Conjugated Ionic Polyacetylenes. 7. Oligomerization of *N*-Methyl-2-ethynylpyridinium (Trifluoromethyl)sulfonate in Methanol and Pyridine

Lajos Balogh and Alexandre Blumstein*

Polymer Program, Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts 01854

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ABSTRACT: Ionic oligomerization of the acetylenic bond in *N*-methyl-2-ethynylpyridinium (trifluoromethyl)sulfonate (triflate) monomer initiated by nucleophiles was investigated in methanol and pyridine at room temperature. Pyridine and pyridine derivatives were used as initiators, and the resulting reactions were monitored by FTIR, UV–visible, and NMR spectroscopy. The monomer is stable in the absence of nucleophiles. In methanol the reaction between the monomer and the solvent is very slow. There is no reaction between the initiator and the monomer if the heteroatom in the initiator cannot be quaternized. After initiation by an appropriate nucleophile, termination by protonation takes place followed by chain transfer to solvent, and the primary zwitterion is converted into 1-pyridiniumyl-2-(*N*-methylpyridiniumyl)ethylene triflate methoxide. Methoxide anions react also with the monomer and form methoxyvinyl(*N*-methylpyridinium) triflates. The initiation was found to be of first order with respect to the initiator and apparent zero order with respect to the monomer in the studied concentration range. Dissolving the monomer in pyridine results in a rapid formation of a black solid. The products are linear zwitterionic polyacetylene oligomers (yield = 96%). Formation of some cyclized byproducts can also be detected. The rate-determining step is the initiation. No obvious mechanism of termination has been identified in pyridine. A general reaction mechanism is proposed for the polymerization of acetylene triple bond activated by the *N*-methylpyridinium group.

Introduction

The aim of this work is to clarify the fundamental mechanistic and kinetic aspects of the polymerization of *N*-methyl-2-ethynylpyridinium (trifluoromethyl)sulfonate (HMTf), particularly in the stage of initiation.

Acetylenic monomers can be polymerized by Ziegler–Natta catalysts, anionic, free radical, or cationic initiators. Acetylenes can also polymerize thermally and under the influence of γ-irradiation. When acetylenic hydrogens are substituted with an electron-withdrawing group such as cyano- or carboxymethyl, the reactivity of the triple bond is greatly enhanced.[1–3] These activated acetylenes are sensitive to nucleophilic attack and react with ease with free or induced 1,3-dipoles or 1,4-dipoles[4] and can also enter Diels–Alder reactions with dienes. The general mechanism is a Michael addition of a carbanion to the triple bond. Activated acetylenic triple bonds when reacted with nucleophiles can form linear and cyclic structures depending on the reaction conditions. The most studied reaction of this type is the addition of two molecules of acetylenedicarboxylic acid dimethyl ester (DMAD) to pyridines, where the electrophilic acetylenic ester attaches itself to the pyridine nitrogen. In an aprotic solvent this primary zwitterion combines with a second molecule of acetylenic ester to form 9a*H*-quinazolines, which easily isomerize to derivatives of 4*H*-quinazolines.[4] In methanol, the isolated products were indolizines.[5] On the contrary, dicyanoacetylene forms linear chains when reacted with anionic initiators.[1]

Activation can also be brought about by quaternization or salt formation of the 2-ethynylpyridine[6–12] and 4-ethynylpyridine.[13] The use of a highly reactive quaternizing agent, such as methyl trifluoromethanesulfonate, enabled us to isolate the 2-ethynylpyridinium salt. Polymerization of this monomer when initiated with nucleophiles such as pyridine resulted in substituted ionic polyacetylenes of low DP. An anionic chain-polymerization mechanism was proposed[14] based on analogy with vinylpyridine.

Spectroscopic methods are of primary importance here because the higher oligomers (DP > 2) cannot be purified by column chromatography due to their reactivity, high charge density, and adsorptivity. In order to be able to identify the reactions as well as to characterize the reaction products, we decided to prepare low molecular mass oligomers as model compounds, preferably dimers. This was attempted both by using a chain-transfer agent (methanol) as solvent and also by dissolving the monomer salt in the initiator, thus providing the highest possible initiator per monomer ratio. Pyridine was used as an initiator because it dissolves both the monomer and the polymer. Selection of pyridine was also justified by the extensive use of this nucleophile in the previous polymerization experiments.

Experimental Section

Materials. 2-Ethynylpyridine, obtained from Lancaster Synth. Inc., was distilled under vacuum in a nitrogen atmosphere before use. Pyridine (anhydrous), methyl trifluoromethanesulfonate, and 4-methyl-2,6-di-*tert*-butylpyridine (MDTBP) were purchased from Aldrich Chemical Co. and were used as received. Spectroscopic-grade methylene chloride and acetonitrile were freshly distilled from P_2O_5 twice, just before the experiment. 1,4-Bis(4-pyridyl)butadiyne was prepared according to the literature.[15] Spectroscopic-grade methanol was purified by distillation from Mg turnings in the presence of I_2 traces. Deuterated solvents were used as received. Other common solvents were distilled before use.

Analytical Instruments and Measurements. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer between CaF_2 plates. UV–visible spectra were obtained on a GBC 916 spectrophotometer at room temperature between 200 and 1000 nm. ^1H, ^{13}C, and ^{14}N NMR measurements

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* To whom correspondence should be addressed.

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were carried out by a Bruker 270 SY multinuclear spectrometer equipped with a temperature controller. Nitromethane in a deuteroacetone solution was used as an external reference in the ^{14}N NMR measurements. Conductivity measurements were carried out by a YSI-50 conductometer using a YSI conductivity cell ($K = 1.0$ cm^{-1}) at room temperature (24 °C). The chloride content was determined by ion chromatography at the Galbraith Laboratories, Inc. Dilute solution viscosity measurements were made in a 1.0 M NaCl solution at 25 °C using a Cannon–Ubbelohde viscometer. η_{inh} in all cases were determined at a concentration of 0.1 g/dL. Thermal analyses were carried out by DSC (Perkin-Elmer DSC 7 series) and TGA (Du Pont TGA 910 thermogravimetric analyzer).

Monomer Synthesis. HMTf was synthesized in a MBraun 150M stainless steel glovebox (Innovative Technology Inc.) equipped with a gas purification system under a dry nitrogen atmosphere (H_2O and O_2 less than 1 ppm). 2-Ethynylpyridine was reacted with a slight (5%) excess of methyl trifluoromethanesulfonate in anhydrous methylene chloride at −20 °C.[16] The precipitated salt was washed with dry methylene chloride and dried under vacuo at room temperature.

Reaction of HMTf with Methanol. A total of 0.13 g (5×10^{-4} mol) of HMTf was dissolved in 5 mL of absolute methanol ($C = 0.1$ M). This solution was moderately stable at room temperature. There was no color change in this solution in 1 week. After 8 weeks, the monomer completely reacted and a dark blue reaction mixture was formed. After evaporation of the solvent, the product is a dark yellow oil. According to ^1H, ^{13}C, and ^{14}N NMR and IR spectra, the products are similar to products of pyridine-initiated reactions, but the "headgroup" is solely methoxide.

