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# Conjugated Ionic Polyacetylenes. 6. Polymerization of 2-Ethynylpyridinium Triflates[1–6]

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ABSTRACT: A new method for polymerization of the acetylenic bond in 2-ethynylpyridine and its trimethylsilyl derivative is described. The acetylenic triple bond is activated by quaternization of the pyridine nitrogen by methyl trifluoromethanesulfonate (triflate). The resulting *N*-methylethynylpyridinium triflate salts polymerize readily to the corresponding poly(*N*-methylethynylpyridinium triflates) when treated with a nucleophilic initiator such as pyridine or with a free-radical initiator (AIBN). The product polymers are substituted ionic polyacetylenes of low DP with extensive backbone conjugation. Spectral data indicate that the conjugation in these systems is extensive.

## Introduction

The introduction of substituents on backbone carbons of *trans*-polyacetylene offers advantages of improved processability and greater oxidative stability compared to the unsubstituted state. It results, however, in substantial lowering of electrical conductivity and of the third-order nonlinear optical susceptibility, $\chi_3$. This is mainly attributed to the loss of conjugation that arises from twisting of the polyene backbone due to unfavorable steric interactions between the substituents. It is hence highly desirable to synthesize substituted polyacetylenes that also possess highly conjugated backbones in view of their potential in optoelectronic applications.

We have reported the synthesis of a new class of mono- and disubstituted ionic polyacetylenes with extensive backbone conjugation.[1–6]. This remarkable structural characteristic is a unique feature that has hitherto not been reported in the literature. The conjugation in these systems despite presence of substituents is attributed to strong electrostatic interactions between the pyridinium ring substituents and the counter ions, which predominate over steric factors that are responsible for twisted backbones in uncharged systems.[7] The synthetic methods outlined by us previously involved a spontaneous polymerization process wherein the acetylenic triple bond in ethynylpyridine was activated via quaternization of the pyridine nitrogen by alkyl halides or methanesulfonates,[3,4] by formation of donor–acceptor complexes with bromine,[5] and by protonation in a strong acid.[6] These monomers (1–7) and some of their polymers have been described previously.[3,4] In all cases, the corresponding monomeric ethynylpyridinium salts are unstable intermediates that are difficult to isolate due to competition between N-alkylation and base-catalyzed polymerization. Such polymerizations lead to low molecular masses (~4000) for the product polymers.[4,6]

In order to effect higher molecular masses, it is desirable to separate the overlapping quaternization (activation) and polymerization processes. This can be accomplished by using a highly reactive quaternizing agent in high concentrations. Rapid formation of the quaternized monomer salt can thus be realized before it has an opportunity to be initiated by nucleophilic attack by unquaternized ethynylpyridine. Such monomeric ethynylpyridinium salts may be readily isolated, purified, and used in controlled polymerization experiments.

Recently, we have reported the isolation of *N*-alkyl-2-ethynylpyridinium salts in their trifluoromethanesulfonate (triflate) form as stable compounds at room temperature.[8] The synthesis and characterization of the corresponding *N*-alkyl-4-ethynylpyridinium triflate salt has also been reported.[9] These compounds polymerize upon melting, resulting in ionic polyacetylenes with conjugated backbones. The similarity of the ethynylpyridinium triflates to the corresponding vinyl analogs[10,11] in terms of their thermal behavior is remarkable, especially since polymerization of acetylenic monomers by thermal methods is normally not a facile process. But unlike their vinyl counterparts, which have also been found to polymerize readily in the presence of nucleophilic or free-radical initiators,[10,11] the susceptibility of ethynylpyridinium salts to these types of polymerization initiators has not been well studied.

The present study describes the polymerization of 1-methyl-2-ethynyl pyridinium triflate and its trimethylsilyl derivative upon treatment with either a nucleophilic initiator such as pyridine or a free-radical initiator (AIBN). The polymerization reaction is quite facile and results in substituted ionic polyacetylenes with extensively conjugated backbones. Their general structure is illustrated in Figure 1.

