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Conjugated Ionic Polyacetylenes. 9. Polymerization of *N*-Methyl-2-ethynylpyridinium Trifluoromethanesulfonate in Aprotic Polar Solvents

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ABSTRACT: Ionic polymerization of the acetylene bond in *N*-methyl-2-ethynylpyridinium trifluoromethanesulfonate (triflate) monomer (HMTf) was investigated at room temperature in aprotic polar solvents such as acetonitrile, DMF, and DMSO. Polymerization was initiated by pyridine and pyridine derivatives and the resulting reactions were monitored by IR, UV–visible, and NMR spectroscopy. Polymerization of HMTf in aprotic polar solvents resulted in incomplete conversions. Conversions were strongly affected by the [monomer]/[initiator] ratio. Reaction rates when initiated with pyridine were not influenced by the polarity of the solvent at the same monomer concentration. Reactivity of initiators decreased in the order alkyl > alkenyl > alkynyl substitution. Ortho-substituted pyridine derivatives were found to be less reactive than the para derivatives. There was no substantial difference with respect to reaction rates and conversions of polymerizations when substituted pyridines were used or the pyridine molecules were linked by ethane, ethylene, or acetylene units. Polymerization of *N*-methyl-2-ethynylpyridinium triflate proceeds according to a complex zwitterionic/anionic mechanism. Two different kinds of chain growth were found and a general reaction scheme was proposed to account for the experimental findings.

Introduction

Synthesis of a new class of thermally and oxidatively stable mono- and disubstituted ionic polyacetylenes was recently reported.[1,2] These polyenes contain pyridinium ring substituents associated with halide, methanesulfonate, or trifluoromethanesulfonate counterions. The structural features of these polymers are unique with respect to their ionic nature, high degree of substitution, and extensive backbone conjugation. They have been prepared by reaction of 2-ethynylpyridines with haloalkanes,[3] methanesulfonic acid,[4] halogen,[5] or halogenic acids.[6] Similar compounds have been synthesized from α-haloethynes,[3] and this reaction route allows the application of virtually all kinds of substituted pyridines. A common feature of these reactions is that the quaternization and polymerization take place simultaneously and, due to the similarity of the reaction rates, interfere with each other.

Using triflic acid esters, it was possible to separate the quaternization step from the polymerization and isolate the *N*-alkyl-2-ethynylpyridinium triflate monomers as stable salts.[7] These monomers polymerize upon melting or upon treatment with either a free-radical initiator (AIBN) or a nucleophilic initiator, such as pyridine.[8] Since radical inhibitors did not affect the nucleophile-initiated polymerization of the triflate salts, an anionic mechanism, based on analogy with 2-vinylpyridine was proposed.[6]

The understanding of the polymerization mechanism and kinetics are the key to the optimization of properties of these polymers with potential applications in the areas of energy storage, nonlinear optics, and permeation. In our recent studies[9,10] we described the initiation stage in the polymerization of HMTf. The study of reactions in polar protic solvents indicated that initiation occurs as a result of quaternization of the initiator by the monomer. Initiation and propagation were found to be of first order with respect to the initiator and zero order with respect to the monomer. Experiments carried out in pyridine as a solvent resulted in a fast reaction and proved that the rate of propagation is at least 1 magnitude higher than the rate of initiation.

However, the rate of propagation decreased with increasing monomer/initiator ratio[10] and polymerization of *N*-methyl-2-ethynylpyridinium triflate with pyridine

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Table 1. IR Valence Stretching Vibrations (cm^{-1}) of 2-Ethynylpyridine, of the Triflate Monomer, and of Poly(HMTf)[a]

	R,=C)-H	(C≡C)−H	Py,C−H	−C≡C−	R, C=C	Py skeleton, I	Py skeleton, II
2EPy in bulk		3293	3053	2109		1583	1561
HMTf salt, solid		3249	3060	2123		1621	1578
polymer, solid	3532		3096		1630	1620	1564
2EPy in CH_3CN		3272	N/A	2114		1584	1562
HMTf in CH_3CN		3238	3100	2123		1620	1577
polymer, in CH_3CN	3623, 3537		3098		1638	1621	1560
2EPy in CH_3OH		N/A	N/A	2113 (3.48)[b]		1592	1584
HMTf in CH_3OH		N/A	N/A	2115 (22.82)[b]		1620	1592

[a] 2EPY, 2-ethynylpyridine; HMTf, *N*-methyl-2-ethynylpyridinium triflate (0.1 M solutions unless otherwise indicated); R, alkene chain; Py, pyridinium ring; N/A, data are not available due to intensive solvent absorption. [b] Intensity in arbitrary area units.

and its derivatives in neutral aprotic polar solvents resulted always in incomplete (0.2−0.6) monomer conversions. Visible spectra of the nucleophile-initiated polymerization products were trailing to 600−1000 nm, often without characteristic peak(s).

The aim of the present paper is to clarify the fundamental mechanistic and kinetic aspects of polymerization of HMTf in polar aprotic solvents, to elaborate the influence of solvent and initiator substitution, and to suggest a general reaction scheme consistent with these experimental results. (Previous results concerning the propagation mechanism have been reported in a communication.[11])

Experimental Part

Materials. 2-Ethynylpyridine (2EPy) obtained from Lancaster Synthesis Inc. and 4-vinylpyridine obtained from the Aldrich Chemical Co. were distilled under vacuum in a nitrogen atmosphere before use. Pyridine, 4-methylpyridine, 2-ethylpyridine, 1,2-bis(4-pyridyl)ethane, 1,2-bis(4-pyridyl)-ethylene, and poly(vinylpyrrolidone) (PVP) (MW = 40 000) were purchased from the 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.

Spectroscopic grade methanol was purified by distillation from Mg turnings in the presence of I_2 traces. Spectroscopic grade DMF and DMSO were stored over molecular sieves. 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. Measurements had been carried out in absolute acetonitrile or methanol after appropriate dilution. ^1H, ^{13}C, and ^{14}N NMR measurements were carried out using a Bruker-270 SY 270 MHz multinuclear spectrometer equipped with a temperature controller. Nitromethane was used as internal reference in the ^{14}N NMR measurements. Conductivity measurements were carried out with a YSI-50 conductometer using a YSI conductivity cell (K = 1.0 cm^{-1}) at 24 °C.

