Articles

On the Importance of the Amide-Bonded Hydrogen Atom in the Cationically Induced Oligomerization of *N*-Vinylamides

A. Madl and S. Spange*

Department of Polymer Chemistry, Institute of Chemistry, Chemnitz University of Technology, Strasse der Nationen 62, D-09111 Chemnitz, Germany

Received December 3, 1999; Revised Manuscript Received April 4, 2000

ABSTRACT: A critical review of former investigations on the cationically induced oligomerization of *N*-vinylformamide points out that some of the results are not in agreement with the model of an cationic propagation mechanism. Special attention in the discussion of the results is given on the chain structure of the oligo(*N*-vinylformamide)s. In comparison with *N*-vinylformamide, the ability of different *N*-vinylamides to undergo a cationically induced polymerization to oligomeric products was investigated. Only the secondary *N*-vinylamides, *N*-vinylformamide (VFA) or *N*-vinylacetamide (VAcA), readily form higher oligomers with various cationic initiators. *N*-Methyl-*N*-vinylformamide and the cyclic *N*-vinylpyrrolidone (VP) dimerize with acidic catalysts, whereas *N*-methyl-*N*-vinylacetamide gives a mixture of low molecular products. The *N*-alkyl-substituted *N*-vinylamides are not able to undergo a oligomerization to higher oligomers ($M_n > 200$) under the conditions investigated. The cationic polymerization of *N*-deutero-*N*-vinylformamide (VFAD) and the ^{2}H NMR analysis of the obtained oligomers show that the nitrogen-bonded hydrogen (deuterium) is strongly involved in the proton transfer as well as the propagation reaction. From these results, we propose an alternative oligomerization mechanism for the oligomerization of secondary *N*-vinylamides. A nonionic pericyclic transition state is potentially suggested involving a *N*-formylimine end group and the monomer rather than a cationically active chain.

Introduction

N-Vinylamides are important monomers for the synthesis of poly(*N*-vinylamides). Poly(*N*-vinylamides) can be hydrolyzed to the corresponding poly(*N*-vinylamines), which offer a great flexibility in tailoring polyelectrolytic properties to fit a broad range of commercial applications[1]. The free radical polymerization of different *N*-vinylamides, including *N*-vinylpyrrolidone (VP), is well established and has reached industrial application.[1,2]

However, only a few examples are reported on the cationically induced polymerization of *N*-vinylamides. The formation of dimers or lower oligomers of VP with solid acids as heterogeneous initiators is reported in a German patent.[3] *N*-Methyl-*N*-vinylacetamide (MVAcA) gave a brown oil with iodine or $BF_3{\cdot}Et_2O$ as catalysts at room temperature as well as a colorless solid with $BF_3{\cdot}Et_2O$ at lower temperatures.[4] *N*-vinylbenzamide (VBzA) was polymerized at room temperature in dry benzene with sulfuric acid as catalyst.[5] But no data for the obtained polymers, such as molecular weights or molecular chain structures, were reported.

The cationic polymerization of *N*-vinylformamide (VFA), initiated with various Lewis and Brønsted acids, has been reported mainly in the patent literature in the past few years.[6]

Only one of the patents gave details on the structure of the oligo(*N*-vinylformamide) (OVFA).[6c] The synthesis of linear oligomeric products with molecular weights between 500 and 2000 and olefinic or cyclic bisamidate end groups obtained by a cationic propagation mechanism was claimed and later published[7] (reaction A in Scheme 1). Despite these results, the formation of a branched oligo(*N*-vinylformamide) (OVFA), caused through an electrophilic attack of the propagating polymer chain upon the amide nitrogen of another chain, was supposed by the inventors in a following publication (see reaction B in Scheme 1).[8] This branching reaction, which is associated with a proton transfer reaction, is only possible with secondary *N*-vinylamides and not with N-alkylated *N*-vinylamides. But as a proof for this mechanistic suggestion, the authors only compared the average molecular weights detected by head-group analysis from ^{1}H NMR spectroscopy and the GPC of the oligomers. No direct evidence for a branched polymer structure was reported.

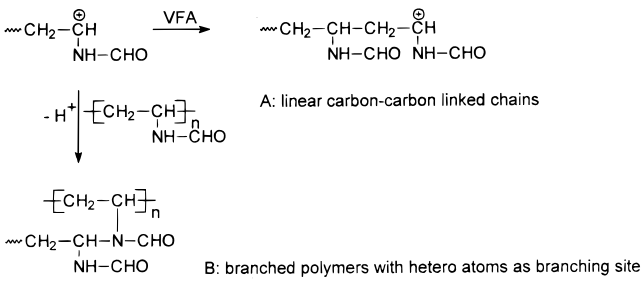
Recently, we reported on a detailed investigation on the cationic polymerization of VFA.[9] Quantum chemical calculations and the influence of the initiator, the solvent, the monomer/initiator ratio, and the reaction temperature on the oligomerization of VFA gave some ambiguous results in relation to a classical cationic propagation mechanism.

The object of this study is a critical review of all experimental data obtained from the cationically induced oligomerization of VFA and the investigation of the influence of the amide nitrogen and its substituents in the mechanism of the cationically induced oligomerization of *N*-vinylamides. For these experiments, the

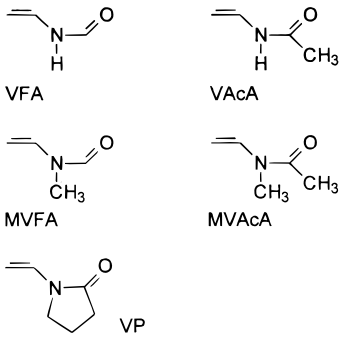
* Corresponding author.

10.1021/ma9920285 CCC: $19.00
Published on Web 07/07/2000

Scheme 1. Propagation Step Leading to Linear Chains and Suggested Alternative Branching Mechanism during Cationic Oligomerization of VFA According to Pinschmidt, Jr., et al.[8]



Scheme 2. *N*-Vinylamides Used for This Study



following monomers were chosen beside the VFA: *N*-vinylacetamide (VAcA) as the next homologous secondary *N*-vinylamide, *N*-methyl-*N*-vinylformamide (MVFA), and *N*-methyl-*N*-vinylacetamide (MVAcA) as N-alkylated, tertiary *N*-vinylamides, and VP as a cyclic *N*-vinylamide (Scheme 2). The last one is fixed at the cis-configuration at the N−CO bond.

Special insight in the participation of the amide-bonded hydrogen in the transfer process should give a polymerization experiment with *N*-deutero-*N*-vinylformamide. From the results of these studies and from previous references we will discuss again the oligomerization mechanism.

Experimental Section

Measurements. NMR spectra were recorded with a Varian Gemini 300 FT-NMR spectrometer using D_2O, $CDCl_3$, or DMSO-d_6 as solvent. IR spectra were recorded on an BioRad FTS 165 instrument. Liquid samples were measured as a thin film between KBr-disks. The oligomer samples were measured as solids with an equipment for diffuse reflection (DRIFT).

Reagents. All solvents were purified and dried by conventional methods. VFA was provided by the BASF Aktiengesellschaft, Ludwigshafen, Germany. MVFA was synthesized from VFA and iodomethane.[10] These monomers and MVAcA from Fluka were distilled under vacuum using a Vigreux column prior to use. VAcA was synthesized according to the literature[1a] and purified by column chromatography prior to use. VP 99$^+$ from Aldrich was used without further purification. Isobutyl vinyl ether from Aldrich was stirred over CaH_2 and distilled under vacuum using a Vigreux column prior to use. Trimethylsilyl triflate, trifluoromethanesulfonic acid, iodine, and bromine were purchased from Merck, Darmstadt, Germany, and used without further purification. Iodine was freshly sublimed prior to use.

Polymerization Procedures. All experiments were carried out under purified argon atmosphere to exclude the effects of oxygen and moisture. The polymerization of the *N*-vinylamides was carried out according to the procedures published for VFA.[9]

A 2.0 mL (2.024 g, 0.028 mol) aliquot of monomer was added to a thermostated solution (273 K) of 71 mg (0.28 mmol) of iodine in 25 mL of toluene in the polymerization tube. The color of the solution changed from violet to brown, and a yellow color appeared after some seconds. Then, the polymerization tube was stored for additional 24 h. After this period, the conversion of the monomer was more than 90%, as proven by ^{1}H NMR spectroscopy. For bromine, trimethylsilyl triflate, and trifluoromethanesulfonic acid as initiator, at first the monomer was added to the solvent and then the initiator was added by a syringe. Besides this, the same procedure as for iodine as initiator was applied.

Oligo(*N*-vinylformamide). Immediately after mixing of the monomer and the initiator, the OVFA precipitated. After storing the reaction tube was stored for an additional 24 h, the supernatant solvent was removed. The crude oligomer was dissolved in dry methanol, reprecipitated in dry acetone, filtered, and washed several times with acetone and dried under vacuum at 333 K. The reported yields are related to these reprecipitated oligomers. The data for characterization of the oligomer (yields, DP, headgroup functionalities) were given before.[9] The acetone soluble part of the reaction product contains, beside a small part not precipitated, low molecular OVFA, addition products of HX upon VFA and decomposition products of the monomer. Dimers of the VFA with olefinic end groups could not be detected.