Reaction of HMTf with Pyridine in Methanol or Acetonitrile. A calculated amount of HMTf was dissolved in 5 mL of solvent in a reaction tube, and anhydrous pyridine was added by means of a microsyringe under vigorous stirring using a Vortex mixer. Reactions were carried out at room temperature typically at 24 ± 1 °C. A sample was measured into a Perkin-Elmer circular demountable cell (0.5 or 0.2 mm, depending on the actual monomer concentration), and disappearance of the $-C{\equiv}C-$ bond was monitored in the successive spectra. UV–visible measurements were taken using absolute methanol or acetonitrile as solvents after appropriate dilution. Typically, 5 μL of the reaction mixture was measured by means of a microsyringe into a 10-mm quartz cuvette containing 3.5 mL of solvent. At lower concentrations 1-mm optical length cuvettes were used without dilution. After reaction the solvent was evaporated on a rotavap under reduced pressure, yielding a dark yellow oily product (oligomer **I**).

When the reaction was performed in acetonitrile, 20 mL of diethyl ether was added and the precipitate was dissolved in methanol, reprecipitated with a 5-fold excess of diethyl ether, and dried *in vacuo*.

Reaction of HMTf with Pyridine in an NMR Tube. A total of 0.13 g (5×10^{-4} mol) of HMTf was measured into a 10-mm-diameter NMR tube. The salt was dissolved in 2.5 mL of deuteromethanol ($C = 0.2$ M), and the reaction was initiated by 10 μL (1.236×10^{-4} mol) of pyridine. The tube was inserted into the magnet, and successive ^1H NMR spectra were recorded at 303 K. A similar sample was prepared in methanol, using the same reagent concentrations ($[M]_0 = 0.2$ M, $[M_0]/[I_0] = 4.0$). After 60 min the solvent was evaporated on a rotavap and the resulting oily product was dissolved in 2.5 mL of deuteromethanol.

Attempted Polymerization of HMTf with 4-Methyl-2,6-*tert*-butylpyridine in Acetonitrile. A total of 0.13 g (4.9×10^{-4} mol) of HMTf was dissolved in 5 mL of anhydrous acetonitrile, and 0.10 g (4.9×10^{-4} mol) of 4-methyl-2,6-*tert*-butylpyridine was added into the solution. In this reaction mixture there was no detectable change in 24 h at room temperature. After the solution was heated for an additional 24 h at 70 °C, the reaction mixture developed a slightly brown color but no polymer formation was observed. Addition of 10 μL of pyridine into the reaction mixture yielded promptly a black solution from which 0.09 g (yield = 70%) of black solid was prepared.

Attempted reaction of HMTf with 4-Methyl-2,6-*tert*-butylpyridine in Methanol. A total of 0.106 g (4.0×10^{-4} mol) of HMTf was dissolved in 5 mL of absolute methanol, and 85 mg (4.0×10^{-4} mol) of 4-methyl-2,6-*tert*-butylpyridine was added into the solution. The reaction was monitored by FTIR. There was no color change or measurable decrease in the intensity of triple bond absorption in 24 h at room temperature.

Oligomerization of HMTf in Pyridine. Thoroughly ground solid triflate salt (54 mmol, 14.45 g) was added into 100 mL of anhydrous pyridine under vigorous stirring in a three-neck flask equipped with stirrer and condenser. After 30 min the solvent was evaporated using a rotavap at 40 °C. The resulting black solid was dissolved in 40 mL of methanol and reprecipitated by 160 mL of diethyl ether. This purification procedure was repeated three times to remove the lowest molecular weight compounds. Finally the product was washed with diethyl ether and dried under reduced pressure at 40 °C to yield the product (oligomer **II**) as a black solid (yield = 96%). Inherent viscosity = 0.05 dL/g.

Fractionation by Precipitation. We have attempted to fractionate this oligomerization product by precipitation from a methanol solution with an increasing amount of diethyl ether. Thus, 1.00 g of a black reaction product was dissolved in 5 mL of methanol, and the first 10 mL of diethyl ether (methanol/ether = $^1/_2$) was added; the precipitate was filtered and dried (0.42 g of product, $\eta_{inh} = 0.08$ dL/g). The resulting solution was diluted by 10 mL of diethyl ether (methanol/ether = $^1/_4$), and the second precipitate was also filtered (0.42 g, $\eta_{inh} = 0.06$ dL/g). Finally, the solvent was evaporated on a rotavap, yielding 0.12 g of a solid residue.

Modification of the Oligomerization Product with Hydrochloric Acid. Concentrated HCl solution (2 mL) was added into the solution of 2.0 g of reaction product dissolved in 10 mL of methanol. The solvent and the excess of the acid were evaporated under reduced pressure. The product was dried under vacuum at 105 °C for 3 days. Determination of the chloride content by ion chromatography gave 3.1% chloride, from which an average DP = 4 can be calculated if we suppose that one chloride is bound to one pyridinium group which had no triflate anion before treatment.

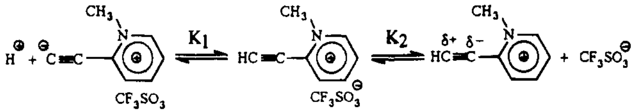
Polymerization of HMTf with 1,4-Bis(4-pyridyl)butadiyne. A total of 38.7 mg (1.89×10^{-4} mol) of 1,4-bis(4-pyridyl)butadiyne was dissolved in the mixture of 1 mL of CH_3CN and 1 mL of CH_2Cl_2 and was added into the solution of 0.26 g (1×10^{-3} mol) of HMTf in 4 mL of acetonitrile. After a 24 h reaction time at room temperature, gel formation occurred. Addition of 20 mL of diethyl ether destroyed the gel, yielding a black precipitate which was insoluble even in boiling polar solvents, such as methanol, DMF, DMSO, and water.

Results and Discussion

Terminal acetylenes have both proton-donating and proton-accepting properties; intermolecular hydrogen bonding is therefore expected especially in the presence of pyridine rings. 2-Ethynylpyridine (2EPy) displays a very broad peak in the ^{14}N NMR spectrum between 20 and 100 ppm (centered around −60 ppm) due to the strong interaction between the acetylenic proton and the pyridine ring. Quaternization of the pyridine ring results in loss of this interaction, and HMTf gives a relatively sharp signal ($D_{1/2} = 10$ ppm) at −176 ppm in the ^{14}N NMR spectrum. Quaternization also polarizes the acetylenic bond in HMTf with respect to 2EPy.

HMTf is a crystalline compound[14] and stable in air at room temperature. Its solution in aprotic solvents such as acetone or acetonitrile is also stable in the absence of nucleophiles. HMTf in solution can display two simultaneous equilibria, one is the dissociation of the weak acid and the other is the dissociation of the salt of a weak base and a strong acid. This double equilibrium is illustrated on Scheme 1. In aqueous

Scheme 1.[a] **Equilibrium I: Double Dissociation of the Triflate Salt in Solution**



[a] Note: there is no experimental evidence for the existence of the monomer zwitterion, $-M^+$.