Synthesis. The synthesis of HMTf has already been described.[7] 1,4-Bis(4-pyridyl)acetylene and 4-ethynylpyridine were prepared according to literature.[12]

General Polymerization Procedure. The HMTf monomer was dissolved in 5 mL of solvent (acetonitrile, DMSO, or DMF) in a reaction tube and the calculated amount of initiator was added at room temperature (24 ± 1 °C) by means of a microsyringe under vigorous stirring using a Vortex mixer.

For IR measurements a sample was measured into a Perkin-Elmer circular demountable cell (0.5 or 0.2 mm, depending on the actual monomer concentration) and the disappearance of the −C≡C− bond was monitored in the successive spectra. In UV−visible measurements typically 5 μL of reaction mixture was added 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 polymerization 20 mL of diethyl ether was added, the precipitate was dissolved in methanol, reprecipitated with 5-fold excess of diethyl ether and dried in *vacuo*.

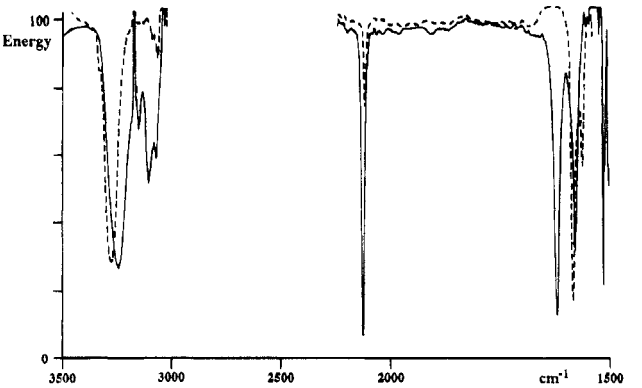


Figure 1. Comparison of IR spectra of 2-ethynylpyridine (2EPy, dashed line) and of *N*-methyl-2-ethynylpyridinium trifluoromethanesulfonate (HMTf, continuous line) in 0.1 M acetonitrile solution.

Reaction of *N*-Methyl-2-ethynylpyridinium Trifluoromethanesulfonate with Nucleophiles in an NMR Tube. Monomer (0.13 g, 5 × 10^{-4} mol) was measured into a 10 mm diameter NMR tube and dissolved in 2.5 mL of CD_3CN or DMSO-d_6 (c = 0.2 M). 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.

Results and Discussion

Dissociation and Polarization of the Monomer. Polarization of the Acetylene Bond in 2Epy. In general, activation of acetylenes by an electron-withdrawing group is well-known.[12−14] 2EPy is a hydrogen-bonded liquid with a high boiling point. Quaternization of the nitrogen changes the nature of the substituent from electron donating to electron withdrawing. This activation is reflected by changes in the IR spectra. The characteristic IR stretching frequencies in 2EPy, HMTf, and the polymer are compared in Table 1. Polarization of the ethynyl group in HMTf due to quaternization is reflected in the −34 cm^{-1} shift of $\nu_{(C\equiv C)-H}$ in CH_3 CN solution and in the increased intensity of the −C≡C− valence stretching and the +37 cm^{-1} shift of the first −C=C− group frequency of the aromatic skeleton. Comparison of the IR spectra of the 2EPy and HMTf in the same solvent and at identical concentration shows that quaternization increases the intensity of the $\nu_{C=C}$ more than 6 times (Table 1, Figure 1).

Solubility of HMTf and Effects of Solvation. N-methylated triflate derivatives of 2EPy are crystalline salts. HMTf is soluble only in polar solvents, such as acetonitrile, DMF, DMSO, water, alcohols, etc. Decomposition of quaternary ammonium salts has been re-

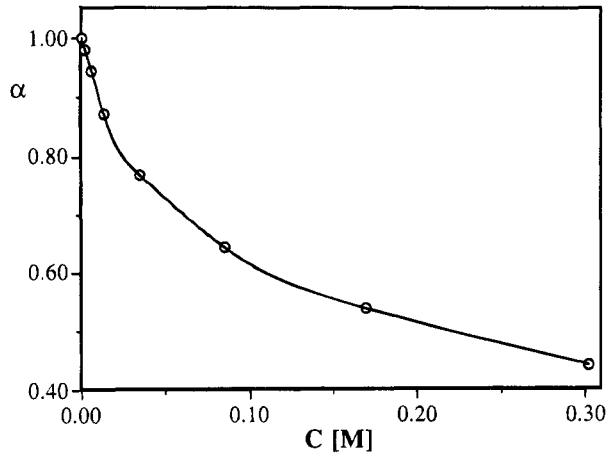


Figure 2. Degree of dissociation (α) of *N*-methyl-2-ethynylpyridinium trifluoromethanesulfonate as a function of concentration (mol/L) in acetonitrile at 25 °C.

ported such as demethylation in DMF[15] and formation of sulfonium ylide in DMSO,[16] but both processes require reflux or high temperature and 6–95 h of reaction time. At room temperature and in the absence of nucleophiles HMTf was stable for days in these solvents.

From conductivity measurements at room temperature, in 0.1 M acetonitrile approximately 60% of the monomer is in its dissociated state (Figure 2). As a consequence of its ionic character, in organic polar solvents both dissociated and undissociated monomer molecules must be present as solvated ions and ion pairs.[17,18] Two cations can contribute to the conductivity of the monomer solution, the acetylene proton, and the *N*-methylpyridinium group. As a consequence of the mass action law, the mobility of the acetylene proton is reduced by the pyridinium-ion formation in a polar solvent. Consequently, the conductivity is mainly due to the dissociation of the monomer[9] into trifluoromethanesulfonate anion and pyridinium cation. Dynamic equilibrium between the different species, among other factors, depends on the polarity of the solvent and its electron-donating strength.

Comparison of the IR data of the solid triflate salt to its acetonitrile solution spectrum (Table 1) reveals that the solvent decreased further the spectral position of the acetylene proton signal ($\nu_{(C\equiv C)-H}$) from 3249 to 3238 cm^{-1} and also shifted the valence band of the aromatic hydrogen by +40 cm^{-1}. Solvation and dissociation of HMTf result in further polarization of the acetylene moiety.[19,20]

Evidence of this polarization can also be found in the ^{13}C NMR spectra where the change in the shielding of C_α and C_β acetylene carbons indicates electronic polarization [(2EPy) C_α = 83.51 ppm, weak; (H−)C_β = 78.5 ppm, strong; (HMTf) C_α = 74.0 ppm, weak; (H−)C_β = 98.1 ppm, strong].