^{1}H NMR (D_2O): δ (ppm) = 1.0−1.3 (C**H**$_3$− headgroup), 1.5−2.3 (−C**H**$_2$− chain), 3.1−3.2 (I−C**H**$_2$− headgroup), 3.2−4.1 (−C**H**−$_{\text{cis and trans}}$ chain),3.2−4.1 (Br−C**H**$_2$− headgroup), 4.4−4.6 (−OC**H**$_3$ terminal group), 5.3−5.6 (−C**H**═ terminal group), 6.7−6.9 (═C**H**− terminal group), and 7.6−8.3 (−C**H**O side groups).

^{13}C NMR (D_2O vs benzene as external standard): δ (ppm) = 17.0−18.5 (−**C**H$_3$ and Br−**C**H$_2$−/I−**C**H$_2$− headgroups), 38.5−42.0 (−**C**H$_2$− chain), 42.5−45.0 (−**C**H− chain), and 162.5−169.0 (−**C**HO side groups). The signals of the olefinic end groups could not resolved from the background.

IR: 3265, 3046, 2866, 2795, 1665, 1533, 1387, 1252, and 1134 cm^{-1}.

Oligo(*N*-vinylacetamide). After the solvent was removed, a white precipitate was obtained. The crude product was dissolved in methanol, reprecipitated in acetone, and dried as reported for OVFA. A white, hygroscopic solid was obtained.

^{1}H NMR (D_2O): δ (ppm) = 1.0−1.1 (C**H**$_3$− headgroup), 1.4−1.7 (−C**H**$_2$− chain), 1.8−2.1 (−CO−C**H**$_3$ side group), 3.6−4.0 (−C**H**− chain), 5.2−5.3 (−C**H**═ terminal group), and 6.6−6.8 (═C**H**−N terminal group).

^{13}C NMR (D_2O vs benzene as external standard): δ (ppm) = 23.2 (−CO−**C**H$_3$− side group), 33.0−42.0 (−**C**H$_2$− chain), 44.0−45.5 (−**C**H− chain), and 174.0 (−**C**O− side group). The signals of the olefinic end groups could not resolved from the background.

IR: 3283, 3082, 2966, 2856, 1645, 1553, 1437, 1375, 1303, and 1033 cm^{-1}.

Dimeric *N*-Methyl-*N*-vinylformamide. All volatile components were removed from the crude product under reduced pressure. A slightly yellow oil was obtained. With HOTf and TMST as initiators, the yield of the dimer was nearby quantitative, with iodine as initiator, the yield was about 80%, and with bromine as initiator, mainly a 1:1 addict of HBr upon MVFA was obtained.

^{1}H NMR (dimer, in DMSO-d_6): δ (ppm) = 1.144 (d, 6.8 Hz, C**H**$_3$−CH), 1.187 (d, 6.9 Hz, C**H**$_3$−CH), 1.275 (d, 6.9 Hz, C**H**$_3$−CH), 1.282 (d, 6.8 Hz, C**H**$_3$−CH), 2616 (s, C**H**$_3$−N), 2.620 (s, C**H**$_3$−N), 2.759 (s, C**H**$_3$−N), 2.766 (s, C**H**$_3$−N), 2.881 (s, C**H**$_3$−N), 2.888 (s, C**H**$_3$−N), 3.000 (s, C**H**$_3$−N), 3.013 (s, C**H**$_3$−N), 4.368 (quintet, 6.6 Hz, −C**H**-), 4.427 (quintet, 6.8 Hz, −C**H**−), 4.947 (quintet, 6.8 Hz, −C**H**−), 4.9−5.1 (interfered, −C**H**−), 5.084 (dvd, 14.1/6.6 Hz, CH−C**H**═), 5.151 (dvd, 14.2/6.2 Hz, CH−C**H**═), 5.164 (dvd, 14.7/6.2 Hz, CH−C**H**═), 5.243 (dvd, 14.6/6.3 Hz, CH−C**H**═), 6.876 (d, 14.1 Hz, ═C**H**−), 6.906 (d, 14.1 Hz, ═C**H**−), 7.067 (d, 14.7 Hz, ═C**H**−), 7.135 (d, 14.7 Hz, ═C**H**−), 7.969 (s, −C**H**O), 7.979 (s, −C**H**O), 8.000 (s, −C**H**O), 8.124 (s, −C**H**O), 8.137 (s, −C**H**O), 8.144 (s, −C**H**O), 1.155 (s, −C**H**O), and 8.403 (s, −C**H**O).

^{13}C NMR (dimer, in DMSO-d_6): δ (ppm) = 16.73, 16.92, and 18.48 (**C**H$_3$−CH), 23.96, 24.70, 26.57, 26.61, 28.91, 28.94, 32.43, and 32.45 (**C**H$_3$−N), 45.82, 45.93, 52.63, and 52.75 (CH$_3$−**C**H−), 108.16, 109.07, 110.65, and 111.56 (CH−**C**H═), 125.65, 125.67, 131.24, and 131.30 (═**C**H−N), and 161.55, 161.70, 161.79, 161.95, 162.03, 162.05, 162.99, and 163.03 (−**C**HO).

^{1}H NMR (HBr adduct, in DMSO-d_6): δ (ppm) = 1.15 (d, 6.2 Hz, C**H**$_3$−CH), 1.30 (d, 6.0 Hz, C**H**$_3$−CH), 2.61 (s, N−C**H**$_3$), 2.77 (s, N−C**H**$_3$), 4.81 (q, 6.0 Hz, CH$_3$−C**H**(NH−CHO)−Br), 5.43 (q, 6.2 Hz, CH$_3$−C**H**(NH−CHO)−Br), 8.14 (s, −C**H**O), and 8.22 (s, −C**H**O).

Dimeric *N*-Vinylpyrrolidone. All volatile components were removed from the crude product under reduced pressure. A yellow-brown oil was obtained. Independent of the nature of the initiator, the yield of the dimer was about 80%.

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.19 (d, 7.0 Hz, C**H**$_3$−CH), 1.89 (quintet, 7.2 Hz, CH$_2$−C**H**$_2$−CH$_2$), 1.99 (quintet, 7.5 Hz, CH$_2$−C**H**$_2$−CH$_2$), 2.43 (??, CO−C**H**$_2$), 2.37 (t, 8.0 Hz, CO−C**H**$_2$), 3.81 (m, 7.6 Hz, N−C**H**$_2$), 3.99 (t, 7.1 Hz, N−C**H**$_2$), 4.47 (quintet, 6.7 Hz, CH$_3$−C**H**−), 5.00 (dvd, 14.5/6.7 Hz, CH−C**H**═), and 6.80 (d, 14.5 Hz, ═C**H**−N).

^{13}C NMR (DMSO-d_6): δ (ppm) = 16.95 and 17.54 (CH$_2$−**C**H$_2$−CH$_2$), 17.56 (**C**H$_3$−CH), 30.53 and 30.77 (CO−**C**H$_2$), 41.57 and 44.60 (N−**C**H$_2$), 45.80 (CH$_3$−**C**H), 110.18 (CH−**C**H═), 137.21 (═**C**H−N), and 172.48 and 172.70 (**C**O).

N-Methyl-*N*-vinylacetamide gave a complex mixture of low molecular products; no dimers nor oligomers could be detected.

H−D Exchange Experiments. VFA was stirred with a 3-fold excess of D_2O for 30 min. The D_2O/HDO/H_2O mixture was removed by an azeotropic distillation with benzene. The same procedure was repeated three times. After that, the crude VFA-D was distilled under vacuum using a Vigreux column. No signals of the NH protons could be detected in the ^{1}H NMR spectra of the sample in CD_2Cl_2. The polymerization procedure and the work up were carried out as described before for OVFA.

^{1}H NMR (D_2O): δ = 1.1−1.3 ppm (−C**H**$_3$ and −C**H**$_2$−D headgroups), 1.5−2.0 ppm (−C**H**$_2$− chain), 3.2−3.3 ppm (I−C**H**$_2$− headgroup), 3.4−4.1 ppm (−C**H**−$_{cis\ and\ trans}$ chain), 5.4−5.8 ppm (−C**H**═ terminal group), 6.6−6.9 ppm (═C**H**− terminal group), and 7.7−8.3 ppm (−C**H**O side groups).

^{2}H NMR (D_2O): δ = 0.8−1.1 ppm (−CH$_2$−**D** headgroups).

IR: 3264, 3050, 2870, 1665, 1534, and 1388 cm^{-1}.

Polymerization in the Presence of $AgSbF_6$. The polymerization was carried out according to the procedure described before. A 2.0 mL (2.024 g, 0.028 mol) aliquot of VFA was added to a chilled solution (253 K) of 70.0 mg (0.28 mmol) of iodine and 96.2 mg (0.028 mmol) of $AgSbF_6$ in 25 mL of dichloromethane in a polymerization tube. Immediately after mixing, the color of the solution is changed from violet to brown, after some seconds a yellow color appeared and a yellow solid precipitated. After 24 h, the solid was filtered off and identified as AgI. All volatile components were removed from the solution under reduced pressure. The obtained residue proved to be a complex mixture of low molecular products. No oligomeric products could be obtained.

