Macromol. Symp. ***161***, *149–157 (2000)*

SYNTHESIS AND APPLICATION OF OLIGO(VINYLAMINE)

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SUMMARY: Oligo(vinylamine) (OVAm) can be synthesized from oligo(*N*-vinylformamide) (OVFA) by hydrolysis of the formamide groups. The cationic polymerization of VFA is initiated with iodine, bromine, trifluoromethanesulfonic acid, or trimethylsilyl triflate in toluene at various temperatures. Chain structures, head group functionality, and MWD of the OVFA are investigated by ^{1}H NMR spectroscopy, MALDI-TOF-MS, and GPC. OVFAs with narrow MWD are obtained in moderate yields (5 - 50 %) at 253 - 313 K. The yields, average molecular weights, and chemical constitution of the OVFAs are strongly determined by the reaction temperature used. The acid or alkaline hydrolysis of the OVFAs leads to OVAm. The structure of the OVAms, based on different precursor OVFAs, is investigated by NMR spectroscopy and GPC. An application of the OVAm as a suitable polyelectrolyte component for organic/inorganic hybrid materials is described.

Introduction

The synthesis of polymers containing stable primary amine functionalities has long been a dream of polymer chemists. The reason is the high reactivity of the primary amino group in derivatization and crosslinking as well as the high cationic charge density of these polymers at low pH values. Poly(vinylamine) (PVAm) is such a desired polymer with primary amino groups near the polymer backbone. But the vinylamine monomer, the simplest precursor to PVAm, is not available, because it tautomerizes to acetaldehyde imine. Therefore, PVAm was always synthesized by indirect routes$^{1)}$.

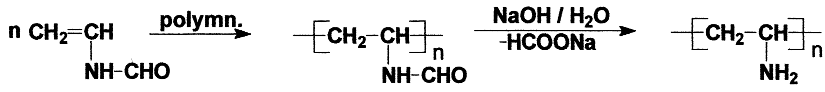

Fig. 1: Polymerization of VFA and hydrolysis of PVFA to PVAm

A suitable and practicable route to PVAm starts from the *N*-vinylformamide (VFA) monomer. The resulting poly(*N*-vinylformamide) (PVFA) is readily prepared with a wide range of molecular weights by radical polymerization and is easily hydrolyzed under alkaline or acid conditions (Fig. 1)$^{2)}$.

CCC 1022-1360/00/$ 17.50+.50/0

Oligomeric products of VFA can be obtained by cationic initiation of VFA using several initiators[3,4]. However, the use of VFA as a monomer in the cationic polymerization brings about several problems. The VFA monomer possesses three different nucleophilic sites: the carbon-carbon double bond (**A**; C-attack), the amide nitrogen (**B**; N-attack), and the carbonyl oxygen (**C**; O-attack) (Fig. 2). All of them can interact with an electrophile. But only the attack of the initiator or growing chain end on the C-C double bond is desired for the cationic polymerization leading to C-C-linked polymer chains. Due to the higher basicity of both heteroatoms, the carbonyl oxygen and amide nitrogen atoms, propagation leading to other than carbon-carbon bonds is also conceivable. Quantum chemical calculations show that the electrophilic attack of the propagating chain end on the carbonyl oxygen of the VFA monomer is kinetically controlled whereas the attack on the carbon-carbon double bond is thermodynamically controlled[5].

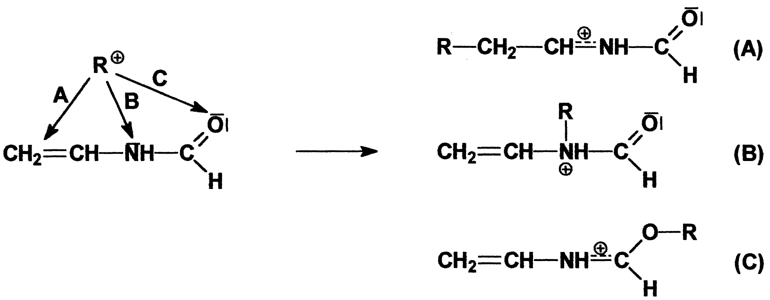

Fig. 2: Three nucleophilic centres of *N*-vinylformamide and possible reaction products after the addition of an electrophile

In this paper, an overview is given about the influence of various parameters, such as solvent, initiator, reaction temperature, and the monomer/initiator ratio on the result of the cationic polymerization. The hydrolysis of OVFA to OVAm is reported as well as the application of OVAm as organic component for producing novel organic/inorganic hybrid materials.