## Experimental Section

**Materials.** 2-Ethynylpyridine and 2-((trimethylsilyl)ethynyl)pyridine were obtained from Farchan Laboratories and distilled under vacuum before use. Methyl trifluoromethanesulfonate was obtained from Aldrich Chemical Company and was used without further purification. AIBN was purchased from Polysciences and recrystallized from aqueous ethanol before use. Anhydrous-grade solvents were obtained from Aldrich Chemical Co. and were dried before use.

**Measurements.** Melting points for monomer samples were determined from DSC and polarizing microscopy. Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform spectrophotometer using KBr plates. UV absorption spectra were obtained at 22 °C in the solvents indicated on an IBM 9420 UV/vis and on a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer. Thermal analyses were carried out under a nitrogen atmosphere on a DuPont TGA 2950 thermogravimetric analyzer. Dilute solution viscosity measurements were made in $CH_3CN$ at 25 °C using a Cannon Ubbelohde dilution-type viscometer. $\eta_{inh}$ in all cases were determined at a polymer concentration of 0.5 g/dL. DSC thermograms were recorded on a Perkin-Elmer 2C differential scanning calorimeter equipped with a cooling attachment. Elemental analyses were performed by the Microanalytical Laboratory at University of Massachusetts, Amherst, MA.

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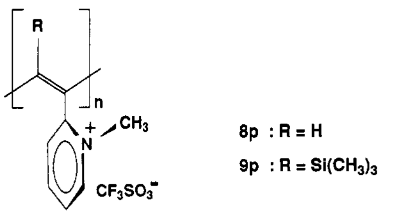


**Figure 1.** General structure of ionic polyacetylenes.

**N-Methyl-2-ethynylpyridinium triflate (8).** Methyl trifluoromethanesulfonate (0.96 g, 5.8 × $10^{-3}$ mol.) was dissolved in dry $CH_2Cl_2$ (10 mL). The solution was cooled to −3 °C, and 2-ethynylpyridine (0.5 g, 4.9 × $10^{-3}$ mol.) dissolved in $CH_2Cl_2$ (5 mL) was added dropwise while the temperature was maintained below 0 °C. The reaction mixture became turbid with the formation of a white precipitate. The reaction mixture was stirred for 10 min at 0 °C after the addition was complete. The solvent was then removed under reduced pressure at 25 °C to yield the crude product as a white solid. This was dried in vacuum and recrystallized from acetone–chloroform to give the title compound as white platelets (0.9 g) that are readily soluble in polar solvents: mp 155 °C (DSC); IR ($cm^{-1}$) 3251 (≡CH stretching), 2121 (C≡C stretching), 1260 (S=O unsymmetric stretch), 1030 (S=O symmetric stretch); UV ($CH_3CN$) $\lambda_{max}$ C=C (nm) 260. Anal. Calcd: C, 40.45; H, 3.00; N, 5.24; S, 11.98. Found: C, 40.29; H, 2.90; N, 5.15; S, 12.4.

**N-Methyl-2-((trimethylsilyl)ethynyl)pyridinium triflate (9)** was prepared in an identical manner using 1.3 g (6.84 × $10^{-3}$ mol.) of 2-((trimethylsilyl)ethynyl)pyridine and 1.0 g (5.7 × $10^{-3}$ mol) of methyl trifluoromethanesulfonate. The crude product was obtained as a white solid that was recrystallized from toluene (1.8 g). It was readily soluble in polar solvents: mp 81 °C (DSC); IR ($cm^{-1}$) 2119 (C≡C stretching), 1274 (S=O unsymmetric stretch), 1030 (S=O symmetric stretch); UV ($CH_3CN$) $\lambda_{max}$ C=C (nm) 256. Anal. Calcd: C, 42.48; H, 4.72; N, 4.13; S, 9.44. Found: C, 42.21; H, 4.72; N, 4.07; S, 9.48.