Attempts on Cationically Induced Copolymerization of VFA with Isobutyl Vinyl Ether. (a) The reaction was carried out according to the procedure described for the synthesis of OVFA. A 1.85 mL (0.014 mol) aliquot of isobutyl vinyl ether and 1.0 mL (0.014 mol) of VFA were used as monomers. The initiator was HOTF, the solvent toluene, and the reaction temperature 273 K. After 1 h, a colorless precipitate was obtained. After the polymerization tube was stored for an additional 23 h, the solvent was removed and the crude product was treated as described for OVFA. In the ^{1}H NMR spectra, the same signals were obtained as detected for OVFA, with one additional signal at 0.85 ppm. No signals of poly(isobutyl vinyl ether) or copolymers could be obtained. The toluene and the acetone soluble fraction contain a complex mixture of low molecular products. No signals of copolymers could be detected in the ^{1}H NMR spectra.

(b) The reaction was carried out according to the procedure described in US Patent 5,373,076.[6c] A 1.85 mL (0.014 mol) aliquot of isobutyl vinyl ether and 1.0 mL (0.014 mol) of VFA were thermostated at 273 K. Under stirring, 0.2 mL of boron trifluoride etherate were added slowly. Immediately, the sample became murky. The temperature was allowed to reach room temperature, and the sample was stored overnight. A slightly yellow solid was obtained. Extraction with toluene followed by removing of the solvent gave a yellow, transparent, rubberlike substance, which was identified by ^{1}H NMR spectroscopy as poly(isobutyl vinyl ether).

^{1}H NMR ($CDCl_3$): δ (ppm) = 0.7−1.0 (−CH(C**H**$_3$)$_2$ side group), 1.0−1.2 (−C**H**$_3$ headgroup), 1.3−1.6 (−C**H**$_2$− chain), 1.6−1.8 (−CH$_2$−C**H**(CH$_3$)$_2$ side group), 2.9−3.4 (O−C**H**$_2$− side group), and 3.4−3.7 (−C**H**− chain); an additional signal is detected at 8.0−8.5 ppm.

The toluene-insoluble part is soluble in water as well as in methanol and contains a complex mixture of low molecular products.

Table 1. Comparison of the M_n and M_w Values of Two Samples of OVFA,[9b] Obtained with MALDI−TOF−MS, Head Group Analysis in the ^{1}H NMR Spectra, and GPC

	sample I		sample II	
analytic method	M_n	M_w	M_n	M_w
MALDI−TOF−MS	860	910	940	1070
NMR	990		630	
GPC	1370	1830	1090	1470

Results

(a) A Critical Review Concerning Former Results. When VFA is mixed with cationically active initiators, e.g. iodine, bromine, trifluoromethanesulfonic acid or boron trifluoride etherate, a oligomeric product is obtained.[6−9] The molecular weights of these OVFAs are in the range between 500 and 1500, as independently reported by different investigators.[6−9] However, different structures for the end groups and the chain structure have been suggested.[6c,8,9] Without doubt the OVFAs bear methyl headgroups and olefinic end groups. When iodine or bromine has been used as initiators, up to 40% of the oligomer fraction bear a halogenomethyl headgroup.[9] Pinschmidt et al. reported on a bisamidate end group, caused by an electrophilic attack of the propagation chain end upon the amide nitrogen of the unit before the penultimate monomeric unit.[6c,7] Signals in the range between 5.2 and 5.4 ppm in the ^{1}H NMR spectra of the OVFA can be assigned to this structure,[6c,9a] but an unambiguous assignment failed, because of the low concentration of these groups and superposition with signals of the other possible end groups. Since the bisamidate end group is a tautomer of a chain end with an olefinic end group, a distinction between these end groups in the MALDI−TOF−MS of OVFA is not possible.

The branching of the OVFA during the oligomerization, as postulated by Pinschmidt et al. in a later publication, occurs via the same electrophilic attack of a propagation chain upon the amide nitrogen. As proof for the suggested branched structure, the authors point to the fact that the molecular weights obtained by GPC are higher than those obtained by ^{1}H NMR analysis of the OVFA. Recently, we were able to could confirm this result.[9c] But like the results from the headgroup analysis, the data for M_n and M_w obtained from the MALDI−TOF−MS are in a region below the molecular weights given by GPC. In Table 1 the obtained data for M_n and M_w of two former published OVFA samples are compared.[9b]

Both the ^{1}H NMR analysis and MALDI−TOF−MS gave molecular weights below 1000. The differences

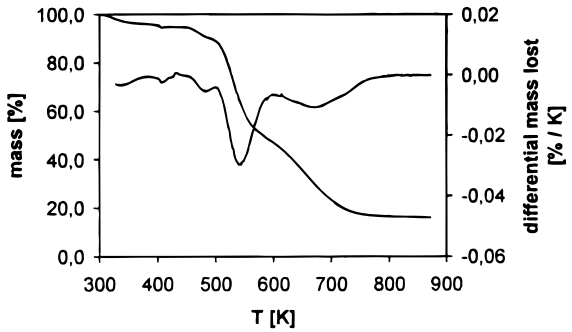


Figure 1. TG and DTG of a sample of OVFA, obtained with iodine as initiator in 1,2-dichloroethane at 273 K ([VFA] = 1.12 mol/L, [M]/[I] = 100).

between the two independent results are within the margin of the error of the two methods. The molecular weight determined by GPC was calculated from the calibration curve of PVP standards. In the referenced publications, PEG standards were used. PVFA standards are still not available. Therefore, it is impossible to calculate absolute molecular weights from the GPC plots. Moreover, it is possible that the highly polar polymer OVFA or PVFA interact specifically with the columns of the GPC and not only separation by size exclusion occurs. This will feign higher molecular weights.

Furthermore, branching sites should drastically cause an increase of the M_w of the OVFA and therefore a broadening of the MWD (with a tailing to higher masses). This is also not observed.

A spectroscopic evidence for the branched structure is not reported, but the bisamidate type branching points should give NMR signals in the same region as the postulated bisamidate end groups. Moreover, a branched OVFA would give the same distribution in the MALDI−TOF−MS as linear ones. A direct proof for or again a branched structure of OVFA is not easy to find. Therefore, we used alternative methods. The thermal decomposition of OVFA should give hints at branched structures. The bisamidate function on the branching point should act as a predetermined breaking-point in the oligomer. If such breaking-points exists in the OVFA, an additional decomposition peak should appear in the TG/DTG of an oligomer in comparison to the TG/DTG of a linear PVFA. As shown in Figure 1, the TG/DTG plot of a OVFA sample agrees with that of a linear PVFA obtained by free radical polymerization.[11]

Summarizing the experimental results, we think there is no direct evidence for the suggested branching mechanism. Moreover, we have discussed the theoretical possibilities for the reaction of a cationic VFA species with another VFA monomer. The quantum chemical calculations show that an electrophilic attack upon the vinyl group leads to the species with the lowest energy, whereas the attack upon the carbonyl oxygen has the lowest activation energy.[9b] An attack upon the amide nitrogen has compared to the other cases high activation energy and leads to the energetic most unfavorable species. Therefore, this reaction should be not of importance in course of a cationic polymerization of VFA. This is also in agreement with theoretical and experimental results published for the regioselectivity of electrophilic additions upon amides (O addition is preferred in comparison to N addition).[12]

The oligomerization occurs well in non polar solvents, such as toluene or halogenated hydrocarbons.[9a] Pinschmidt, Jr., et al. often worked in highly concentrated (neat) solutions or in a two-phase system VFA/*n*-pentane.[6a,c] We carried out also some polymerization experiments in the two-phase system VFA/*n*-hexane (see Experimental Section). Compared with the other solvents, the highest yields and DPs are obtained. However, we reached no quantitative yields. A critical review concerning the yields given in the landmarks shows that often yields of the crude oligomer are given.[13] It should be mentioned that a part of the obtained OVFA is insoluble in MeOH but soluble in water. This may be caused by higher molecular weight fractions of the obtained OVFA. A structural peculiarity of this OVFA fraction could not be detected.

No oligomers or only oligomers with very low yields and low DPs could be obtained in the polar donor solvents acetonitrile, dimethylformamide, or diethyl ether.[9a] In the strong ionizing solvent 1,1,1,3,3,3-hexafluoropropan-2-ol, where OVFA is soluble, no cationic polymerization was observed.[14] If VFA is polymerized in bulk, than it serves as solvent as well as monomer. In this case, the high polar "solvent" VFA does not disturb the formation of oligomers. But the fact that the electronic similar DMF completely inhibits the polymerization hints at the special role of VFA in its cationically induced polymerizations.