Cationic polymerization of *N*-vinylformamide

Recently, we reported on the cationic initiation of oligomerization of VFA with iodine, triphenylmethyl chloride/silica, and trimethylsilyl trifluoromethanesulfonate as initiators in different solvents[4]. The choice of the solvent influences the result of the cationic polymerization of VFA. Suitable solvents are *n*-hexane, toluene, and halogenated hydrocarbons like dichloromethane or 1,2-dichloroethane. The cationic polymerization is suppressed in diethyl ether, acetonitrile, dimethylformamide, and 1,1,1,3,3,3-hexafluoropropan-2-ol.

More recently, a systematic study of the influence of the reaction temperature and the monomer/initiator ratio on the cationic polymerization of VFA for iodine, trifluoromethanesulfonic acid and trimethylsilyl trifluoromethanesulfonate as initiators was carried out[5]. We found that bromine acts as an initiator in the cationic polymerization of VFA[6]. A general statement on the mechanism of the cationic polymerization can be made from a comparison of the experimental results obtained with the structurally different initiators. At that, however, qualitatively similar results were obtained.

The ^1H NMR spectra of the obtained oligomers clearly show that the purified OVFA is polymerized via the carbon-carbon double bond and not via the O or N heteroatoms. In every case, a rather intense signal at 1.15 ppm indicates methyl head groups. They are due to proton transfer reactions of the propagating chain end to the monomer. If the cationic polymerization of VFA was initiated with iodine or bromine, iodomethyl or bromomethyl head groups, respectively, were found. Both alkenyl and methoxy groups were detected as end groups. Alkenyl end groups are formed through the chain transfer reaction from the chain end to the monomer. The methoxy end groups are formed by the termination reaction with the halide counter-ion, followed by methanolysis during the work-up (see Fig. 3).

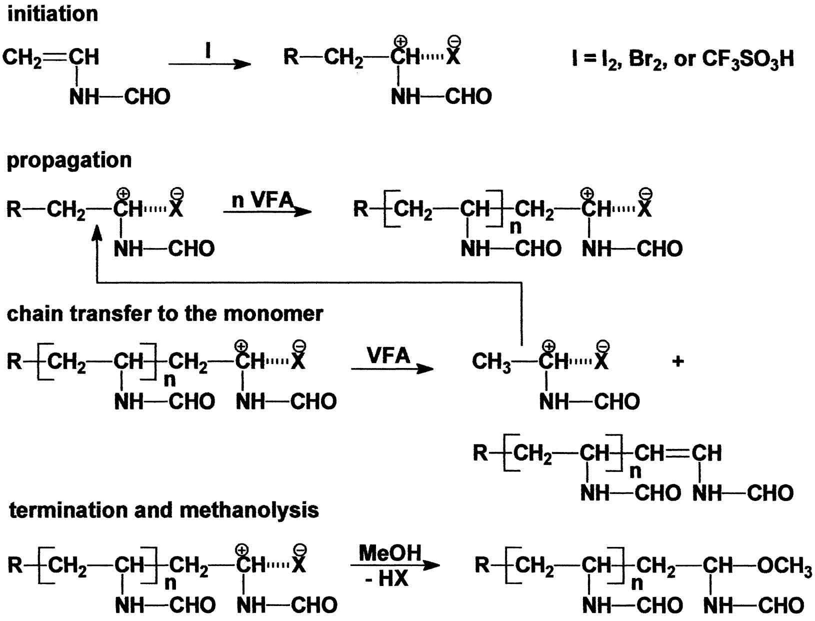

Fig. 3: General reaction scheme for the cationic polymerization of *N*-vinylformamide

The MALDI-TOF-MS analysis of selected samples confirms the results obtained from the NMR analysis. Molecular weight distributions with a repeating-unit MW of 71 corresponding to the monomer unit, methyl head groups, and both alkenyl and methoxy end groups were detected. The oligomers with iodomethyl or bromomethyl head groups could not be detected in the MALDI-TOF-MS because of decay of these groups under MALDI conditions7). Both NMR spectroscopy and MALDI-TOF-MS show that the oligomers obtained at different reaction temperatures differ only in their DPs and mole fractions of iodo- or bromomethyl head groups when initiated with iodine or bromine, respectively. According to the results, a general reaction scheme for the cationic polymerization of VFA was proposed (Fig. 3).