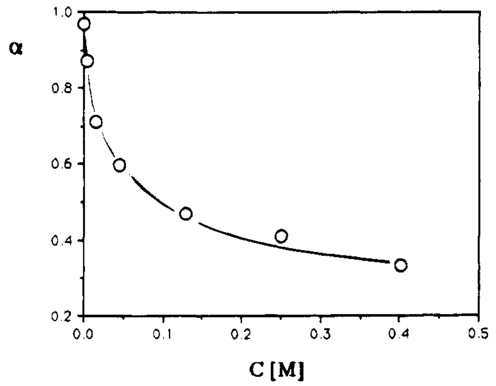


Figure 1. Degree of dissociation (α) of *N*-methyl-2-ethynylpyridinium (trifluoromethyl)sulfonate as a function of concentration in methanol at 25 °C.

solution, K_1 appear to decrease with increasing dilution: at 0.1 M (pH = 3.22) $K_{1,0.1} = 3.65 \times 10^{-6}$ and at 0.01 M (pH = 4.08) $K_{1,0.01} = 6.97 \times 10^{-7}$, respectively. Triflic acid is a much stronger acid than the acetylene derivative, therefore, dissociation of the salt is favored to the dissociation of the weak acid. Dissociation of the salt increases with increasing dilution. This process decreases the concentration of HMTf; therefore, the acidity of the solution also decreases. In methanol (Figure 1) which is a less polar solvent than water, dissociation of the acetylenic proton is still retained as it is indicated by the ^{1}H NMR spectra of HMTf in CD_3OD. After dissolving the monomer in deuteromethanol, the intensity of the acetylenic proton signal slowly decreases (in hours) due to the hydrogen–deuterium exchange. This slow exchange indicates that the measurable conductivity in MeOH is primarily due to the dissociation of the triflate anions and the pyridinium cations (Scheme 1, right side equilibrium). In this solvent [HM$^+$] and [HMTf] are comparable (α = 0.5 at [M_0] = 0.1 M and at room temperature), but [H$^+$] is very low. In ethynylpyridinium cations the positive charge on the pyridinium ring generates a partial negative charge on the C_α carbon and a partial positive charge on the C_β carbon atom of the ethynyl group.[4] As a consequence, the proton is not mobile in these cations, and that is why $-CH{=}C(MePy^+)-$ is the repeating unit in the polymer.[6-8]

Anionic polymerization initiated by pyridine has been observed in several systems. In the polymerization of cyanoacrylate esters by pyridine,[18] the pyridine consumption was very low, which was explained later[19] by the subsequent formation of hydroxide anions which were the real initiators (rather than the pyridine itself). Pyridine has been found to be a real initiator in the polymerization of nitroethylene[20] and in the polymerization of 2- and 4-vinylpyridinium salts.[16,21] It was reported[13] that approximately 50% cyclotrimerization occurred when *N*-methyl-4-ethynylpyridinium triflate was heated in DMSO or water. In this case the formation of (*N*-alkylpyridinium)acetylide zwitterions were thought to be responsible for the trimerization of that monomer salt; therefore, in the case of quaternized ethynylpyridines we have also to consider the possibility of initiation by the acetylide anions (species $^-$MTF in Scheme 1).

To clarify the role of pyridine in the initiation step, we have attempted to react an equimolar amount of *N*-methyl-2-ethynylpyridinium triflate with 4-methyl-2,6-di-*tert*-butylpyridine (MDTBP). MDTBP is known as an effective proton trap in the living carbocationic polymerizations.[22] Due to the steric hindrance of the *tert*-butyl groups, the nitrogen in this compound cannot be quaternized by the ethynyl group of the monomer. In an anhydrous solvent, trapping the dissociated protons of the monomer must increase the dissociation of the acetylene proton, producing a higher concentration of acetylenic anions (see Scheme 1, left side). If the polymerization had been initiated by the acetylenic anions, this reaction should produce at least dimers. In acetonitrile no oligomer formation was observed in the absence of pyridine even at elevated temperature (3 days at 70 °C was the longest attempt). From this solution HMTf was recovered quantitatively, which means that the acetylide anions are not able to initiate this reaction. Similarly, HMTf was stable in the presence of 4-methyl-2,6-di-*tert*-butylpyridine (MTDTP) in methanol. No triple bond consumption could be detected by FTIR in this system at room temperature for 24 h. HMTf in acetonitrile at 70 °C was also stable for 1 day. The light brown color in the acetonitrile solution may be due to the contaminations of MDTBP (purity claimed by manufacturer: 98.87%), but this coloration was negligible and HMTf was recovered.

Initiation by hydroxide ions can be ruled out by using 1,4-bis(4-pyridyl)butadiyne as an initiator for the following reason: If the initiation happens as a consequence of the hydroxyl ion generated by pyridine,[19] the polymer must be linear and therefore soluble. This reaction resulted in formation of a cross-linked gel. This can only happen if the nitrogens in the initiator have become quaternized, activating both triple bonds in the initiator molecule making them accessible to cross-linking.

The lack of polymerization of *N*-methyl-2-ethynylpyridinium (trifluoromethyl)sulfonate in the absence of pyridine and the formation of a cross-linked gel in the reaction mixture when the polymerization was initiated with 1,4-bis(4-pyridyl)butadiyne prove that pyridine is a real initiator, and the first step of the initiation is the quaternization of the pyridine nitrogen.

Kinetic measurements were carried out at room temperature by monitoring the disappearance of the triple bond from the IR spectra, i.e., the monomer consumption. Methanol itself reacted very slowly with the monomer (100% conversion in 8 weeks). According to ^{1}H, ^{13}C, and ^{14}N NMR and IR spectra, the products of this reaction are methoxyvinylpyridinium triflate and its derivatives. This reaction therefore can be attributed to the methoxide anions present in the alcohol due to the self-ionization. Initiation by solvent can be neglected on the time scale of the experiments. When reaction was initiated by pyridine (or its derivatives), the colorless monomer solution at 0.1 M concentration turned to yellow, red, green, and finally dark blue. The conductivity of the reaction mixture continuously decreased (from 4.90 to 4.72 mS) during this reaction. As the total concentration of pyridinium ions is increasing in this reaction and there is no reason for the degree of dissociation to decrease, this conductivity change can

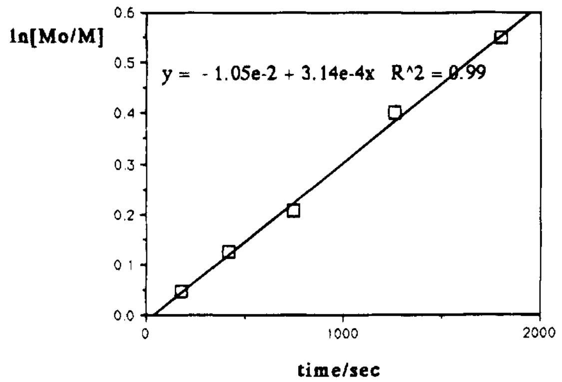


Figure 2. Reaction of *N*-methyl-2-ethynylpyridinium triflate with pyridine in methanol at room temperature. $[M]_0 = 0.10$ M; $[M]_0/[I]_0 = 8.22$. Only the first stage is plotted, up to 42% conversion.

