1990]; Chem. Abstr. **1992**, *117*, 49 443
[64] E. Senogles, R. A. Thomas, J. Chem. Soc., Perkin Trans. II, **1980**, 825
[65] V. M. Csizmadia, K. M. Koshy, K. C. M. Lau, R. A. McClelland, V. J. Nowlan, Th. T. Tidwell, J. Amer. Chem. Soc. **1979**, *101*, 974
[66] M. Lederer, Chem. Ber. **1972**, *105*, 2169
[67] S. Sugita, R. Ishioka, K. Marumo (Showa Denko); JP 61 191 672 [1985]; Chem. Abstr. **1987**, *106*, 66 745
[68] S. Sugita, K. Marumo, R. Ishioka (Showa Denko); JP 61 282 354 [1985]; Chem. Abstr. **1987**, *107*, 9 351
[69] T. Hayashi, L. S. Hegedus, J. Amer. Chem. Soc. **1977**, *99*, 7093
[70] L. S. Hegedus, R. E. Williams, M. A. McGuire, T. Hayashi, J. Amer. Chem. Soc. **1980**, *102*, 4973
[71] L. S. Hegedus, M. A. McGuire, Organometallics **1982**, *1*, 1175
[72] Y. Becker, A. Eisenstadt, J. K. Stille, J. Org. Chem. **1980**, *45*, 2145
[73] R. K. Pinschmidt, W. E. Carroll (APC); US 5 373 076 [1992]; Chem. Abstr. **1995**, *122*, 315 375
[74] S. Spange, A. Madl, U. Eismann, J. Utecht, Macromol. Rapid Commun. **1997**, *18*, 1075-1083
[75] J. W. Lynn, B. D. Ash (UCC); US 3 008 992 [1959]; Chem. Abstr. **1962**, *56*, 8 573g
[76] J. W. Breitenbach, F. Galinovsky, H. Nesvadba, E. Wolf, Mh. Chem. **1956**, *87*, 580
[77] M. Hojo, R. Masuda, Y. Kokuryo, H. Shoida, S. Matsuo, Chemistry Letters (Chem. Soc. of Japan), **1976**, 499
[78] F. Engelhardt, K. Kühlein, U. Riegel, S. von Halasz, J. C. Jeffrey, A. R. Reed (Casella); WO 82 02, 073 [1980]; Chem. Abstr. **1982**, *97*, 200 545
[79] N. Chen, W. L. Renz, R. K. Pinschmidt (APC); US 5 463 110 [1994]; Chem. Abstr. **1996**, *124*, 147 111
[80] R. K. Pinschmidt, Jr., Ning Chen, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **1998**, *39 (1)*, 639–640
[81] S. Sugita, K. Marumo, M. Akashi (Showa Denko); JP 03 227 310 [1990]; Chem. Abstr. **1992**, *116*, 42 567
[82] Pankaja K. Kadaba, J. Org. Chem. **1992**, *57*, 3075

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