**Poly(N-methyl-2-ethynylpyridinium triflate) (8p).** Polymerization was carried out by three methods: (α) initation with 1–2 mol % of pyridine in $CH_3CN$ or in DMSO at 20 °C for 24 h, (β) initiation with 0.5 mol % of 2,2′-azobis(isobutyronitrile) (AIBN) at 70 °C for 15 h, and (γ) thermally by heating at 170 °C for 1 h in a sealed ampule under argon atmosphere. (Note: The monomer salt polymerizes when heated in air to its melting point.) The product polymers were purified by removal of solvent followed by extraction with ether. They were then dissolved in acetonitrile and reprecipitated in ether. All samples were dried in vacuum at 40 °C for 24 h. The polymer structures were confirmed by spectral methods and elemental composition.

8pα: IR ($cm^{-1}$) 1613 (backbone C=C stretch), 1260 (S=O unsymmetric stretch), 1030 (S=O symmetric stretch); UV $\lambda_{max}$ C=C (nm), 598; $\eta_{inh}$ (dL/g) 0.25. Anal. Calcd: C, 40.45; H, 3.00; N, 5.24. Found: C, 42.55; H, 3.90; N, 6.19.

8pβ: IR ($cm^{-1}$) 1620 (backbone C=C stretch), 1260 (S=O unsymmetric stretch), 1029 (S=O symmetric stretch); UV ($CH_3CN$) $\lambda_{max}$ C=C (nm), 384, 908 (710 in $H_2O$); $\eta_{inh}$ (DMSO) 0.05 dL/g. Anal. Calcd: C, 40.45; H, 3.00; N, 5.24; S, 11.98. Found: C, 39.04; H, 3.13; N, 5.12; S, 11.98.

8pγ: IR ($cm^{-1}$) 1622 (backbone C=C stretch), 1260 (S=O unsymmetric stretch), 1029 (S=O symmetric stretch); UV ($CH_3CN$) continuous band trailing to 900 nm; $\eta_{inh}$ ($CH_3CN$) 0.05 dL/g.

**Poly(N-methyl-2-((trimethylsilyl)ethynyl)pyridinium triflate) (9p)** was prepared in a similar manner using method α. The polymer was isolated as a black lustrous solid that was soluble in chloroform but insoluble in ether: IR (method α) $cm^{-1}$ 1620 (backbone C=C stretch); UV ($CH_3CN$) $\lambda_{max}$ C=C (nm), 574 (shoulder), 610; $\eta_{inh}$ ($CH_3CN$) 0.2 dL/g. Anal. Calcd: C, 42.48; H, 4.72; N, 4.13. Found: C, 43.53; H, 3.59; N, 6.63.

## Results and Discussion

**Thermal Properties.** Monomer triflate salts 8 and 9 are crystalline solids that are thermally stable at room temperature in the solid state and as solutions in nonnucleophilic solvents. The DSC thermogram of 8 shows two endotherms at 100 and 155 °C upon heating that arise from a crystal–crystal and a crystal–isotropic transition, respectively. This is immediately followed by a broad exotherm likely resulting from thermal polymerization in the melt (Figure 2). The crystal–crystal transition at 100 °C is completely reversible through successive heating and cooling scans below the crystal melting temperature. The TGA thermogram of monomer 8 shows no weight loss until 360 °C [Figure 2 (inset)], which precludes the possibility of loss of hydrated water that might contribute toward this endothermic transition. Furthermore, it is evident that the large exotherm is not due to a degradative decomposition of the monomer, since no weight loss is detected at this temperature. This is confirmed by the thermal behavior of polymers 8pα, β and γ, all of which show a major weight loss starting at 360 °C. The thermal stability of these poly(ethynylpyridinium triflates) is substantially higher than that of the corresponding iodides.[4] Their oxidative stability is similar to the iodides (TGA thermograms in air and in nitrogen are identical with respect to the degradation temperature for respective polymers). The thermal behavior of the ethynylpyridinium triflate monomers is similar to the corresponding N-alkyl-4-vinylpyridinium triflates which also undergo spontaneous polymerization upon melting to give poly(N-alkyl-4-vinylpyridinium triflates).[10,11]