Polymer Formation. The polymerization process and the influence of initiator structure and substitution, of initiator concentration, and of solvent were studied at room temperature by conductivity measurements, FT-IR, UV–visible, and ^1H NMR spectroscopy.

Conductivity. Conductivity of HMTf solutions was decreasing after initiation by pyridine (Figure 3), as is expected when ionic mobility decreases due to the increasing molecular mass.

FT-IR Spectroscopy. FT-IR was the preferred method to monitor the disappearance of the −C≡C− bond. A characteristic intense band at 3600–3400 cm^{-1}

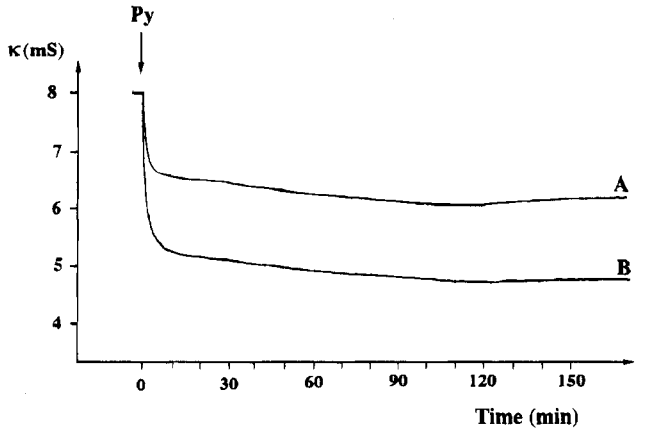


Figure 3. Change of specific conductivity (κ) during polymerization of HMTf. Initiator: pyridine. $[M]_0$ = 0.1 M; $[M]_0/[I]$ = 4.08 (A) and 2.0 (B). Solvent: acetonitrile.

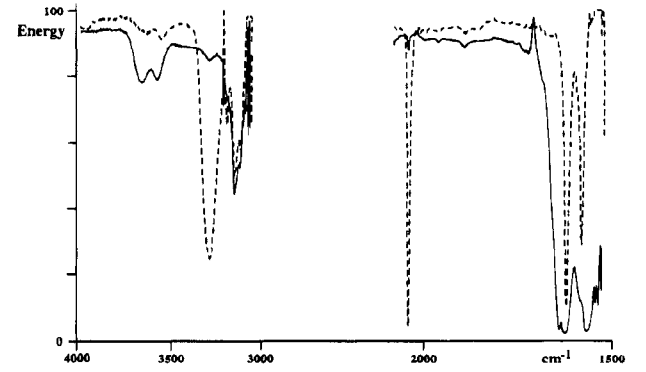


Figure 4. Comparison of FT-IR spectra of HMTf (dashed line) and poly(HMTf) (continuous line) in acetonitrile solution. Reaction mixture, t = 0 and 23 h. Initiator: 4-methylpyridine. $[M]_0$ = 0.1 M, $[M]_0/[I]$ = 4. Excessive absorption (blackout) ranges of solvent have been eliminated from the spectra.

appears in the IR spectra of these polymers in the solid state. Different explanations were proposed for the presence of this band.[5,21,22] In the solution spectrum of the polymer two resonance frequencies (3623 and 3537 cm^{-1}) can be observed (Figure 4). Similar, splitted absorption peaks are present at 3563 and 3496 cm^{-1} in the IR spectra of the protonated primary zwitterion (1-pyridiniumyl-2-(*N*-methylpyridiniumyl)ethylenetriflate methoxide) which displays a cis and a trans form.[9] Nevertheless, there is no significant difference between the absorption of aromatic C–H resonances in the solution of the monomer and of the polymer. We believe that these absorption bands belong to hydrogen on the alkene backbone ($\nu_{(C=C)-H}$) and the splitting represents the symmetric and asymmetric =C–H valence bond stretching.

UV–Visible Spectroscopy. The UV–visible absorption peaks increased in intensity with a similar rate at every wavelength during polymerization, suggesting a fast propagation accompanied by an effective termination process (Figure 5). Visible absorption trailing up to 800 nm confirms that these polyenes possess possibly a high degree of conjugation. This observation also suggests a trans–transoid or a cis–transoid configuration for the backbone, because low-wavelength absorption maxima are expected of the cis–cisoid isomers.[23] The formed polymers are dark brown or black solids. Their color indicates that there is no dominating chromophore present and the product contains a broad distribution of different chromophores.

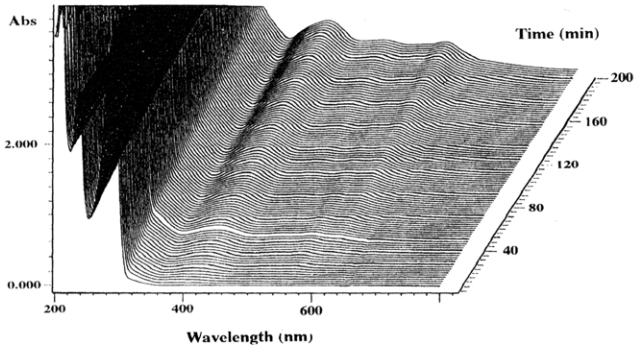


Figure 5. Evolution of the UV–visible spectra of the HMTf + pyridine reaction system at room temperature. Quartz cuvette: l = 1.0 mm. $[M]_0$ = 0.004 M, $[M]_0/[I]$ = 1. Solvent: CH_3CN.