Moreover, the addition of $AgSbF_6$ disturbs completely the oligomerization of VFA with iodine as initiator. No oligomeric products could be obtained in this case (see Experimental part).[15] Usually, the addition of $AgSbF_6$ strongly accelerates the cationic polymerization of vinyl ethers with iodine as initiator.[16]

The polymerization behavior of VFA was strongly determined by the reaction temperature, but not by the nucleophilicity of the counterion.[9b,9c] Moreover, the monomer/initiator ratio has only an influence on the headgroup functionality but not on the degree of polymerization.[9b] These are unexpected results in relation to a cationic propagation mechanism (see Discussion). Consequently, we concluded that the cationically induced polymerization of VFA is controlled by the intrinsic electronic structure of the monomer as well as by chain transfer processes to the monomer.

In former publications, we discussed different options for an electrophilic attack upon the heteroatoms of VFA during a cationic polymerization.[9] Such disturbing side reactions are expected owing to the electronic structure of VFA. The quantum chemical calculations showed that the attack upon the vinyl group (chain propagation) is thermodynamically controlled and the attack upon the carbonyl oxygen is kinetically controlled.[9b] In fact, we found a strong influence of the reaction temperature on the yield of OVFA. But independent of the reaction temperature, the chain structure of the obtained OVFA remains unchanged. This means a competing attack upon the carbonyl oxygen leads to low molecular byproducts but not to defects in the polymer backbone. This result is supported by the fact, that the backbone of the OVFA remains stable during hydrolysis to the corresponding oligo(vinylamine).[6a,14]

Surprisingly, VFA does not cationically copolymerize with neither vinyl ethers, styrene, *N*-vinylcarbazole, nor 1,3-divinylimidazolidin-2-one.[17] Despite these results, the cationic copolymerization of VFA with vinyl ethers is shortly reported.[6c,7] But the synthesis of copolymers could not be confirmed by own experiments. A copolymerization set up according to the oligomerization of VFA

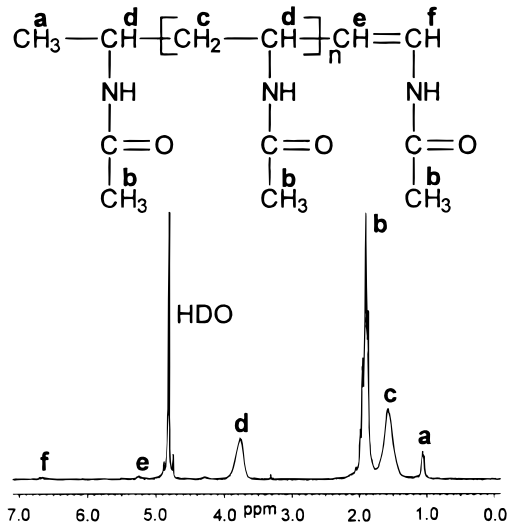


Figure 2. ^{1}H NMR spectrum (D_2O) of OVAcA, obtained by cationically induced polymerization of VAcA with HOTf as initiator ([VAcA] = 1.12 mol/L, [M]/[I] = 100, T = 273 K), with signals assigned to the shown structure of the oligomer.

gives only OVFA and a complex mixture of low molecular products. Signals of copolymers could not be detected in the ^{1}H NMR spectra of the products.

A copolymerization set up according to the referred landmark[6c] gives a solid product. The ^{1}H NMR spectra of this part of the solid, which is soluble in organic solvents, like toluene, acetone, or tetrahydrofuran, shows only signals of poly(isobutyl vinyl ether), with one additional signal at 8.0−8.5 ppm. Signals of −C**H**$_2$−C**H**(NH−CHO)− structure elements could not be obtained. The toluene insoluble part represents a complex mixture of low molecular products, including VFA units. From these results, we suggest that the product is not really a copolymer of VFA and isobutyl vinyl ether despite the occurrence of signals of both VFA and isobutyl vinyl ether structure units in the ^{1}H NMR spectra of the crude product.

(b) Experiments on the Cationically Induced Polymerization of Different Substituted *N*-Vinylamides. The polymerization experiments for the *N*-vinylamides were carried out under the same conditions as reported for the cationic polymerization of VFA.[9] In all cases the solvent was toluene, the reaction temperature T = 273 K, and the concentration of the monomer was [M] = 1.12 mol/L. As initiators, iodine, bromine, trifluoromethanesulfonic acid (HOTf), and trifluoromethanesulfonic acid trimethylsilyl ester (TMST) were used. The monomer/initiator ratio was [M]/[I] = 100.

Altogether, the various *N*-vinylamides rapidly react with the cationic initiators used. In the case of iodine and bromine as initiators, the color of the initiator solution disappeared immediately after mixing with the monomer. But from all of the investigated *N*-vinylamides, beside VFA, only VAcA yields an oligomeric product with M_n > 200 (in acetone insoluble fraction). The yields of the obtained oligo(vinylacetamides) (OVAcA) are about 25%. Approximately the same yield was obtained for OVFA under the same reaction conditions. The obtained OVAcA was characterized by the ^{1}H and ^{13}C NMR spectra in accordance with a spectrum published for poly(vinylacetamide).[18] Figure 2 shows the ^{1}H NMR spectrum of a typical OVAcA sample.

Signals of the polymer backbone and the −CO−CH$_3$ side group could be detected both in the ^{1}H and ^{13}C NMR spectra. Analogous to OVFA, rather intense signals for methyl headgroups were detected at δ = 1.0 ppm in the ^{1}H NMR spectra of OVAcA. Obviously, the cationic polymerization of VAcA seems to be dominated by chain transfer reactions to the monomer, as reported for VFA, too. The signals of the formed olefinic terminal groups were detected at δ = 5.2−5.3 and 6.6−6.8 ppm. The average degree of polymerization (DP) of the OVAcA can be calculated from the ratio of the normalized integral (NI) of the −CO−CH$_3$ side group to the NI of the CH$_3$- headgroups. The calculated DPs are in the range between 5 and 10. Thus, they are in the same range as for OVFA produced under the same reaction conditions.

MVFA yields different products in dependence on the initiator used. With bromine MVFA forms a mixture of low molecular products, mainly the adduct of H−Br upon MVFA because the dibromide is unstable at higher temperatures than 253 K, eliminating H−Br.[9a] No oligomeric products could be detected in the NMR spectra of the mixture. With iodine as initiator, the corresponding HI adduct has only a share of about 20% of the reaction mixture. Besides it, only one new product is obtained. The same product was found nearly quantitative in the reaction mixtures for HOTf and TMST as initiators.

The ^{1}H and ^{13}C NMR spectra of the new product are shown in Figure 3. A 4-fold signal set was obtained for each structure element. The assignment of the signals in the ^{13}C NMR spectra to primary, secondary, and tertiary carbons was confirmed by a DEPT 135 experiment as well as by a gated spectrum. The chemical shifts, splitting patterns and coupling constants, as well as the relative integral intensities lead to the conclusion, that the obtained compound is the dimer of MVFA.

There are two stereoisomers possible, because of the different substituents on the olefinic double bond. But from the coupling constants for the CH=CH coupling between the olefinic protons of about 14.1−14.7 Hz, it can be concluded that the dimeric MVFA only occurs in the *E*-configuration. Because of the hindered rotation of the amide bond, there are four rotamers according to the two rotamers found for the MVFA.[19] For this reason, four signal sets were obtained in the NMR spectra. This leads to a superposition of the signals, which makes the quantitative analysis of the spectra difficult.

VP formed also a dimer with the initiators used, but not in such a quantitative yield as found for MVFA. Because of the fixed conformation at the amide bond, the dimeric VP gives a single signal set in the NMR spectrum. The ^{1}H NMR spectrum of the product is shown in Figure 4. The assignment of the signals to the structure elements is analogous to the dimeric MVFA. From the coupling constants for the CH=CH coupling between the olefinic protons of 14.5 Hz, it can be concluded that the dimer only occurs in the *E*-configuration. Beside the signals of the dimer also some low intense signals of byproducts are observed.

The reaction of MVAcA with any initiators, respectively, leads to mixtures of low molecular products. The conversion of the monomer was nearly quantitative, but neither dimeric nor oligomeric products could be obtained. The ^{1}H NMR spectra of the mixture hints at an acid-induced cleavage of the amide bond. The qualitative results for checking the cationically induced polymerization of different *N*-vinylamides and VP with various initiators are collected in Table 2.