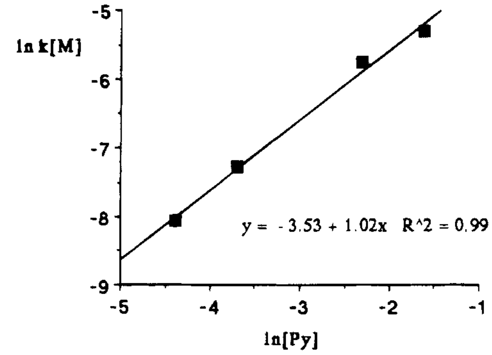


Figure 3. Dependence of the reaction rate on the initial initiator concentration. $[M]_0 = 0.10$ M; $[M]_0/[I]_0 = 1.0, 2.0, 4.1,$ and 8.2, respectively.

Table 1. Representative Kinetic Data in Absolute Methanol at Room Temperature

no.	$[M]_0$ (mM)	[Py] (mM)	$10^4 k$ (1 M^{-1} s^{-1})	$[M_0]/[I]$
LB-29	101	99	31.8	1.0
LB-102	259	124	25.7	2.1
LB-165	47	25	5.57	1.9
LB-167	101	25	5.81	4.1
LB-166	400	49	5.60	8.1
LB-32	262	26	5.37	10.1
LB-168	394	25	2.05	15.9

be attributed to the decreased mobility of the cations. Conversions were 100% in methanol.

The ln $[M_0/M]$ versus time function of the reaction (Figure 2) is linear up to 50% conversion, which suggests a first-order dependence. However, at lower $[M_0]/[I]$ ratios the rate of monomer consumption slightly accelerated with increasing conversion; i.e., the concentration of active centers is slowly increased. This indicates that pyridine is a slow initiator. A similar tendency was experienced in the case of 2-ethynylpyridine or 4-*tert*-butylpyridine initiators.

Varying the concentration of the reactants, the kinetic orders can be determined (Table 1). According to Figure 3, ln $k[M]$ (the first derivative of the ln($[M_0]/[M]$)−time curve) versus ln [Py] function is linear. From the slope first-order behavior was obtained at the same monomer concentration. Using different pyridine derivatives as the initiator, the stronger nucleophile gives a higher reaction rate (Figure 4).

If we plot ln($k[I]$) as a function of $[M_0]$, we obtain a zero-order behavior between 0.05 and 0.25 M monomer concentrations (Figure 5), suggesting that the initiation is the rate-determining step in the polymerization of the *N*-methyl-2-ethynylpyridinium triflates.[14]

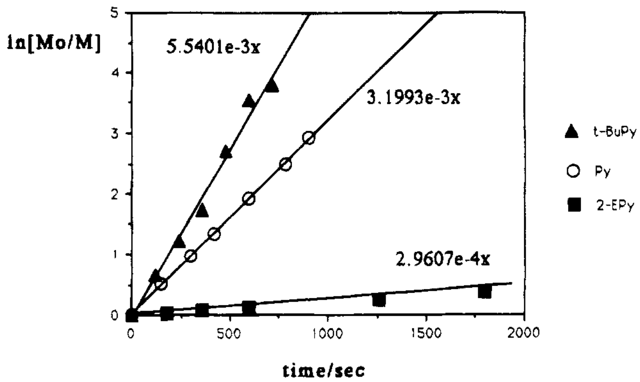


Figure 4. Comparison of the reaction rates with different initiators. $[M]_0 = 0.10$ M; $[M]_0/[I]_0 = 4.0$. 2-EPy: 2-ethynylpyridine. Py: pyridine. t-BuPy: 4-*tert*-butylpyridine. Solvent: methanol.

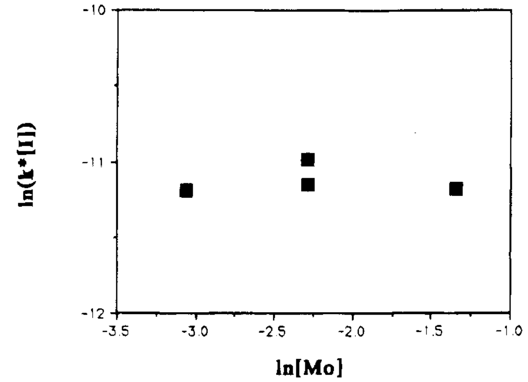


Figure 5. Dependence of the reaction rate on the initial monomer concentration. $[I]_0 = 0.025$ M; $[M]_0 = 0.047$, 0.1, and 0.26 M, respectively.

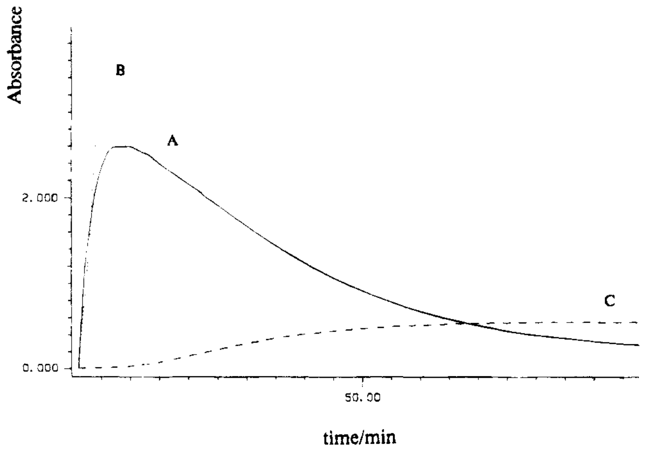


Figure 6. Evolution of the UV−visible spectrum of oligomer **I** at different wavelengths as a function of time. $[M]_0 = 0.039$ M. Initiator: pyridine. [I] = 0.0123 M. Dotted line: 330 nm (peak B + 10 nm). Full line: 430 nm (peak A + 28 nm). Dashed line: 580 nm (peak C).

Oligomerization in methanol was also monitored by UV−visible spectroscopy (Figure 6). Changes in the UV−visible spectra of the reaction mixture in methanol displayed both concentration and pH dependence. In the case of dilute solutions (4×10^{-3} M) two peaks were observed in the successive spectra (peak B at 322 nm, and peak A at 402 nm with pyridine and 420 nm with 4-*tert*-butylpyridine). In more concentrated solutions (0.1−0.25 M) an additional peak was also observed (peak C at 580 nm with pyridine and 595 nm with 4-*tert*-butylpyridine). First, peak A appeared and its intensity passed through a maximum (Figure 6, full line), indicat-