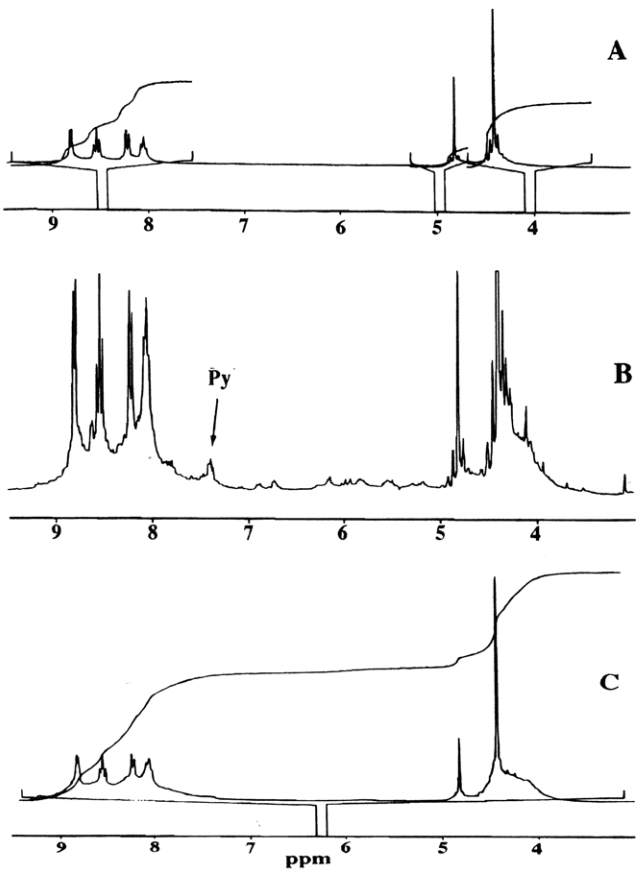


Figure 6. ^1H NMR spectra of the poly(HMTf) formation reaction in CD_3CN. Initiator: pyridine. $[M]_0$ = 0.2 M. Reaction time: (A) t = 0 min; (B) t = 4 min (enlarged by a factor of 8); (C) t = 1 day. Peak assignment: 8–9 ppm; pyridinium protons; 4.74, ≡C–H; 4.34, $=N^+-CH_3$.

Cycling of pH of the polymer solution by means of acid–base addition produced reversible changes in the UV–visible spectra.[9] These changes were attributed to the subsequent protonation and deprotonation of the anionic chain end. Pyridine was also able to perform this deprotonation; consequently, the anionic site should be less nucleophilic than the pyridine.

NMR Spectroscopy. Polymerization of the monomer in deuterioacetonitrile and DMSO-d_6 solution was monitored also by ^1H NMR (Figure 6). The position of the acetylene proton signal in HMTf spectra depends on the ability of the solvent to form H bonds (CD_3CN 4.74 ppm, CD_3OD 5.26 ppm, deuterioacetone 5.32 ppm, DMSO 5.77 ppm). After initiation distinct signals developed in the 5 and 7 ppm range with low but

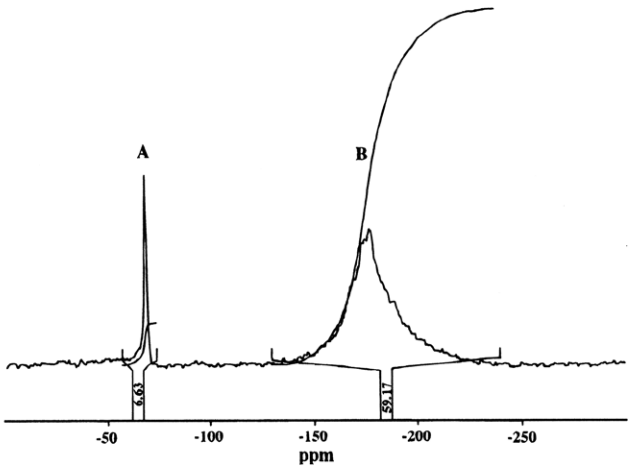


Figure 7. ^{14}N NMR spectra of poly(HMTf) in deuterioacetone: (A) uncharged nitrogenes; (B) charged nitrogenes. Initiator: pyridine. $[M]_0$ = 0.1 M, $[M]_0/[I]$ = 4.

constant intensity, indicating different intermediates in low concentrations (Figure 6B). A gradual decrease of the initiator concentration was observed at 7.4 ppm (pyridine $C_{2,5}$–**H** proton). This signal was still present in the spectrum of the polymerization reaction mixture after 1 day, although in low intensity. The $>N^+-$**CH_3** resonance in the polymer appeared at lower ppm values than in HMTf, and they partially overlapped with the monomer signals. The pyridinium aromatic resonances became broader and overlapped with the backbone =CH– signals. This effect may represent a broad charge distribution, which can be the consequence of molecular association at the concentration of 0.2 M.

The ^{13}C NMR spectrum of the polymer contains only the characteristic resonance of aromatic, $(>N^+)-CH_3$, and $-CF_3$ carbons. Because the conjugated backbone is very similar to an aromatic compound, this is also further evidence of the proposed linear structure.

A broad distribution of the $>N^+-$signal was observed in the ^{14}N NMR spectra of the products. However, a low-intensity signal of uncharged nitrogen can also be found in every ^{14}N NMR spectrum of the product polymers (Figure 7). This weak peak at −69 ppm could be the result of the presence of cyclic byproducts, might be caused by initiator contamination, or may be the consequence of a possible partial demethylation of the *N*-methylpyridinium rings.

It is known that activated acetylenes are able to give cyclic and/or linear products.[24,25] For example, dimethylacetylene dicarboxylate led to cyclic products upon reaction with pyridine,[13] but dicyanoacetylene gave linear chains when reacted with nucleophiles.[26,27] Quinolizidine-type cyclic products form by "back-biting", i.e., by the attack of the dimer anion on the loosened meta-position of the pyridine. Intramolecular cyclization leads to an uncharged nitrogen in the formed heteroaromatic condensed rings. The spectra of the above polymers were characterized by a dominant signal of a charged nitrogen; therefore polymerization of 2-ethynylpyridinium methyl triflate results dominantly in linear structures.