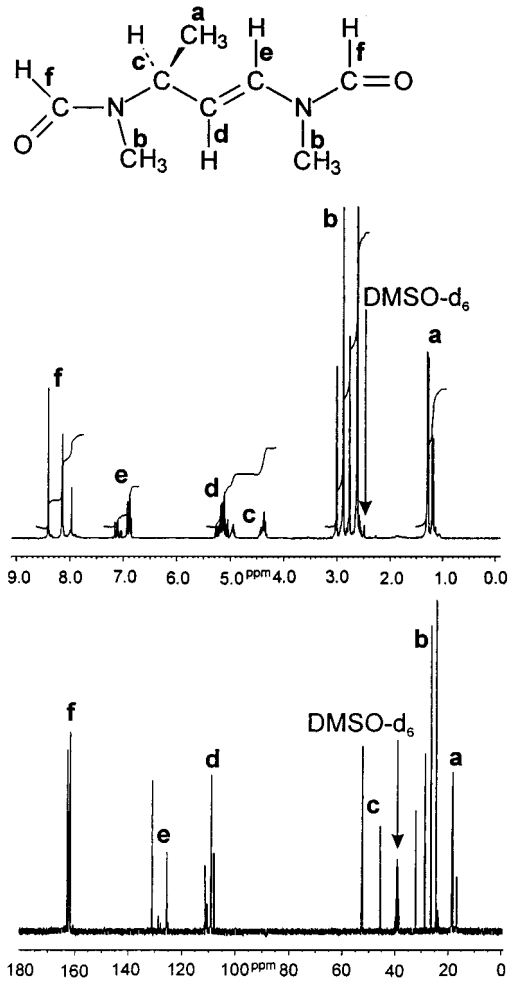


Figure 3. ^{1}H and ^{13}C NMR spectra (DMSO-d_6) of dimeric MVFA, obtained by cationic dimerization of MVFA with TMST as initiator ([MVFA] = 1.12 mol/L, [M]/[I] = 100, T = 273 K, solvent: toluene), with signals assigned to the shown structure of the dimer. The assignment in the ^{13}C NMR spectrum was confirmed by a DEPT 135 experiment as well as by a gated spectrum.

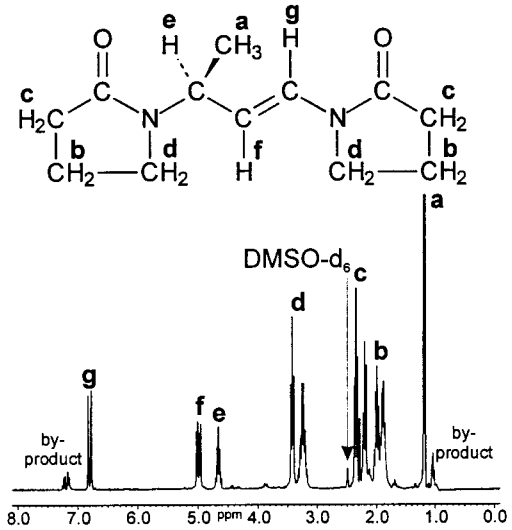


Figure 4. ^{1}H NMR spectrum (DMSO-d_6) of dimeric VP, obtained by cationic dimerization of VP with HOTf as initiator ([VP] = 1.12 mol/L, [M]/[I] = 100, T = 273 K, solvent: toluene), with signals assigned to the shown structure of the dimer.

The use of *N*-deutero-*N*-vinylformamide (VFA-D) should give a better insight in the role of the amide bonded substituent on the polymerization mechanism. The experiments were set up analogous to the described experiments for the cationically induced polymerization of the other *N*-vinylamides. The ^{1}H and ^{2}H NMR analysis of the obtained oligomeric products show that the deuterium is incorporated in the methyl headgroups ($D-CH_2-$) of the obtained oligomers (Figure 5) but not in the polymer chain (neither CH nor CH_2 groups). The formation of $D-CH_2-$ headgroups is only possible when the amide-bonded deuterium directly participates in the chain transfer mechanism.

Table 2. Qualitative Results of Cationically Induced Polymerizations of Different *N*-Vinylamides and *N*-Vinylpyrrolidone with Various Initiators[a]

monomer	HOTf	TMST	iodine	bromine
VFA	O	O	O	O
VAcA	O	O	O	O
MVFA	D	D	D/A	A
VP	D/X	D/X	D/X	D/X
MVAcA	X	X	X	X

[a] Key: O = oligomer; D = dimer; A = 1:1 adduct of the monomer with HX; X = neither dimeric nor oligomeric products obtained. Reaction parameters: solvent, toluene; [M] = 1.12 mol/L; [M]/[I] = 100; T = 273 K.

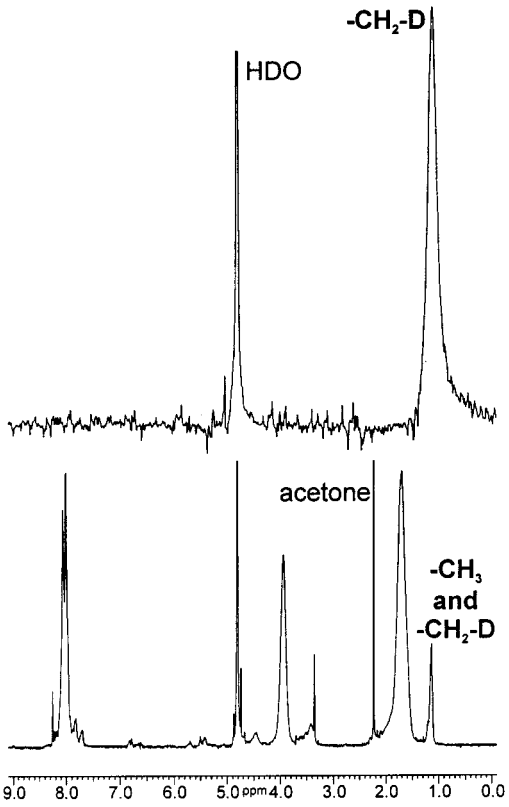
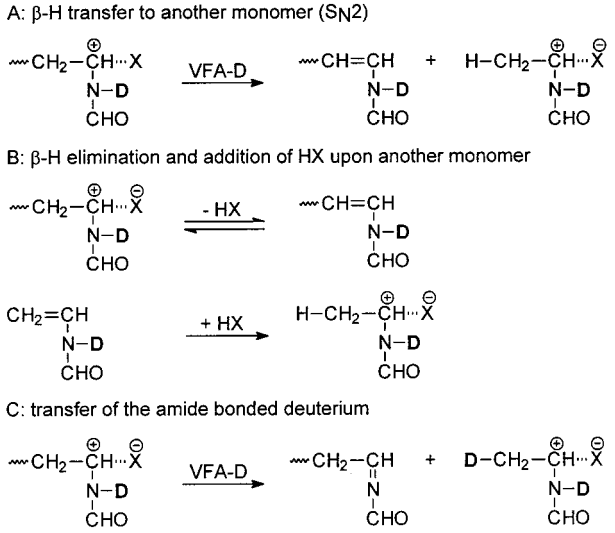


Figure 5. ^{1}H and ^{2}H NMR spectrum (DMSO-d_6) of OVFA-D, obtained by cationic induced oligomerization of VFA-D with iodine as initiator at 273 K ([VFA-D] = 1.12 mol/L, [M]/[I] = 100).

Discussion

Only the secondary *N*-vinylamides VFA and VAcA give oligomers with cationic initiators. The oligomerization is significantly determined by proton-transfer processes, and the DPs as well as the yields of the products are limited. Taking into account all the experimental results and theoretical calculations, it can be concluded that the oligomers exhibit a linear, nonbranched chain structure.

Scheme 3. Possible Transfer Reactions for the Cationically Induced Oligomerization of VFA-D

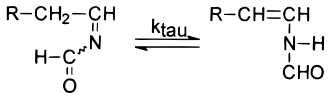


MVFA and VP gave only the dimer with cationic initiators and MVAcA a complex mixture of low molecular products. This means, the substitution of the amide hydrogen by a methyl group prevents a propagation to higher oligomers.

Why does such a little change in the chemical constitution of the monomers cause such a great influence on the polymerization behavior? On one hand, a steric hindrance by the methyl group during the propagation can be excluded. It is well established that all the investigated *N*-vinylamides as well as VP easily undergo a free radical polymerization to high molecular products.[1,2] Moreover, in contrast to MVAcA, the steric positions of the substituents at the nitrogen of VP are fixed by the ring structure. Therefore, the steric claim of VP should not be greater than for *N*-vinylcarbazole, which forms readily polymers with cationic initiators.[20] On the other hand, the difference of the strength of the inductive effect between a hydrogen and a methyl group is not sufficient to explain the profound difference in the ability to undergo a cationic polymerization for otherwise the same molecule.

Is the N−H acidity of the secondary *N*-vinylamides the key for the explanation of this behavior? The N−D labeling experiment clearly showed, that the deuterium is incorporated in the headgroups of the oligomers. This means, it is involved in the transfer processes during the polymerization. The well-known β-H-transfer, which occurs directly to the vinyl group of another monomer (S_N2, reaction A in Scheme 3), leads to methyl headgroups. Otherwise, an elimination of HX from the active chain end is also possible (S_N1, reaction B in Scheme 3). The produced "free" HX can add upon the vinyl group of another monomer. Then, chains with methyl headgroups are formed, too. An addition of HX to the amide nitrogen, followed by an elimination of DX, seems not of importance according to the quantum chemical calculations for the protonation of VFA and the known regioselectivity for the protonation of amides.[9b,12] Moreover, if such a rapid H−D exchange on the amide nitrogen will occur during the oligomerization of VFA-D, free DX is formed. In a free equilibrium, the DX may also add to the olefinic end groups and the tautomeric form of VFA. Consequently, deuterium should be incorporated in the polymer backbone. This was not found in the ^{2}H NMR analysis of the oligo(VFA-D). Considering the arguments given in the analysis of the chain structure (see Results, part a), the transfer of generated D^+, caused by the branching reaction on the amide nitrogen seems not of importance.