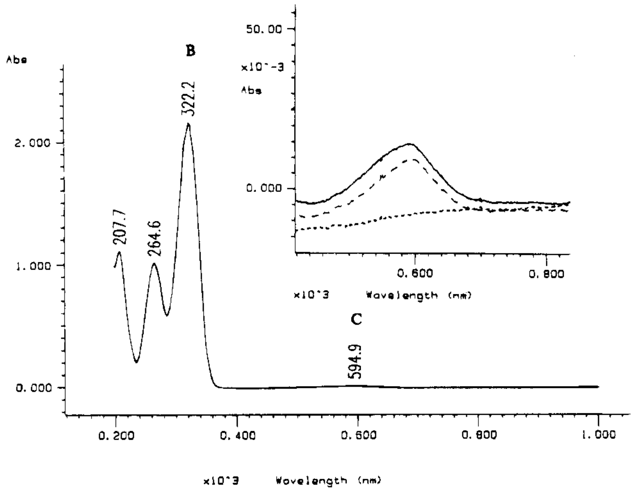


Figure 7. UV–visible spectrum of oligomer **I** in methanol. $[M]_0 = 1.4 \times 10^{-5}$ M. Initiator: *tert*-butylpyridine. Inset: peak C in different solvents (continuous line, methanol; long dashed line, acetonitrile; short dashed line, chloroform).

ing that it belongs to an intermediate compound in the reaction mixture. The intensity of the peak B continuously increased; it belongs therefore to a reaction product (Figure 6, dotted line). The intensity of peak C remained constant after the consumption of the monomer (Figure 6, dashed line), and further monomer addition only slightly increased its intensity. (At higher concentrations a sampling technique was used to obtain the successive spectra. Several minutes after dilution by methanol to 7.7×10^{-5} M concentration, peak A disappeared from the diluted samples.) Acidifying the samples with HCl changed the color from blue to yellow, and both A and C peaks disappeared. The blue color and both peaks reappeared again when an excess of pyridine (or any other base) was added to the sample.

The dark blue solution of the final reaction product (0.1 M in methanol) had two characteristic absorptions in the visible range (peaks B and C, Figure 7). Peak C was present when methanol or acetonitrile was used as solvent for spectroscopy, but it was absent in chloroform (Figure 7, inset).

On the basis of these observations, peak B at 322 nm was assigned to the $-CH{=}CH-$ aliphatic double bond in conjugation with the pyridinium ring (proton-terminated zwitterion HP_1 in Scheme 3), peak A was assigned to the primary zwitterion (P_1 in Scheme 2), and peak C was assigned to the dimeric anions (P_2 and P_2').

The reaction system was also monitored by taking successive ^1H NMR spectra in deuteromethanol. The signal of the acetylenic proton disappeared from the spectra after pyridine addition, as a result of the exchange of hydrogen with deuterium. In the aliphatic region the $>NCH_3$ signal of the monomer at 4.46 ppm gradually decreased and the $>NCH_3$ signals of the products increased (see Figure 8: main peak at 4.21 ppm; additional minor signals at 4.39 and 4.08 ppm). The aromatic region became complicated. A comparison of spectra of the reaction products prepared in methanol and deuteromethanol is demonstrated on Figure 8. Characteristic doublets of the proton-terminated anionic species can be found in the spectrum of products prepared in methanol: 6.3 and 7.9 ppm for the protonated primary zwitterion (HP_1), $J = 12$ Hz; 5.7 and 7.2 ppm for the protonated dimer (HP_2), $J = 6$ Hz; area ratio HP_1:HP_2 = 9:1. These doublets and the two methoxy signals in the proton spectra (3.5 and 3.9 ppm) were absent when the reaction was carried out in deuteromethanol. Addition of a small amount of $NaOCD_3$ solution into the deuterated NMR sample simplified the aromatic region of the proton spectra of oligomerization products (Figure 8, inset). A possible explanation is that the addition of the strong base breaks the intermolecular associations between the cationic and anionic sites, thus providing separate zwitterions.

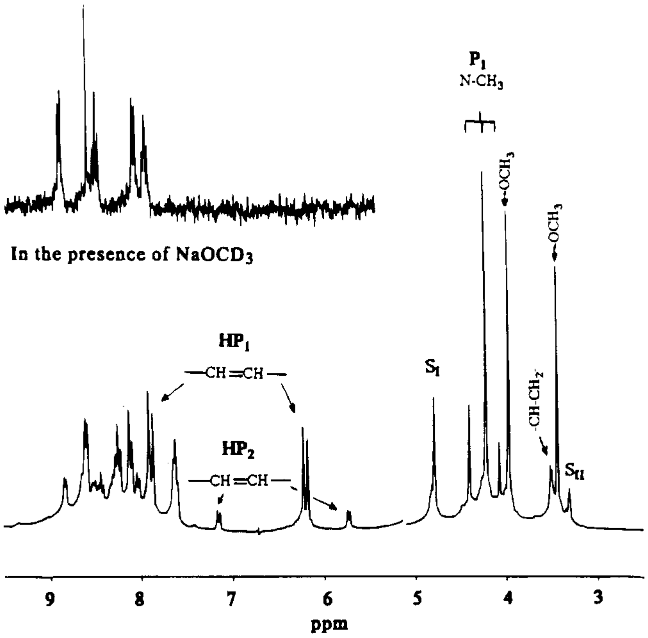


Figure 8. ^1H NMR spectrum of oligomer **I**. $[M]_0 = 0.2$ M. Initiator: pyridine. $[M]_0/[I]_0 = 4.0$. Solvent: CD_3OD. The 9.5–5.0 ppm region is magnified by a factor of 2. Peaks marked by arrows were missing when the reaction was carried out in deuteromethanol. Inset: In the presence of $NaOCD_3$.

The main primary products were *cis*- and *trans*-1-pyridiniumyl-2-(*N*-methylpyridiniumyl)ethylene triflate methoxide (HP_1), methoxyvinyl(*N*-methylpyridinium) triflate (HP_1') and the corresponding protonated dimers (HP_2 and HP_2'). In the proton NMR spectra of the final reaction mixture the presence of secondary reaction products also can be detected. In deuteroacetone a doublet at 3.6 ppm ($-\mathbf{CH_2}CH-$) and a triplet at 4.9 ppm ($CH_2\mathbf{CH}-$) indicate that ionic addition to the 1-methoxyvinyl(*N*-methylpyridinium triflate) does occur, giving rise to $(CH_3O)_2CHCH_2$ Py^+ fragments. Similar double addition of methanol across the triple bond was also observed in the esterification of monopotassium acetylenedicarboxylate.[23] In the ^{13}C NMR spectra of oligomer **I** (Figure 9), the presence of a $-CH_2-$ signal (38 ppm) and the different $-CH{=}$ signals (around 100 ppm) also refer to these secondary reactions. The C_β carbon signal in the $\rangle N^+\mathbf{C_\beta(H)}{=}C_\alpha(H)C^+{}_{ar}\langle$ unit (HP_1, P_1, HP_1', and P_1') appears at 165 ppm. This signal shifts further lowfield in the dimers due to the increased conjugation, and $\mathbf{C_\beta}$ can be found at 161 ppm.