We believe that the presence of an uncharged nitrogen in the purified samples of the polymer cannot be explained by cyclic side products or initiator contamination. Both the initiator and the cyclic byproducts were soluble in ether–ethanol or ether–acetonitrile 4:1 solvent mixtures and were removed during purification. Partial demethylation of pyridinium nitrogen offers an

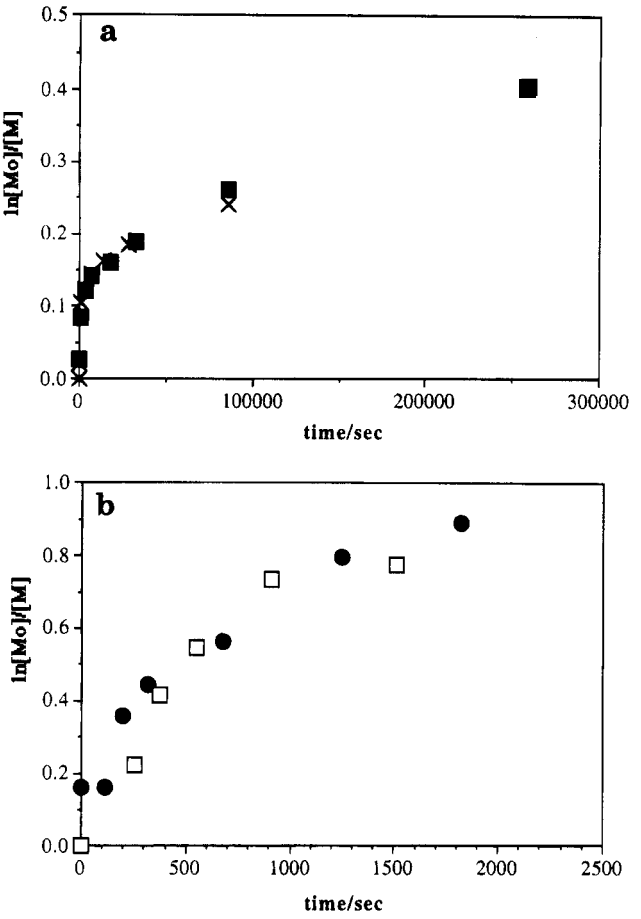


Figure 8. Comparison of ln $[M]_0/M$ versus time functions in HMTf polymerizations. (a) In acetonitrile (×) and DMF (■); Initiator: pyridine. $[M]_0 = 0.2$ M, $[M]_0/[I] = 4.08$. Method: solution FT-IR. (b) In deuterioacetonitrile (●) and DMSO-d_6 (□). Initiator: pyridine. $[M]_0 = 0.20$, $[M]_0/[I] = 4.0$. Monitoring method: ^{1}H NMR. Integration of acetylene proton signals was transformed into conversion data as a function of time.

alternative explanation, but demethylation attempts, including one with 5 M NaOH solution in water at 60 °C for 2 days, were unsuccessful. Consequently, demethylation of the pyridinium rings at room temperature by pyridine is highly unlikely.

We think that formation of a radical ion may also be considered as another possible reason for the loss of charge. A more detailed study of this phenomenon is in progress.

Influence of Solvent. Polymerization experiments in different solvents indicated that the reaction rate is not sensitive to the polarity of the solvent. Under the same experimental conditions in acetonitrile and DMF (Figure 8a), or deuterioacetonitrile and DMSO-d_6 (Figure 8b), the reaction rates were similar.

According to conductivity and permittivity studies performed on solutions of inorganic electrolytes[28] and tetraalkylpyridinium salts,[29] the average permittivity of salt solutions in organic solvents is determined by both the dipole momemt of the pure solvent[30] and the ion-pair concentration in the solution. We have shown that the degree of dissociation of HMTf is similar in different polar solvents;[9] it follows that the ion-pair concentration is approximately similar. As our experiments were carried out in a narrow monomer concentration range, this may explain the insensitivity of the polymerization rate to the solvent polarity.

Influence of Initiator. The effect of initiator substitution on the reaction rate was systematically investigated in acetonitrile with different initiators.

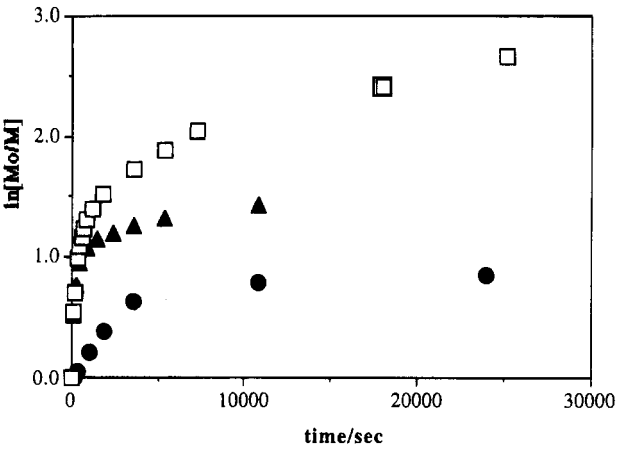


Figure 9. Comparison of ln $[M]_0/M$ versus time functions during polymerization. Initiators: 4-methylpyridine (□), 4-vinylpyridine (▲), and 4-ethynylpyridine (●). Solvent: CH_3CN, $[M]_0 = 0.1$ M, $[M]_0/[I] = 2.5$. Monitoring method: solution FT-IR.

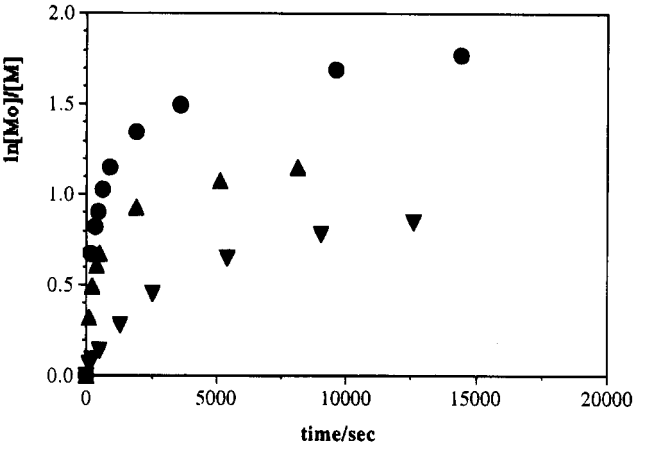


Figure 10. Comparison of ln $[M]_0/M$ versus time functions during polymerization. Initiators: 1,2-bis(4-pyridyl)ethane (●), 1,2-bis(4-pyridyl)ethylene (▲), and 1,2-bis(4-pyridyl)acetylene (▼). Solvent: CH_3CN. $[M]_0/[I] = 5$ (2.5 per pyridine nitrogen). Monitoring method: FT-IR.