Scheme 4. Tautomerization Equilibrium between *N*-Formylimine and Enamide Structures



We think that the formation of the D−CH_2− headgroups is caused by a direct transfer of the deuterium under formation of a *N*-formylimine structure (reaction C in Scheme 3). Stronger bases than VFA, like triethylamine, can release the amide bonded hydrogen of VFA which leads to the anionic dimerization/oligomerization of this monomer.[21] Since a cationically activated form of VFA is present, the NH acidity should be drastically increased. As a consequence, the weaker base VFA, compared to triethylamine, is suitable to abstract the proton from the positively charged amide nitrogen.

N-Acylimines are highly unstable on account of their strong polarizability. *N*-Methylene formamide and *N*-methylene acetamide are the simplest compounds with this structure. They decompose slowly even at 173 K.[22] In the absence of any solvent, polymerization occurs at 77 and 123 K respectively.[22] Furthermore, *N*-acylimines tautomerize, when possible, into the corresponding enamides (Scheme 4).

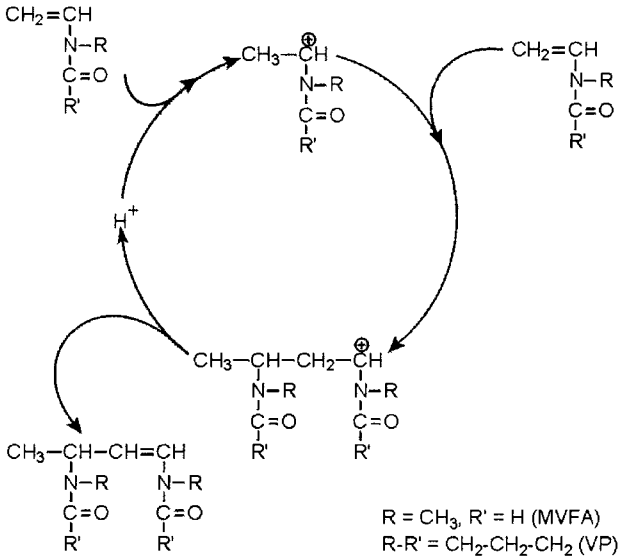
The elimination of the amide-bonded hydrogen alone is only another proton transfer in the course of the cationic polymerization and no sufficient for explanation the unprecedented behavior of the secondary *N*-vinylamides in the course of a cationically induced polymerization.

Our investigations on the cationically induced oligomerization of VFA gave some results which are not in agreement with a cationic propagation mechanism. The most convincing result is the independence of the polymerization behavior on the nucleophilicity of the generated counterion in conjunction with the presumed cationic species.[9b,c] Despite this result, the dimerization of MVFA is suppressed with increasing nucleophilicity of the counterion ($OTf^- < I^- \ll Br^-$). With bromine, no dimerization is observed. It should be mentioned, that the dimerization of VP with all initiators used show similar activity. Attempts to improve the conditions for cationic polymerizations for VFA (polar or ionizing solvents; addition of $AgSbF_6$) lead to a suppression of the oligomerization. This result was surprising.

The DPs of the OVFA are nearly independent of the monomer/initiator ratio, despite the observed high transfer ratio. Despite the high transfer ratio, the MWD of the OVFA remains narrow (MWD < 1.3). Moreover, the yield of OVFA is decreased at high and at very low monomer/initiator ratios.

We could not confirm the published results on a copolymerization of VFA with vinyl ethers.[6a,c] There are no publications on a cationic copolymerization with other vinyl monomers. For cationically induced polymerization's, we have found that VFA did never form copolymers independent of the electronic structure of the comonomer.[17] Of course, with styrene as comonomer, the failure may be caused by electronic issues. But this argument failed for *N*-vinylcarbazole or 1,3-divinylimidazolidin-2-one. Both monomers are electronic similar to VFA in order to produce copolymers by a cationic

Scheme 5. Suggested Reaction Mechanism for the Proton-Catalyzed Dimerization of MVFA and VP



polymerization. However, since a cationic polymerization via a $-CH^{+}-NH-CHO$ carbenium should take place, a copolymerization should be possible in principle.

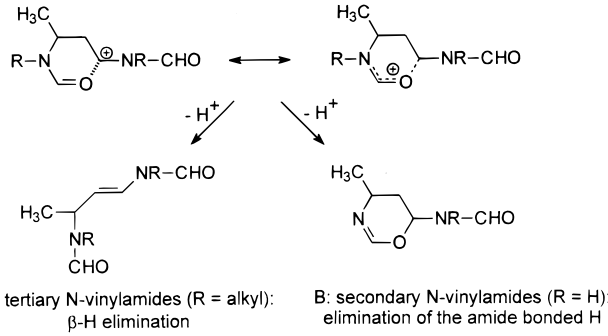
Tying all these results together, we will now discuss a new mechanistic interpretation for the dimerization/oligomerization of the *N*-vinylamides, but especially for VFA. We think that it is possible that the dimerization of MVFA and VP, and also of VFA and VAcA, proceeds via a classical cationic mechanism. Obviously, the first step of the dimerization of MVFA and VP is a protonation of the monomer. Dimers with a halogenomethylene headgroup, as found for iodine or bromine as initiators for the oligomerization of VFA,[9] were not obtained with the tertiary *N*-vinylamides. Instead of that, the addition product of HX upon the monomer is found in the reaction product. The formation of a 1,2-diiodide followed by a HI transfer to another monomer has been established supposed for the cationic polymerization of vinyl ethers, styrene, and acenaphthylene.[23] The formed HX addition species seems to be the real initiator for the polymerization.

The protonated *N*-vinylamide adds upon the carbon−carbon double bond of a second monomer, followed by a proton transfer to another monomer under maintenance of the kinetic chain. After that, the dimerization proceeds self-catalyzed in a three-step reaction (initiation through a proton, addition of one monomeric unit, and transfer of a proton starting a new cycle; see Scheme 5). A dimeric product with a methyl headgroup and an olefinic terminal group is obtained.

A further propagation to higher oligomers could not be observed. An explanation for this result may be the formation of a cyclic species during the dimerization step (Scheme 6). The carbonyl oxygen of the first monomeric unit coordinates upon the carbocation through the internal donor bridge and prevents a further propagation of the chain. In this cyclic species, the cationic center is stabilized by a charge delocalization via different resonance structures including the amide nitrogen and the carbonyl group of the first monomeric unit.

The quantum chemical calculations for the dimerization of VFA support the formation of the supposed cyclic, oxygen bridged species.[9b] The cyclic dimer (species 13 in ref 9b, the same species as shown in Scheme 6) is

Scheme 6. Cyclization of the Dimeric *N*-Vinylamide Species after the First Cationic Propagation Step and Different Possible Proton Elimination Reactions for Secondary and Tertiary *N*-Vinylamides, Stabilizing the Cationic Dimer



the species with the lowest free energy (because of the wide charge distribution). In tertiary *N*-vinylamides, a further stabilization of the cationic species only can occur through the β-H elimination (reaction A in Scheme 6). This reaction obviously explains the exclusive *E*-configuration at the olefinic double bond in the dimers.

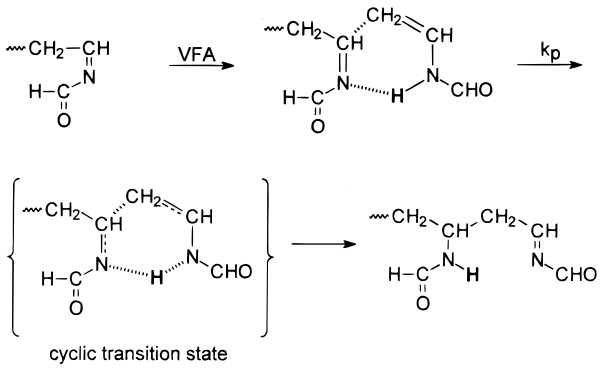
Despite the tertiary *N*-vinylamides structure, the stabilization of the cyclic dimereric species can occur via the β-H elimination as well as the elimination of the acidic amide-bonded hydrogen of the first monomeric unit (reaction B in Scheme 6). The cationic dimerization of VFA leads in the second case to a 4-methyl-6-formyl-5,6-dihydro-4*H*-1,3-oxazine but not to linear oligomers. Because of the low stability of this product, it may decompose and remain in the fraction of the low molecular byproduct (acetone-soluble part).

It should be mentioned that the quantum chemical calculations were performed for single molecules in gas phase. In a real system, the dimeric species has other possibilities to find an energy minimum rather than to form the cyclic product. Nevertheless, both the experimental results for the dimerization of MVFA and VP as well as the quantum chemical calculations support the formation of cyclic species for the cationically induced dimerization of *N*-vinylamides. But the oligomerization of VFA and VAcA leads to higher oligomers with a linear chain structure, which do the tertiary *N*-vinylamides not. Is the formation of *N*-formylimine species the key to explain the open questions?