In the ^{14}N NMR spectrum (Figure 10) three signals are present (signal $A_M = -69$ ppm, signal $B_M = -176$ ppm, and signal $C_M = -189$ ppm). In the case of pyridines a correlation exists between the chemical shift of the neutral nitrogen and the change of this shift on protonation or quaternization. Removal of the diamagnetic shielding of the lone electron pair shifts the resonances upfield;[24] i.e., the ppm values are decreasing with increasing positive charge on the nitrogen. Signal B_M is in an identical position to the only peak found in the spectrum of the monomer. Both B_M and C_M are

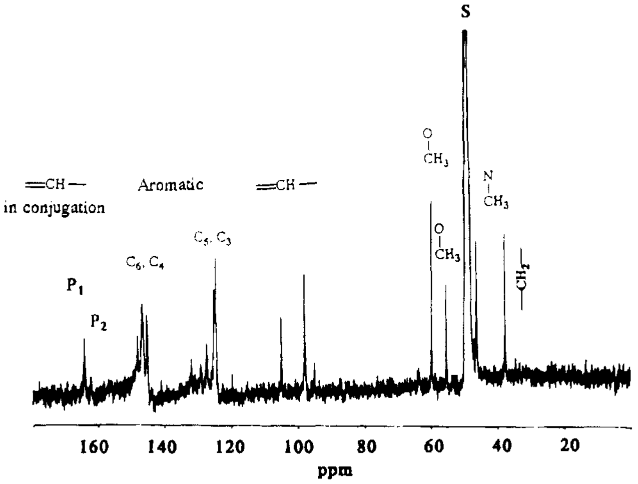


Figure 9. ^{13}C NMR spectrum of oligomer **I**. Solvent: CD_3OD. Peak assignment was achieved by a coupling experiment.

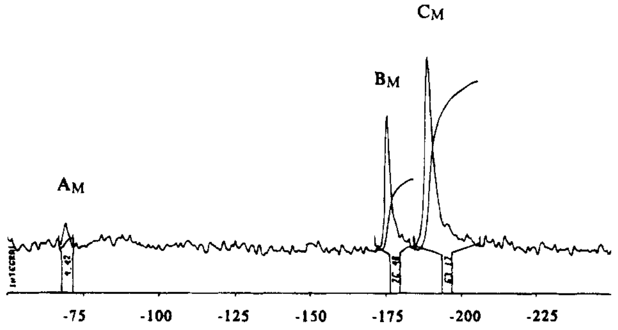


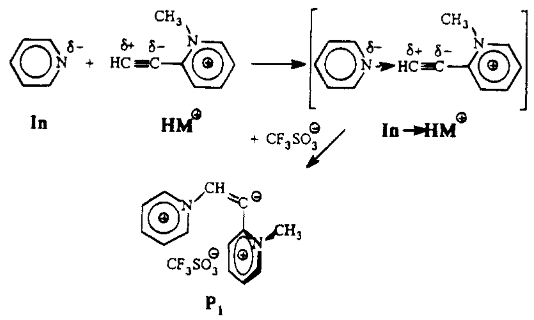
Figure 10. ^{14}N NMR spectrum of oligomer **I**. Solvent: CD_3OD. Nitromethane in deuteroacetone was used as the external standard.[27]

present in the reaction product formed in pure methanol; they belong therefore to the *cis*- and *trans*-pyridinium isomers. These peaks do not change when the solution is acidified. However, signal A_M disappeared when HCl had been added to the sample. Pyridine has a resonance at −62 ppm; therefore, the −69 ppm value indicates the presence of an uncharged nitrogen. A similar peak was found in the ^{14}N NMR spectrum of the cyclization product of DMAD with pyridine prepared according to the literature;[25] therefore, signal A_M possibly indicates the formation of a small amount of cyclic byproduct, probably a substituted indolizine. Consequently, this peak is missing from the ^{14}N NMR spectrum of the product formed in pure methanol because there is no possibility of cyclization in this case. The amount of formed cyclic byproduct in the oligomerization of HMTf is surprisingly low, compared to the reaction of DMAD with pyridine in methanol in which they are the main products.

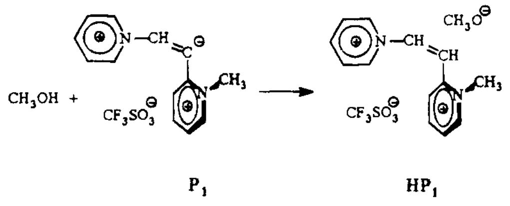
On the basis of the above observations, we propose the following scheme for the reaction of *N*-methyl-2-ethynylpyridinium (trifluoromethyl)sulfonate with pyridine in methanol (Schemes 2−5).

Initiation by pyridine involves the quaternization of the pyridine nitrogen by the ethynyl group of the monomer and yields zwitterions with pyridinium headgroups (Scheme 2). Fast and complete deuterium−hydrogen exchange in a methanol solution in the presence of pyridine indicates a possible salt formation between the pyridine and the undissociated HMTf. Introduction of any base into the HMTf solution creates an additional equilibria (eq II).

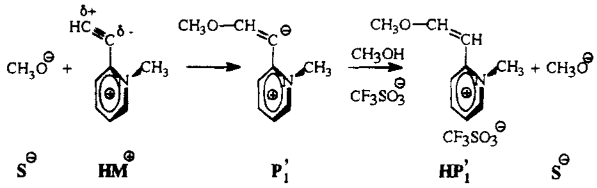
Scheme 2. Initiation with Pyridine



Scheme 3. Termination of the Initial Zwitterion by Protonation

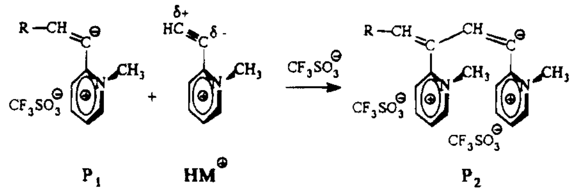


Scheme 4.[a] **Chain Transfer to Solvent**

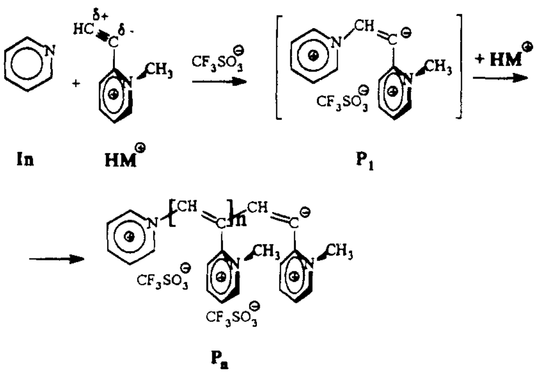


[a] Triflate dissociation equilibria are not shown for the sake of simplicity.