In the case of *para*-substituted pyridines the reaction rate decreased in the order alkyl > alkenyl > alkynyl derivatives (Figure 9). The same order was observed with bis(pyridyl) compounds linked by ethane, ethylene, and acetylene units (Figure 10). There was no significant difference between the mono- and bis-substituted nucleophiles (Figure 11) when the concentration of pyridyl groups was identical. Therefore, it appears from our results, that in the case of *para*-substituted pyridines the nucleophilicity and the concentration of the quaternizable heteroatom determine the rate of polymerization.

Ortho-substituted pyridines are less reactive in nucleophilic substitutions than the meta and para derivatives because of their steric hindrance.[31] Comparison of reaction rates with the unsubstituted pyridine and 2-ethyl- and 2-ethynylpyridine initiators shows almost identical rates for the similarly hindered ethyl and ethynyl substituents (Figure 12). This corroborates the importance of steric hindrance in the initiation process.

Ethynylpyridines (EPy) and vinylpyridines (VPy) represent a special class of initiators within this group of nucleophiles. Quaternization of the nitrogen in Epy or Vpy activates its acetylene or vinyl bond. As a

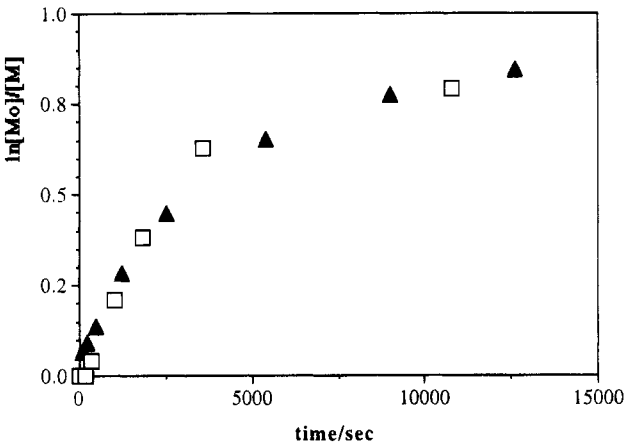


Figure 11. Comparison of the polymerization of HMTF with 4-ethynylpyridine (□) and 1,2-bis(4-pyridyl)acetylene (▲) initiators. $[M]_0$ = 0.1 M, $[M]_0/[I]$ = 2.5 per functional group. Solvent: acetonitrile. Monitoring method: FT-IR.

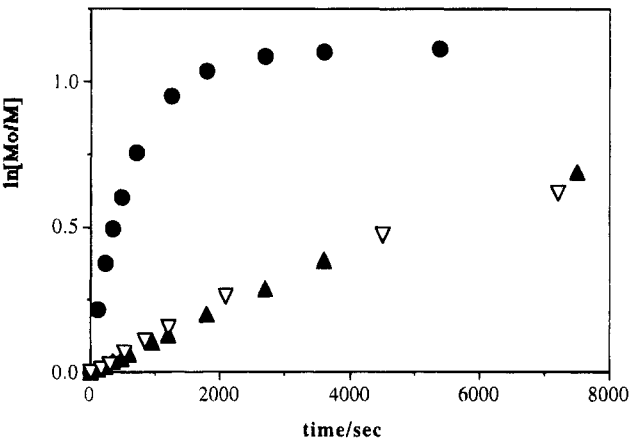


Figure 12. Influence of steric hindrance at the quaternization site of the initiator on the polymerization rate. Solvent: CH_3CN. $[M]_0$ = 0.10 M, $[M]_0/[I]$ = 2.5. Initiators: pyridine (●), 2-ethylpyridine (▲), and 2-ethynylpyridine (▽). Monitoring method: solution FT-IR.

consequence, the growing chain behaves as a macromonomer and can react at both its ends with the monomer in the polymerization process. This is reflected in the UV–visible spectra of these systems, which are characterized by a slow but continuous change, indicating a slow increase of the conjugation length. When 2EPy or 4EPy was used as initiator, the triple bond of the initiator was also consumed in the polymerization reaction together with the monomer. This difunctional character of EPy and VPy should result in the formation of branched structures.

Polymerization Mechanism. General Polymerization Scheme. Polymerization of *N*-methyl-2-ethynylpyridinium triflate with pyridine and its derivatives in all studied aprotic polar solvents resulted in incomplete (0.2–0.6) monomer conversions. This feature of the activated acetylene polymerization is known from the literature.[24,26] Figure 13 illustrates the general characteristics of this process: after a rapid reaction the disappearance of the triple bonds continues only slowly. The shape of curves suggests a complex reaction mechanism. Conversion is strongly affected by the $[M]_0/[I]$ (monomer/initiator) ratio. A general scheme should explain the slow and the fast polymerization stages as well as the incomplete conversion in aprotic polar solvents and the fast polymerization with a 100% monomer conversion in pyridine.

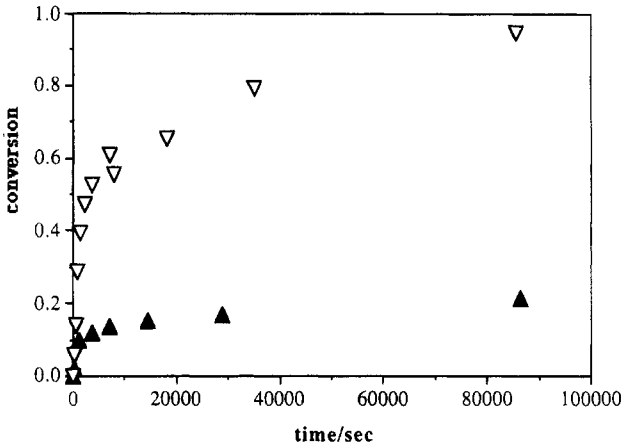
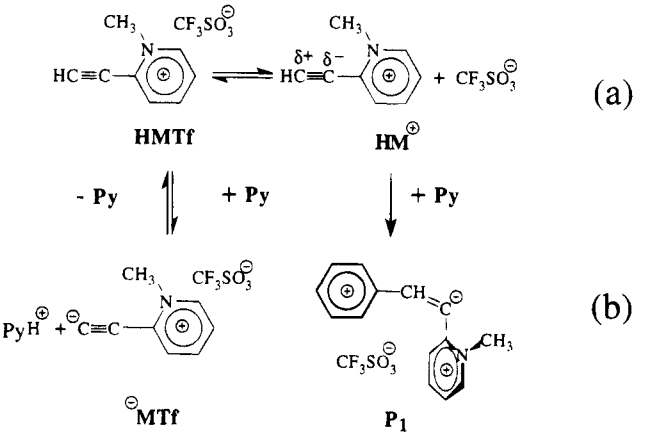


Figure 13. Conversion of HMTf to polymer in acetonitrile as a function of time. Initiator: pyridine. $[M]_0$ = 0.1 M, $[M]_0/[I]$ = 2.06 (△) and 4.11 (▲). Method: solution FT-IR.