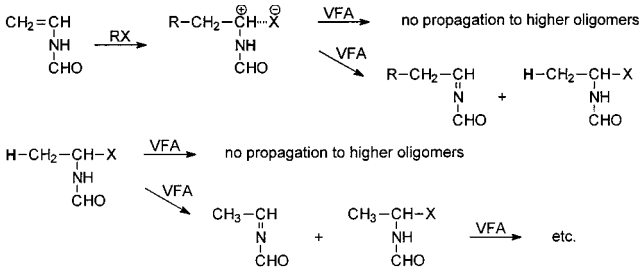
We suppose that the cationically induced oligomerization of *N*-vinylamides proceeds such as the en-reaction[24] via a nonionic cyclic transition state, incorporating a chain end with a *N*-formylimine structure and a second VFA molecule (Scheme 7) with an orbital interaction between the HOMO of VFA and the LUMO of the *N*-formylimine species. Compared with nonactivated imines, the *N*-acylimine derivatives easier participate in en-reactions.[25] The electron-withdrawing effect of the *N*-acyl group lowers the energy of the $LUMO_{Imin}$, which decreases the energy difference between the $HOMO_{En}$-$LUMO_{Imin}$ in the transition state and consequently accelerates the reaction. During the reaction, the amide-bonded hydrogen is transferred to the penultimate unit and the *N*-formylimine structure as the active center is restored.

N-Acetylimine derivatives as intermediates in the formation of oligonitriles have been reported recently.[26] However, this reaction proceeds via an activation of the *N*-acetylimine with alkylating reagents and the con-

Scheme 7. Supposed Cyclic En-Reaction Like a Transition State Incorporating a Chain End with a *N*-Formylimine Structure and a VFA Monomer



Scheme 8. Supposed Reaction Scheme for the Cationically Induced Formation of the N-formylimine Species[a]



[a] The HX-adduct at the carbonyl oxygen of VFA is not considered in this scheme but it limits the yield of OVFA.

densation of the obtained cationic intermediates with nitrogen nucleophiles.

We think that the classical addition of VFA upon the active cationic chain end (reaction A in Scheme 1) does not really play a role in forming OVFA. We suppose that this transition state is the explanation for the special reactivity of the secondary *N*-vinylamides in the course of a cationically induced oligomerization.

The first step in the supposed oligomerization mechanism is the addition of the initiator to the vinyl group of VFA (Scheme 8). This may cause a cationically inactive species (addition of bromine) or an cationically active one. If a cationic propagation is possible (and it cannot be neglected), the reaction is suppressed after the formation of the dimer.

However, in the next step, HX is transferred from the formed species to another monomer under formation of the active *N*-formylimine. From the formed HX/VFA addition product, the next HX elimination will occurs, and so on (Scheme 8). The coupling of the formation of the active species with a transfer process is a special effect of the supposed mechanism. This explains the fact, that both high and low monomer/initiator rations decrease the yield of OVFA. With high monomer/initiator ratios, there is not enough initiator present to induce the formation of the active species. Using a low monomer/initiator ratio, the main fraction of the monomer is consumed during the first transfer steps, and therefore, the "transfer cascade" is suppressed.

The chain propagation proceeds via the postulated cyclic transition state. The active *N*-formylimine species is in a rapid tautomeric equilibrium with the enamide species (see Scheme 4). In that way, the olefinic end groups will be formed without a transfer process. Quantum chemical calculations for the VFA/*N*-formylacetimine equilibrium show that the energy difference between the most stable conformers of each tautomer is 2.8 kcal/mol with respect to VFA as the species with the lower energy.[27] Accordingly, a VFA/*N*-formylacetimine ratio of about 99:1 is present at room temperature. Therefore, the *N*-formylimine species is not detectable in the NMR spectra of the monomer. In increasing the temperature the fraction of the *N*-formylimine also increases. It is known, that the VFA monomer tends to self-polymerizations at temperatures above 313 K, even in the presence of radical scavengers.[28] This may be also caused by the fractions of *N*-formylimine, which initiates the oligomerization of the VFA.

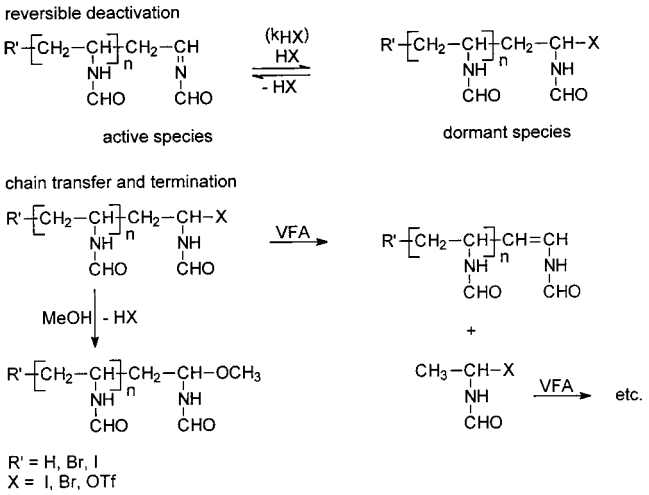
Beside it, a deactivation of the active *N*-formylimine species is possible by a reversible addition of HX. From this inactive species, a "normal" chain transfer forming olefinic terminal groups and an irreversible termination

Table 3. Arguments against and for a Cationic or a Pericyclic Mechanism of Cationically Induced Oligomerization of VFA[a]

		active species	
experimental result	ref	cationic	nonionic
1. higher oligomers only obtainable with secondary N-vinylamides, not with tertiary ones	p	−	++
2. amide-bonded deuterium of the VFAD found to be incorporated in the methyl headgroups of the oligomer	p	0	+
3. VFA neither cationically copolymerizes with vinyl ethers, styrene, or *N*-vinylcarbazole nor with 1,3-divinylimidazolidin-2-one	17	−	++
4. cationically induced polymerization of the secondary *N*-vinylamides unaffected by the kind of initiator: iodine, bromine, HOTf, and TMST	9b, 9c	−	+
5. an effect of the counterion observed for the dimerization of MVFA	p	++	−
6. an added salt ($AgSbF_6$) disturbs the polymerization	15, p	−	++
7. the oligomerization of VFA occurs well in nonpolar solvents; in the highly polar and strong ionizing solvents (except VFA), the polymerization is suppressed	9a, 14	0	+
8. no oligomers obtained below 253 K; yield of OVFA increases with increasing reaction temperature	9b, 9c	0	+
9. the degree of polymerization slightly decreases with increasing reaction temperature	9b, 9c	+	0
10. headgroup functionality decreases with increasing reaction temperature	9b, 9c	+	0
11. degree of polymerization not influenced by the monomer/initiator ratio	9b	−	+
12. only linear OVFA obtained; no branched oligomers could be detected	9, 14, p	0	++

[a] Key: p, this paper; −, result against this mechanism; 0, no special preference for this mechanism; +, hint for this mechanism; ++, strong hint for this mechanism.

Scheme 9. Deactivation of the Active *N*-Formylimine Species and Formation of the End Groups



with methanol may be possible (Scheme 9). The methanolysis of such counterion terminated species is described for vinyl ethers.[29]

Because the *N*-formylimine species is a tautomer of the enamide form of VFA species, the concentration of the active species in the polymerization system is rather low. Therefore, a controlled oligomerization will occur. This explains that the OVFA bear methyl headgroups caused by a transfer reaction but exhibit narrow MWD. The experimental result that the M_n is independent of the monomer/initiator ratio is attributed to the intrinsic ratio of the rate constant for tautomerization (k_{tau}, see Scheme 4) or HX addition (reversible deactivation, k_{HX}, see Scheme 9) and propagation (k_p, see Scheme 7). Thus, only the k_{tau}/k_p and the k_{HX}/k_p values are the important constants for controlling the molecular weight, and not the monomer/initiator ratio.

It can be concluded that the oligomerization of VFA is controlled despite the high transfer ratio, because the transfer reaction is associated with the formation of the active species and not with a competition reaction of the chain propagation.

Table 3 collects all experimental results and argumentations for or against a cationic or a pericyclic propagation mechanism of cationically induced polymerization of VFA.

As you can see, the experimental results strongly hint at the nonionic, pericyclic, en-reaction like propagation mechanism. Preferably, the arguments 1−4 in Table 2 are absolutely consistent with the suggested novel oligomerization mechanism for VFA. Also the molecular structure of the OVFA and the results of the temperature influences do not disturb the explanation. The novel mechanism also explains all discrepancies observed for the oligomerization of VFA by cationic initiators.

Although the supposed mechanism explains all the experimental results, a direct proof is not yet given in the moment. The *N*-formylimine species are incorporated in fast equilibria and therefore a direct experimental (spectroscopic) proof for the evidence of this species failed. Because VFA is a very reactive monomer it is difficult to synthesize model compound for an investigation of the HX elimination.

Special attention should be given in the future to the reaction of VFA with enophiles, because a reaction of these compounds with VFA will give an indirect proof for the supposed mechanism.