Studies of the influence of the initiator structure, reaction temperature, and the monomer/initiator ratio on the results of cationic polymerization of VFA show that the yield, the degree of polymerization, and the amount of iodomethyl or bromomethyl head groups are strongly influenced by the intrinsic electronic structure of the VFA monomer. The propagation, transfer, and termination mechanisms are unaffected by the nature of the initiator. Unfortunately, the proton transfer reaction of the propagating chain end to the monomer is the predominant side reaction even in this temperature interval (253 - 320 K) suitable for cationic VFA polymerization.

According to predictions of quantum chemical calculations, at reaction temperatures below 253 K, the kinetically controlled O-attack is preferred. This reaction leads to undesired low-molecular-weight by-products and to chain structures with heteroatoms in the polymer backbone. Thus, the yields of OVFA are restricted to less than 5 %. Oligomer chains without heteroatoms in the backbone were produced in higher yields only at higher reaction temperatures because the thermodynamically controlled attack of the growing chain end on the carbon-carbon double bond gain in importance. In contrast, even at higher reaction temperatures, the well-known chain transfer reaction to the monomer limits the amount of head groups and the DP8).

Synthesis and application of oligo(vinylamine)

Advantageously, the acid or alkaline hydrolysis of OVFA yields water-soluble OVAm. A representative ^{1}H NMR spectrum of OVAm, obtained by alkaline hydrolysis of OVFA, is shown in Fig. 4. It can be clearly seen that the backbone of the oligomers remains stable toward hydrolysis, indicating the carbon-carbon linked chain. The aldehyde signals derived from the formamide groups disappeared and a new aldehyde end group is observed due to hydrolysis of the chains containing the former -CH=CH-NH-CHO end group[4]. Additionally, the signals of sodium formate, the by-product of the hydrolysis, appear.

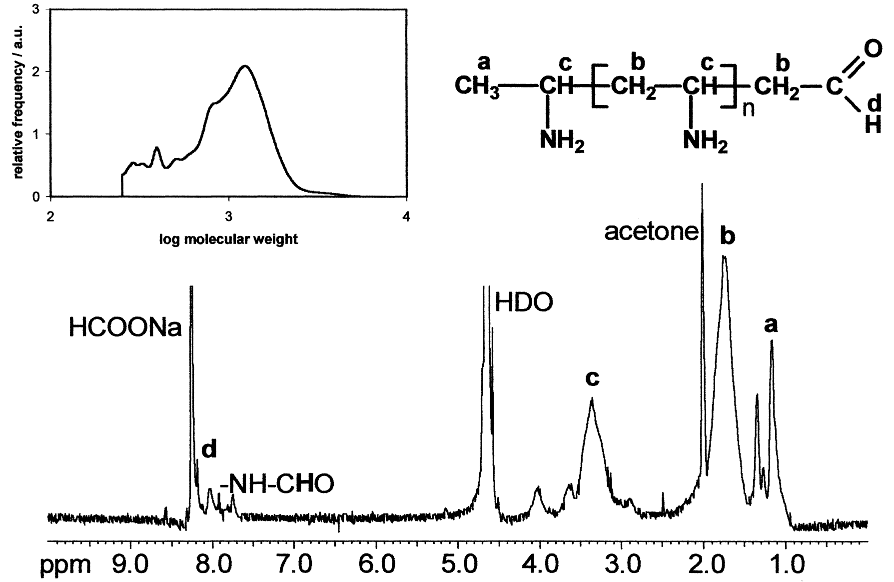

Fig. 4: ^1H NMR spectra (D_2O) of OVAm, obtained by alkaline hydrolysis (3 M NaOH in water, 343 K, 6 h) of OVFA, neutralisation with 1 M HCl, and reprecipitation from methanol into acetone. Inset: GPC trace (MWs calculated by poly(vinylpyrrolidone) calibration)

As expected, the GPC traces of the obtained OVAm show that their molecular weights are between 300 and 1500, while the MWDs remain small. The inset of Fig. 4 shows the GPC trace of a typical sample of the obtained OVAm.

The acid hydrolysis of OVFA yields oligo(vinylamine) hydrochloride (OVAm•HCl) and formic acid as by-product (Fig. 5).