Scheme 1. Dissociation States of the Monomer in the Absence (a) and in the Presence (a and b) of Nucleophilic Initiator

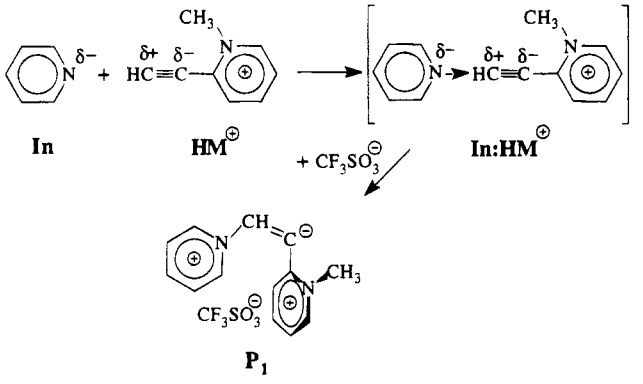


To construct a reasonable reaction mechanism consistent with the experimental facts, we have to consider the ionic dissociation of the monomer, the potentially acidic character of the monomer, and the nucleophilic character of the initiator.

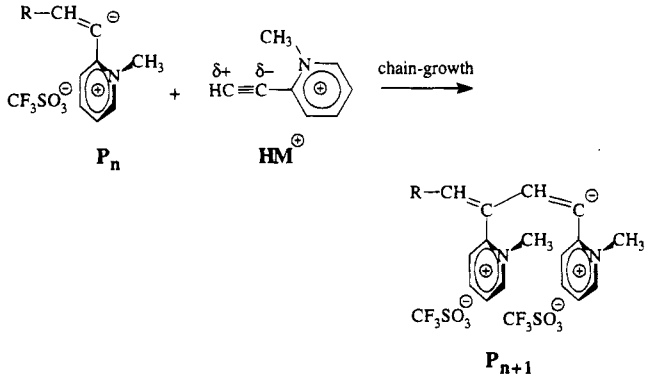
Due to the ionic salt character of the monomer in the initial solution the degree of dissociation in the equilibrium state is a function of solvent polarity, solute concentration, and temperature. Addition of a nucleophile into this solution perturbs the equilibrium and brings about a transient state (Scheme 1a). When a base is added to the solution of HMTf, initiation and salt formation take place simultaneously. Due to the weakly acidic character of HMTf, a nucleophile can react with the acetylene hydrogen, leading to an additional acid–base equilibrium between the protonated base and the acetylide anions. (Scheme 1b). The polymerization will be illustrated with the example of a pyridine initiator.

It is known that formation of primary zwitterions proceeds through a charge-transfer complex between the initiator and the monomer cation.[19] In our case, in the initiation reaction of pyridine (In) with the dissociated monomer (HM^+), the first step is the formation of a charge-transfer complex ($In{:}HM^+$) by an internal nucleophilic rearrangement. The result is the formation of a primary Michael zwitterion (P_1) from the initiator and the monomer (Scheme 2). This initiation competes with the acid–base reaction between pyridine and the undissociated monomer (HMTf). The latter reaction

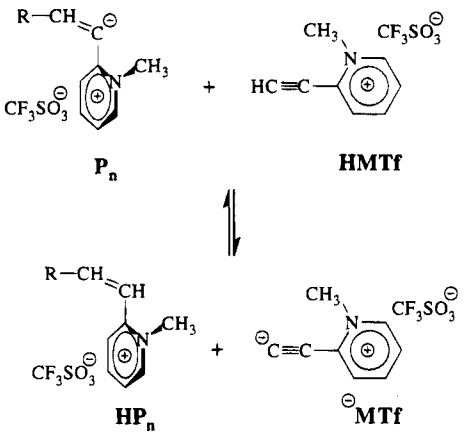
Scheme 2. Mechanism of Initiation: Formation of Charge-Transfer Complex and the Primary Michael Zwitterion



Scheme 3. Propagation Mechanism



Scheme 4. Termination by Monomer

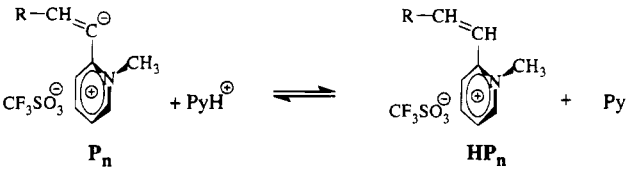


results in an equilibrium between protonated pyridine (InH^+) and acetylide anions (^-MTf).[9] The triple bond in the acetylide anion is not polymerizable by nucleophiles.