Scheme 5. Chain Growth (R = CH_3O or *N*-Pyridiniumyl)



Scheme 6. Oligomerization in Pyridine



$$\mathrm{PyHMTf} \overset{K_4}{\leftrightarrow} \mathrm{Py} + \mathrm{HMTf} \overset{K_5}{\leftrightarrow} \mathrm{Py{:}HM^+} + \mathrm{Tf^-} \quad \mathrm{(II)}$$

Because PyHMTf is a salt of a weak base (Py) and a weak acid (HMTf), its degree of dissociation must be very small. Formations of PyHMTF and $Py{:}HM^+$ are competitive reactions when nucleophile is added into the solution of HMTf. After initiation equilibrium I and II coexist; therefore, the observed rate will depend also on the $[M]_0/[I]_0$ ratio (Figure 11). The rate of In → HM^+ complex formation depends on $[M]_0$, $[I]_0$, and the initiator nucleophilicity. Solvation of HM^+ plays an impor-

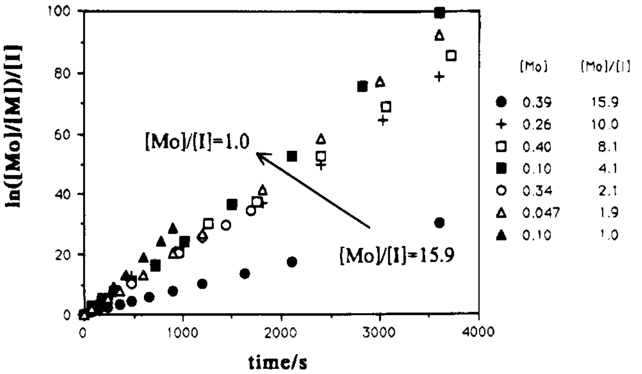


Figure 11. Dependence of the reaction rate on the initial $[M]_0/[I]$ ratios.

tant role in the reactivity of the acetylene bond, because the positive charge on the ring enhances the partial negative charge density on the neighbor carbon, similar to the case of enamines.[25]

Reaction of the monomer with the Lewis base is of the first order with respect to the initiator. The pyridine-initiated zwitterions (P_1) are reactive intermediates, and they can undergo different simultaneous and consecutive reactions. P_1 can react either with the solvent (Scheme 3 and 4, termination and chain transfer) or with HM^+ (Scheme 5, chain growth). Due to the high excess of protic solvent, termination by protonation takes place and methoxide anions are generated (Scheme 3). These methoxide anions yield also zwitterions which will be terminated by the solvent, regenerating the methoxy anions (Scheme 4). This termination–chain transfer cycle leads to the simultaneous formation of methyl vinyl ethers. The rate of this vinylation reaction depends on the momentary concentration of alkoxide anions. The amount of methoxide anions will always be proportional to the amount of quaternized initiator molecules. After the chain-transfer cycle began, the monomer consumption is the result of reactions both between the pyridine and HMTf and between the methoxide anions and HMTf. Both nucleophiles contribute to the measured rate; therefore, only apparent rate constants can be calculated. Although the numerical values of the reaction rate constants determined in methanol will differ from the expected values in a nonprotic solvent, the general relationships and reaction orders will be the same, because the chain transfer to solvent does not change the concentration of the active species.

The Lewis base gradually incorporates into the reaction product, and the concentration of the active species slowly increases. Finally the reaction yields the mixture of 90% of *cis*- and *trans*-1-pyridiniumyl-2-(*N*-methyl pyridiniumyl)ethylene triflate methoxide (HP_1) and 1-methoxy-2-(*N*-methyl pyridiniumyl)ethylene triflate (HP_1'). The actual ratio depends on the experimental conditions. Further reaction of P_1 and P_1' with HM^+ leads to the formation of approximately 10% of the corresponding protonated dimers, i.e., to the triflate salts of the 1-pyridiniumyl-2,4-bis(*N*-methylpyridiniumyl)-1,3-butene (HP_2) and 1-methoxy-2,4-bis(*N*-methylpyridiniumyl)-1,3-butene (HP_2'). The more dilute the solution, the smaller is the concentration of HP_2 and HP_2'. The presence of 10% dimer in the final reaction mixture at $[M]_0 = 0.2$ M demonstrates the high reactivity of the pyridinium-activated triple bond. Both kinds of vinyl ether salts are reactive intermediates, and formation of a small amount of other compounds as products of consecutive reactions can also be detected. Vinyl ethers reacts with methanol, yielding 1-dimethoxy-2-(*N*-methylpyridiniumyl)ethane triflate. The dimeric zwitterion of 1-pyridiniumyl-2,4-bis(*N*-methylpyridiniumyl)-1,3-butene can also provide some cyclic byproduct, as is witnessed by the ^{14}N NMR spectra of the reaction mixture.

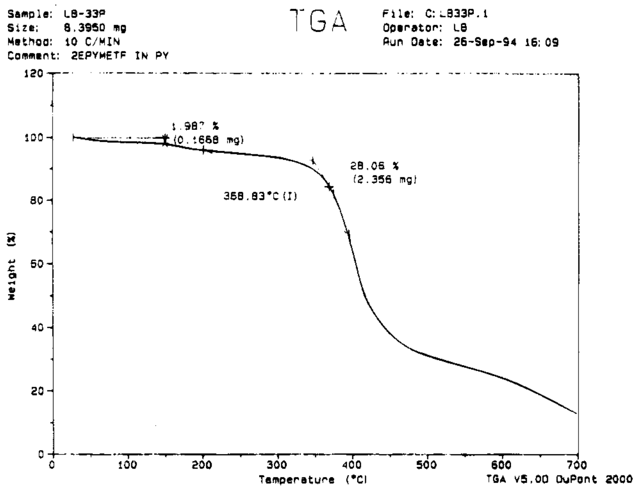


Figure 12. TGA thermogram of oligomer **II** in nitrogen; heating rate 10 °C/min.

When the reaction was carried out in anhydrous pyridine, i.e., using the initiator itself as solvent, a black compound was formed instantaneously in a rapid exothermic reaction with a practically 100% conversion.

The FTIR spectrum of the product showed that all triple bonds were converted into double bonds. According to TGA, the thermal stability of oligomer **II** is similar to that of the previously reported polyacetylene triflates,[14] i.e., weight loss is only 2% up to 150 °C, and the product decomposes around 368 °C (Figure 12). DSC thermograms gave no sign of any thermal events before decomposition. This suggests an amorphous structure of the polysalt. Treatment of this reaction product with concentrated hydrochloric acid followed by evaporation of the volatile acid and determination of the chloride content gave an average DP of 4.

UV–visible spectra of different fractions precipitated with an increasing amount of diethyl ether show that the compound precipitated from more polar solvent mixtures has higher wavelength values, i.e., longer conjugation length. However, inherent viscosities of the fractions were low in all cases (see the Experimental Section).

Characteristic doublets of the protonated chain ends are absent from the proton NMR spectra of this material (Figure 13A). (Note: The protic termination in the case of the thermally polymerized 2-ethynylpyridinium hydrochloride is clearly detectable by the ^{1}H NMR spectrum of the thermal polymerization product.)

^{13}C NMR spectrum (Figure 13B) confirms that only aromatic and conjugated CH groups are present except for the $N-CH_3$ signals of the pyridinium ring. This means that chain polymerization takes place even in pyridine with this monomer.