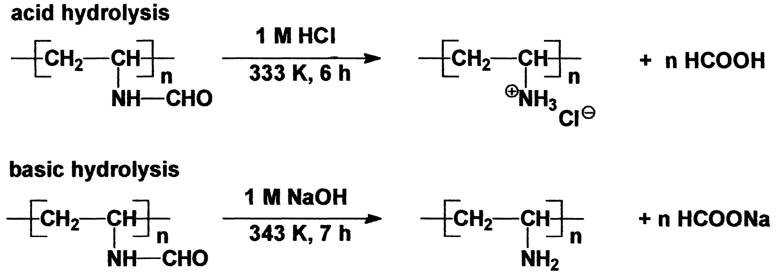

Fig. 5: Acid and alkaline hydrolysis of poly(vinylformamide) to poly(vinylamine)

The alkaline hydrolysis with NaOH leads to pure OVAm, with sodium formate as by-product (Fig. 5)2). The undesired by-products can be removed by dialysis of aqueous solutions of poly(vinylamine)s. This procedure, however, is not suitable for oligomers. Dissolution of OVAm or OVAm•HCl in methanol followed by reprecipitation into acetone may reduce the by-products in the oligomer but a complete removal of low-molecular-weight by-products was not possible.

The chain conformation of PVAm also depends on pH. At neutral pH, PVAm chains contain both the protonated and unprotonated forms of the monomer unit. Strong interaction between protonated amino groups leads to a stiff chain structure involving the formation of relatively stable six-membered rings along the polymer backbone1). For these reasons, it is difficult to interpret ^{1}H NMR spectra of OVAm and complete characterization of OVAm still remains an unsolved problem.

The synthesized OVAms possess molecular weights below the critical limit of M_n = 5 000 suitable for radical polymerization. Therefore, some special applications, resulting from properties of short OVAm chains will be discussed. We found that OVAm, in contrast to PVAm, is suitable as an organic component for the synthesis of novel OVAm/silica hybrid materials through the sol-gel process. The OVAm-containing hybrid materials were characterized by elemental analysis after a tempering process. The reaction parameters and analytical results for the obtained materials are collected in Table 1.

Table 1: Organic/inorganic hybrid materials from oligo- and poly(vinylamine)s a) and silica

Oligomer (polymer)	Oligomer (polymer) in the sol-gel solution, wt-%	C %	N %
OVAm	0.010	0 b)	0 b)
OVAm	0.033 c)	0.886	0.177
OVAm	0.500 c)	1.771	0.446
PVAm (MW 5 000)	0.005 d)	- e)	- e)
PVAm (MW 400 000)	0.005 d)	- e)	- e)
PVAm (MW 400 000)	0.500 d)	- e)	- e)

TEOS/water/0.1 M HCl = 2/1/0.05, 1.0 % oligomer (polymer) solution in water, 3 h stirring. Provided by the BASF Aktiengesellschaft; b) not detectable; c) the gelation process was significantly accelerated; d) the polymer precipitates, giving a heterogeneous, opaque material; e) no analysis was performed due to the heterogeneity of the materials.

For producing the hybrid materials, a stock solution of tetraethoxysilane (TEOS), water, and 0.1 M HCl was mixed with a 1.0 % solution of OVAm or PVAm in water[9]. In the case of PVAm (M_n 5 000 – 400 000), the solutions immediately become opaque and the polymer precipitates. Obviously, large coils of the high-molecular-weight PVAm form agglomerates, interfering with the gel formation (Fig. 6).