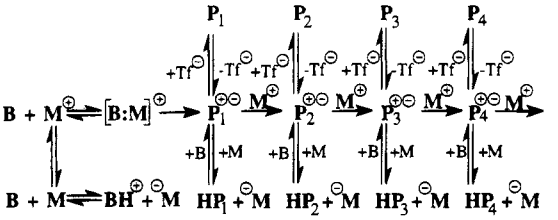
After initiation there are two different nucleophiles available in the polymerizing system: pyridine and the anionic centers. The concentration of pyridine is decreasing, while the concentration of growing centers is increasing. The carbanionic center, when it reacts with HM^+, provides the chain-growth step (Scheme 3). Reaction of the growing chain (P_n) with HMTf leads to a protic termination step (Scheme 4). This termination is reversible as long as the initiator is present in excess (Scheme 5), because pyridine is able to abstract the terminal proton from the protonated chain end and reactivate the propagation.[9,10]

However, incorporation of pyridine into the polymer gradually decreases the concentration of the stronger

Scheme 5. Reactivation of the Chain End by a Nucleophile



Scheme 6. General Reaction Scheme of Polymerization in Aprotic Solvent[a]



[a] Key: B, base; M, monomer; [B:M], initiator:base complex; BH^+, protonated base; M^+, monomer cation (net positive charge); ^-M, monomer anion (acetylyde anion); Tf^-, triflate counterion; P_n, polymer zwitterion molecule with DP = n (net zero charge); P^{+-}, cationic polymer zwitterion (net positive charge); HP_n, protonated polymer molecules (net zero charge).

nucleophile. Due to the decrease in the concentration of the available initiator, the reaction between the less nucleophilic growing center (P_n) and HM^+ becomes dominant, and the monomer consumption slows down. Finally, the polymerization proceeds slowly.

Presence of adventitious proton sources increases the conversion but decreases the chain length due to chain transfer.[9]

A general scheme may be formulated by taking into account the complexation, polymerization, and the acid-base equilibria in the reaction system (Scheme 6).

Polymerization When [Py] > [HMTf]. When the solid monomer was dissolved in pyridine, polymer was formed in a fast exothermic reaction, giving 100% conversion with no triple bond present in the final product.[10]

In order to explain the polymerization in pyridine, we have to assume that the $In:HM^+$ complex is also able to polymerize. This $In:HM^+$ complex has to be more reactive than HM^+ because of the double polarization effect of two electron-withdrawing substituents in the vicinity of the triple bond. Reaction of M^+ into $In:HM^+$ is nothing else than a base-catalyzed monomer activation. Both nucleophilic (the strong Py and the weak P_1) and both forms of monomer (the more active $In:HM^+$ and the less reactive HM^+) participate in the polymerization when pyridine is present in excess.

The propagation in this case may proceed by the reaction of the more reactive $In:HM^+$, and polymer formation occurs instead of dimers. Protic termination is impossible in pyridine due to the high excess of base, yet a decrease in the polymerization rate was observed in the reaction system, similar to other polar aprotic solvents. Quaternization of one pyridine moiety per polymer molecule means the formation of one extra positive charge in P_n, which has to be balanced in the pyridine solution by either association with an active anionic chain end or an internal radical-ion formation. Pyridinium compounds tend to form radical-ionic species, and according to ^1H NMR measurements, even the dimers of HMTf are strongly associated in solution.[10] Loss of this extra charge may also happen during purification, as these polymers can accept both cations

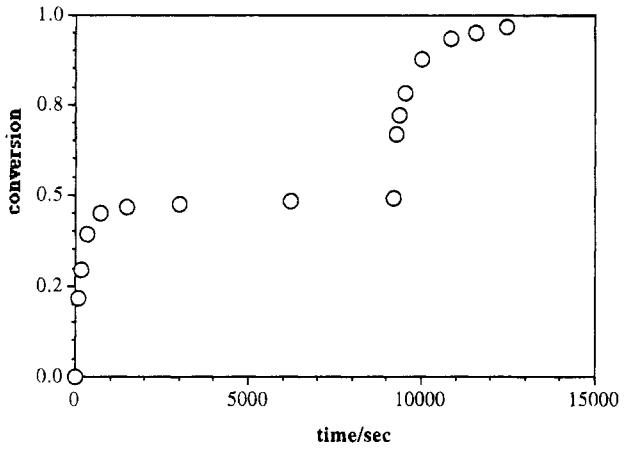


Figure 14. Polymerization of HMTf in acetonitrile initiated by pyridine in the presence of poly(vinylpyrrolidone). $[M]_0$ = 0.125 M, [PVP] = 0.127 M, $[M]_0/[I]$ = 3.46 and 1.73, respectively. Monitoring method: solution FT-IR.

and anions from solvents and they are eager to react with both acids and bases.

When the concentration of initiator and the concentration of the monomer are comparable, the propagation begins first between P_1 and In:HM^+ and gradually changes toward the reaction between P_1 and HM^+.

Polymerization When [Py] < [HMTf]. When the nucleophile is not in excess with respect to the monomer, the only available source of a free base in the system is the equilibrium described in Schemes 1 and 5. Consequently, termination by the monomer (Scheme 4) becomes more emphasized, and the rate of propagation decreases. A decrease in the concentration of the initiator also results in slower initiation. The protic termination remains reversible as long as unreacted initiator is available in the system, but at the coast of the reaction rate. Due to the equilibrium character of their complexation and dissociation processes, free pyridine and protonated pyridinium ions are both present in the system for a relatively long time. By the time all the pyridine is consumed, only a very slow growth and termination occur.

This is illustrated by the following experiment. An equimolar amount of poly(vinylpyrrolidone), which can give strong hydrogen bonds with PyH^+, was added to the solution of HMTf in acetonitrile. The polymerization was initiated by pyridine (Figure 14). Polymer was formed, but the polymerization stopped in a relatively short time at 50% conversion. The polymerization was reinitiated by adding further pyridine into the system. In this case, the added poly(vinylpyrrolidone) immobilized the protonated pyridine, and depletion of pyridine halted the polymerization process.

It appears that the weak acidic character of this monomer and its participation in the termination process are factors responsible for the difficulties in reaching high DP's by ionic polymerization of HMTf.

Summary

Kinetic and mechanistic investigations were carried out using *N*-methyl-2-ethynylpyridinium trifluoromethanesulfonate monomer, pyridine, and pyridine derivative initiators in different sovlents at room temperature. The highly ionic character of the monomer was demonstrated. The reaction rate increased with increasing nucleophilicity of monofunctional (para-substituted pyridines) and difunctional initiators (bis(pyridyl)ethane, ethylene, and acetylene). Initiator efficiency was affected by the nucleophilicity and the steric hindrance of the nitrogen atom. The polymerization proceeds according to a complex zwitterionic/anionic mechanism, which requires the presence of free nucleophilic initiator in the system. Chain growth occurs by the reaction of the propagating anionic center with the polarized ethynyl group of the dissociated monomer triflate causes termination, giving rise to acetylide anions that cannot polymerize.

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