The ^{14}N NMR spectrum of this material (Figure 14) consists of two signals, a small sharp signal at −69 ppm (signal A_P, uncharged N) and a broad one (signal B_P, positively charged N), centered at −176 ppm. Signal A_P has an identical position to signal A_M, the lowest field peak in the ^{14}N NMR spectrum of the oligomerization product in methanol. The area ratio of the two different

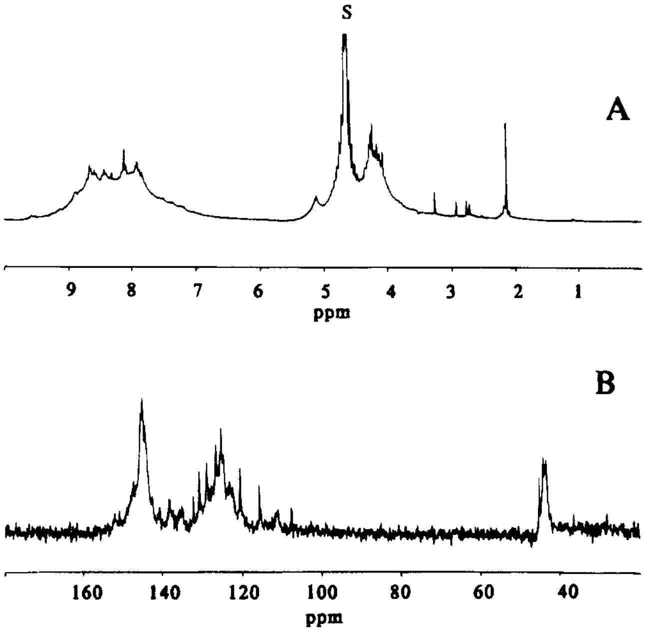


Figure 13. ^1H NMR and ^{13}C NMR spectra of oligomer **II**. Solvent: D_2O.

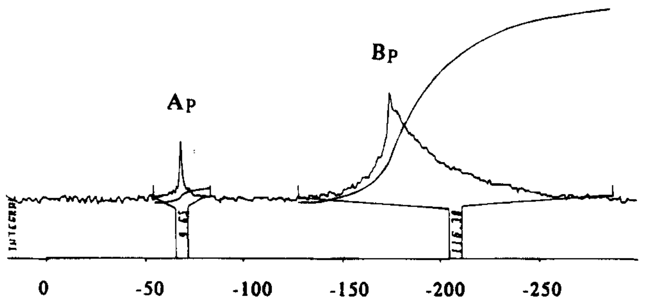


Figure 14. ^{14}N NMR spectrum of oligomer **II**. Solvent: CD_3-OD.

kinds of nitrogens is 16/1. Signal B_P was assigned to the pyridinium cations in the chain. The broadness of this peak indicates a scatter in the positive charges on nitrogens. Acidification of this oligomerization product with hydrochloric acid led to the disappearance of signal A_P. As the known cyclization process of DMAD with pyridine yields 4*H*-quinolizines, we assume that this −69 ppm peak is due to the formation of a small amount of cyclic byproduct, such as 4*H*-1,3-bis(*N*-methylpyridiniumyl)quinazoline triflate.

In order to confirm the zwitterionic character of the products, the effect of pH on the behavior of the polymer UV−visible spectrum was also investigated. Aqueous concentrated HCl solution and pyridine were used to vary the pH of the UV sample of the product in subsequent additions (Figure 15). While the original UV−visible spectrum of the polymer cannot be restored after the first acidification, the additional acid−base cycles produced reversible changes comprised between curves 2 and 3. Protonation of any heterocyclic ring is not expected to change the visible spectral region, while a possible hydrohalogenation[26] would not be reversible. The reversible absorbance change at 445 nm supports the zwitterionic character. Because the dissociated anions have their own absorption in this spectral region, they also contribute to the spectral shifts and their absorption has to be taken into account.

Initiation in pyridine involves a quaternization of the pyridine by the activated ethynyl group of the monomer. The primary zwitterion can only react with the monomer. In pyridine the result of this reaction is a mixture of linear oligomers of low DP. Pyridine is a slow initiator, so the molecular mass distribution should be broad. As a result of the quaternization of the initiator, there is one more pyridinium cation than triflate anion present, and the additional anion must come from the solvent. In solution, due to the dynamic equilibrium between all pyridinium cations and all triflate anions, the triflate counterions must be randomly distributed between the available pyridinium groups. As a consequence, the pyridinium cationic sites are indistinguishable. Nevertheless, pyridine cannot provide anions; therefore, some other mechanism is necessary to keep the principle of electroneutrality. It is possible that stable radicals had been formed, and investigations in this field are in progress.

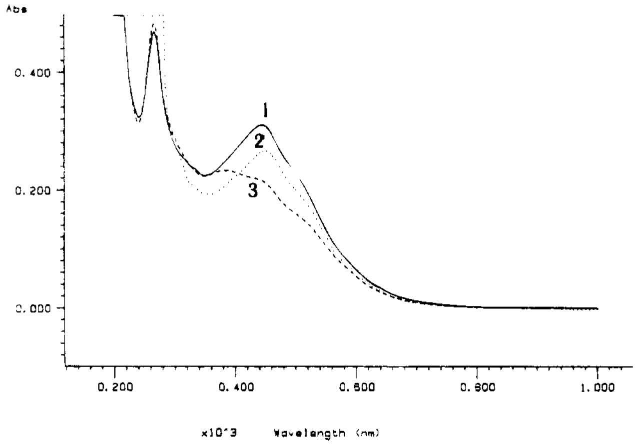


Figure 15. Effect of pH on the UV−visible spectrum of oligomer **II**. Solvent: CH_3OH. (1) Neutral solution (continuous line). (2) Solution acidified with HCl (dashed line). (3) Excess of Py added into the acidic solution (dotted line).

Formation of oligomers using the initiator itself as solvent reveals that the rate of propagation is much higher than the rate of initiation and therefore the initiation is the rate-determining step even in pure pyridine. The high excess of the initiator assures 100% conversion. The degree of polymerization is governed by the k_p/k_i ratio if there is no termination present. Protic termination is impossible in pyridine. No other obvious termination process was observed, yet a termination must account for the low DP's of such ionic polyacetylenes.

The nature of the termination is not yet completely understood, and it is under investigation.

Summary

Kinetic and mechanistic investigations were carried out on the *N*-methyl-2-ethynylpyridinium (trifluoromethyl)sulfonate using pyridine as the initiator in methanol or pyridine as the solvent at room temperature. Addition of pyridine into the monomer solution in methanol generates rapid exchange of the acetylenic protons with deuterium. Initiation by nucleophiles involves quaternization of the initiator producing zwitterions as primary intermediates. Termination occurs by protonation followed by chain transfer to methanol. The main products are 1-pyridiniumyl-2-(*N*-methylpyridiniumyl)ethylene and methoxyvinyl(*N*-methylpyridinium) triflates. Formations of protonated dimers have also been observed despite the large excess of protic solvent. The initiation is of first order with respect to the initiator and apparent zero order with respect to the monomer in the studied concentration range. Dissolving the monomer in pyridine results in fast formation of oligomers, indicating that the rate of propagation is much higher than the rate of initiation; therefore, the latter is the rate-determining step. No obvious mechanism of termination has been identified in this case. Pyridine proved to be a slow initiator. The zwitterionic character of oligomers was confirmed in both solvents. The oligomerization proceeds according to a complex zwitterionic/anionic mechanism which requires the presence of quaternizable heteroatom in the initiator.

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