Conclusion

The surprising formation of oligomeric products by a cationically induced polymerization of secondary *N*-vinylamides is probably caused by the formation of *N*-formylimine intermediates, because the N−H acidity of the immonium $CH_3-CH{=}NH^+-CHO$ plays a more important role than does the Lewis acidity of the mesomeric carbenium $CH_3-CH^+-NH-CHO$. The addition of a further VFA monomer to the *N*-formylimine species can be simply explained by a cyclic transition state where the amide bonded hydrogen of the added monomer migrates to the penultimate unit, and the active species is reproduced. This is a novel polymerization mechanism for NH-substituted vinyl compounds because the disturbing tautomerization reaction, well-known for enamines, can be circumvented.

Thus, the initiation takes place cationically, then a proton transfer takes place, and the resulting *N*-formylimine is suitable to add further VFA monomer. Because both mechanisms, cationic initiation as well as cyclic transition state propagation, are associated, the total yield of OVFA is rather low because the initiation reaction requires a distinct fraction of the VFA monomer for producing the *N*-formylimine intermediate.

Acknowledgment. We thank Dr. M. Hagedorn, Department of Organic Chemistry, Chemnitz University of Technology, for measuring the ^2H NMR spectra. We thank Prof. Dr. E.-U. Würthwein, University of Muenster, for the fruitful discussions on the supposed enreactionlike mechanism and the quantum chemical calculations. Financial support by the DFG, the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft, Ludwigshafen, Germany, is gratefully acknowledged.

References and Notes

(1) a) Dawson, D. J.; Gless, R. D.; Wingard, E. W., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 5996−6000. (b) Badesso, R. J.; Nordquist, A. F.; Pinschmidt, R. K., Jr.; Sagl, D. J. *Adv. Chem. Ser.* **1996**, *248*, 489−504.

(2) a) Kirsh, Y. E.; Berestova, S. S.; Aksenov, A. I.; Karaputadze, T. M. *Russ. J. Phys. Chem.* **1990**, *64*, 1894−1898; (b) Nagata, M.; Yoshikawa, O.; Sakai, M.; Sakakibara, Y.; Uchino, N. *Nippon Kagaku Kaishi* **1975**, *10*, 1819−1822 [*Chem. Abstr.* **1976**, *84*, 5731]. (c) Pinschmidt, R. K., Jr.; Sagl, D. J. In *Polymeric Materials Encyclopedia*; Salamone, J. C. Ed.; CRC Press: New York, 1996; Vol. 9/P, p 7095. (d) Barabas, E. S. In *Encyclopädia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; John Wiley & Sons: New York, 1989; Vol. 17, p 199ff.

(3) DE 19,642,490 A1 (1996). Inventors: Breitenbach, J.; Schade, C.; Sigwart, C.; Müller, U.; Hesse, M.; Negele, A.; Rübenacker, M.; Eller, K., assigned to BASF AG [*Chem. Abstr.* **1998**, *128*, 270985].

(4) US patent 2,231,905 (1941); Inventors: Hanford, W. E.; Stevenson, H. B., assigned to duPont [*Chem. Abstr.* **1941**, *35*, 3267].

(5) Ben-Ishai, D.; Giger, R. *Tetrahedron Lett.* **1965**, *50*, 4523−4526.

(6) a) US patent 5,280,077 (1994). Inventors: Carroll, W. E.; Pinschmidt, R. U., Jr., assigned to Air Products Chemicals [*Chem. Abstr.* **1994**, *120*, 299557]. (b) DE 44 03519 (1994). Inventors: Kobayashi, S.; Uyama, H.; Sawayama, S.; Satoh, K., assigned to Mitsubishi Kasai Corp. [*Chem. Abstr.* **1995**, *122*, 56829]. (c) US patent 5,373,076 (1994) Inventors: Pinschmidt, R. U., Jr.; Carroll, W. E., assigned to Air Products Chemicals [*Chem. Abstr.* **1995**, *122*, 315375].

(7) Pinschmidt, R. K., Jr.; Wasowski, L. A.; Orphanides, G. G.; Yacoub, K. *Prog. Org. Coatings* **1996**, *27*, 209−218.

(8) Pinschmidt, R. K., Jr.; Renz, W. L.; Carroll, W. E.; Yacoub, K.; Drescher, J.; Nordquist, A. F.; Chen, N. *J. Macromol. Sci.—Pure Appl. Chem.* **1997**, *A34*, 1885−1905.

(9) a) Spange, S.; Madl, A.; Eismann, U.; Utecht, J. *Macromol. Rapid Commun.* **1997**, *18*, 1075−1083. (b) Madl, A.; Spange, S.; Waldbach, T.; Anders, E.; Mahr, N. *Macromol. Chem. Phys.* **1999**, *2000*, 1495−1505. (c) Madl, A.; Spange, S.; Mahr, N. *Polym. Bull.* **2000**, *44*, 39−46.
(10) DE 2919755 (1979). Inventors: Jensen, H.; Schmidt, E.; Mitzlaff, M.; Cramer, J.; Pistorius, R.; Pietsch, H.; Dehmer, C., assigned to Hoechst AG [*Chem. Abstr.* **1981**, *94*, 174381].
(11) Product information NVF, Mitsubishi Kasai.
(12) a) Homer, A. B.; Johnson, C. D. In *The Chemistry of Amides*; Zabicky, J., Ed.; Interscience Publishers: London, 1970; p 188ff. (b) Cho, S. J.; Cui, C.; Lee, J. Y.; Park, J. K.; Suh, S. B.; Park, J.; Kim, B. H.; Kim, K. S. *J. Org. Chem.* **1997**, *62*, 4068−4071. (c) Lin, H.-Y.; Ridge, D. P.; Uggerud, E.; Vulpius, T. *J. Am. Chem. Soc.* **1994**, *116*, 2996−3004. (d) Antonczak, S.; Ruiz-López, M. F.; Rivail, J.-L. *J. Am. Chem. Soc.* **1997**, *116*, 33912-3921.
(13) US 5,373,076 (ref 6c). See example 8, polymerization of VFA (neat) with trifluoroacetic anhydride: 3.59 g of VFA feed, 2.3 g of crude OVFA (64%), and 1.6 g of OVFA after reprecipitation (45%)
(14) Madl, A.; Spange, S. *Macromol. Symp.* **2000**, in press.
(15) Madl, A. Master of Chemistry Thesis, 1996, Chemnitz University of Technology.
(16) Heublein, G.; Helbig, M. *J. Prakt. Chem.* **1972**, *314*, 1−14.
(17) (a) See ref 15. (b) Spange, S.; Meyer, T. *Macromol. Chem. Phys.* **1999**, *200*, 1655−1661.
(18) Murano, M.; Harwood, H. J. *Macromolecules* **1970**, *3*, 605−609.
(19) Kirsh, Y. E.; Kalnish, K. K.; Pestov, D. V.; Shatalov, G. V.; Kuznetsov, V. A.; Krylov, A. V. *Russ. J. Phys. Chem.* **1996**, *70*, 802−806.
(20) Sawamoto, M.; Fujimori, J.; Higashimura, T. *Macromolecules* **1987**, *20*, 916−920.
(21) DE 4030380 A1 (**1990**). Inventors: Fikentscher, R.; Kröner, M., assigned to BASF AG [*Chem. Abstr.* **1992**, *117*, 49443].
(22) Lasne, M.-C.; Ripoll, J.-L.; Thuillier, A. *J. Chem. Res., Synop.* **1982**, 214−215.
(23) (a) Gandini, A.; Cheredame, H. *Adv. Polym. Sci.* **1980**, *34/35*, 81. (b) Giusti, P.; Andruzzi, F. *Makromol. Chem.* **1966**, *98*, 170−178.
(24) Hoffmann, H. M. R. *Angew. Chem.* **1969**, *81*, 597−618.
(25) Borzilleri, R. M.; Weinreb, S. M. *Synthesis* **1995**, 347−360.
(26) (a) Beckmann, A.; Fröhlich, R.; Würthwein, E.-U. *Tetrahedron Lett.* **1997**, *38*, 5481−5484. (b) Aust, N. C.; Fröhlich, R.; Hecht, J. W.; Würthwein, E.-U. *Liebigs Ann./Recl.* **1997**, 1593−1602.
(27) B3LYP/6-31+G*//B3LYP/6-31+G* ab initio calculations, performed by Würthwein, E.-U. Unpublished results, 2000, communicated to the authors.
(28) (a) BASF Aktiengesellschaft, Ludwigshafen. Unpublished results, communicated to the authors. (b) Madl, A.; Spange, S. Unpublished results, 1999.
(29) (a) Higashimura, T.; Miyamoto, M.; Sawamoto, M. *Macromolecules* **1985**, *18*, 611−616. (b) Van Meirvenne, D.; Haucourt, N.; Goethals, E. J. *Polym. Bull.* **1990**, *23*, 185−190. (c) Nuyken, O.; Rie*β*, G. *Macromol. Rep.* **1995**, *A32*, 25−38.

MA9920285