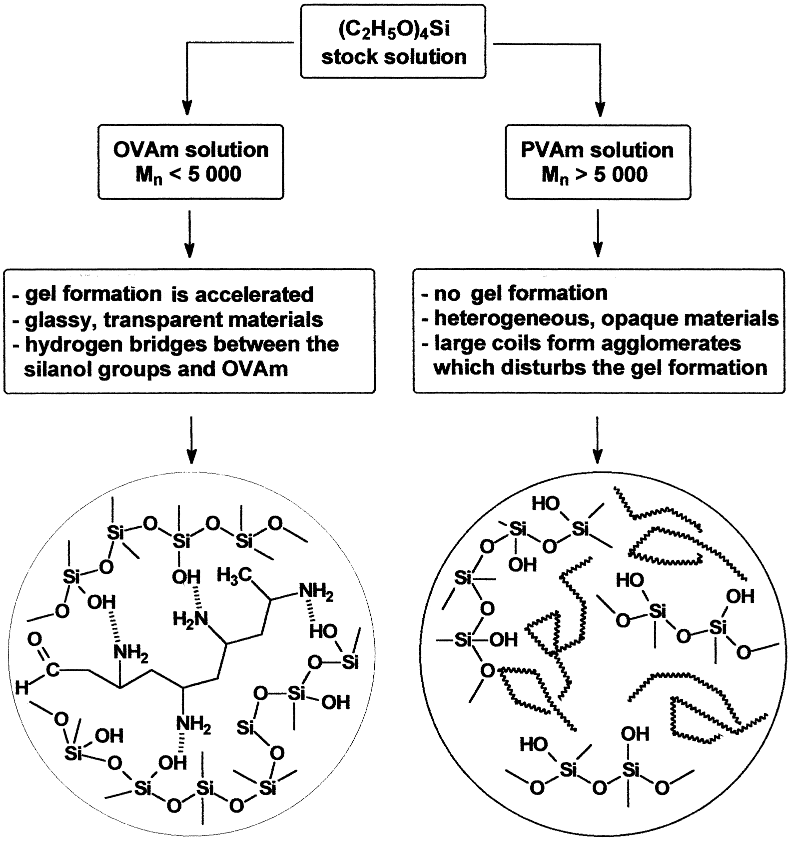

Fig. 6: Proposed mechanism of the influence of the molecular weight of oligo(vinylamine) and poly(vinylamine) on the silica network formation during the gelation process (diameter of PVAm chains is much larger than shown)

The OVAm-containing solutions remain transparent and become solid within a time period of 24 h. After heating at 333 K (20 kPa) for 48 h, brittle, transparent, yellowish, and glassy materials were obtained. When the OVAm content in the reaction system is higher than 0.033 %, a significant acceleration of the gel formation was observed. It is suggested that a small portion of OVAm catalyzes the gelation process because of the presence of free primary amine functions (Fig. 6). The influence of amino-group-containing catalysts on the gel formation of silica was recently reported[10,11,12]. The proposed mechanisms involve the reaction of primary amino groups with silanol groups. For an IR spectroscopic proof of the formation of hydrogen bonds between primary amino groups of OVAm and silica gel[11], the concentration of OVAm in the hybrid material was too low.

Conclusions

Oligo(*N*-vinylformamide)s with molecular weights between 500 and 1500 were obtained by cationic polymerization of VFA with different initiators at 253 - 313 K. Characteristics of the OVFA by different analytical methods show that the chains are carbon-carbon-linked. If iodine or bromine were used as initiators, up to 50 % of the chains bear iodomethyl or bromomethyl head groups, respectively. The structure, yield, degree of polymerization, and the amount of head groups of OVFA are strongly influenced by the reaction temperature. Surprisingly, the structure of the initiator and the monomer/initiator ratio have no or only a slight influence on the cationic polymerization of VFA. The most restricting factors influencing the chain growth are the proton transfer reactions and electrophilic reactions on the carbonyl oxygen of VFA at low reaction temperatures. These restricting factors are associated with the intrinsic electronic structure of the monomer itself and cannot be circumvented by modification of reaction conditions. This means that VFA as monomer acts as a "self-controlling" reagent in the cationic polymerization due to its basicity and enhanced dipolar / polarizability properties.

The alkaline or acid hydrolysis of the obtained OVFA leads to OVAm. The structure of the OVAm was confirmed by ^{1}H NMR spectroscopy and GPC. It could be demonstrated that the oligomer chains remain stable under hydrolysis conditions. The OVAm were used as an organic component for the synthesis of novel organic/inorganic hybrid materials by the sol-gel process. It was found that OVAm catalyzes the sol-gel process even at low concentrations. In contrast, the synthesis of such materials was impossible using PVAm with higher molecular weights because these polymers precipitate during the sol-gel process. The obtained hybrid materials - brittle, transparent solids - were characterised by elemental analysis. Further investigation of the structure and properties of these materials is under way.

Acknowledgement

We thank Dr. Thomas Waldbach and Prof. Dr. Ernst Anders for performing the quantum chemical calculations of the electronic structure of VFA and its reaction with electrophiles. In addition, we thank Dr. Norbert Mahr and the BASF Aktiengesellschaft, Ludwigshafen

(Germany) for supporting characterisation of the oligomers. Financial support by the DFG, the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft, Ludwigshafen, Germany, is gratefully acknowledged.

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