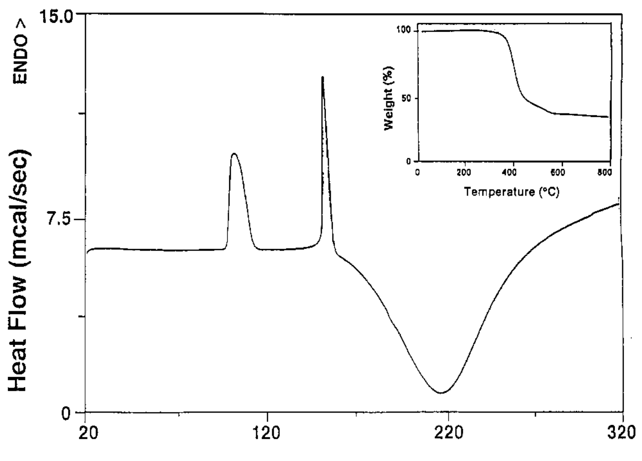


**Figure 2.** DSC and TGA (inset) thermograms of N-methyl-2-ethynylpyridinium triflate (8) in nitrogen; heating rates 20° and 10°/min, respectively.

Melt polymerization in an inert atmosphere of monomer 8 resulted in a black, polymeric product which is indicative of a conjugated polyene backbone. Its infrared spectrum shows a band at 1622 $cm^{-1}$ (C=C stretch), while the acetylenic bands of the starting monomer are absent. The UV/vis spectrum exhibits a continuous absorption band trailing to 900 nm in the near-infrared region. This is perhaps indicative of a wide distribution of conjugated polyene segments coupled with the ionic nature of side groups.

The thermal behavior of monomer salt 9 is markedly different from that of 8. Figure 3 shows that DSC thermogram for the monomer, which shows a possible crystal–crystal transition at 70 °C that is immediately followed by crystalline melting. The crystal–isotropic transition occurs at a much lower temperature (ca. 81 °C) and results in a stable isotropic melt. No thermal polymerization was observed until its decomposition temperature (150 °C) as is evidenced from the TGA thermogram of the monomer [Figure 3 (inset)]. The relatively lower crystalline melting temperature and the poor thermal reactivity for 9 can both be attributed to steric factors introduced by the bulky trimethylsilyl substituent, which is also responsible for its lower decomposition temperature. Table I lists the crystal–crystal transition, melting, and decomposition temperatures to-

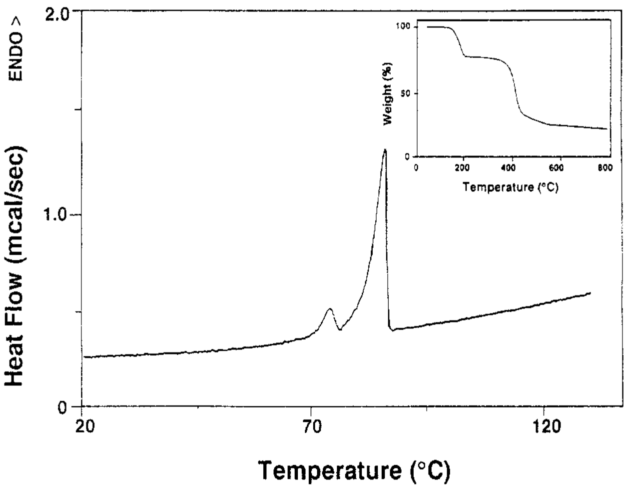


**Figure 3.** DSC and TGA (inset) thermograms of *N*-methyl-2-((trimethylsilyl)ethynyl)pyridinium triflate (9) in nitrogen; heating rates 2.5° and 10°/min, respectively.

**Table I. Transition Temperatures (°C) and Enthalpies of Transition (J/g) for 2-Ethynylpyridinium Triflate Salts**[a]

| monomer | $T_{K\text{-}K}$ | $\Delta H_{K\text{-}K}$ | $T_m$ | $\Delta H_m$ | $T_p$ | $\Delta H_p$ | $T_d$[b] |
|---|---|---|---|---|---|---|---|
| 8 | 100 | 49.9 | 157 | 33.2 | 170 | -570 | 360 |
| 9 | 70 | 5.8 | 81 | 57.8 | | | 150 |

[a] Transition temperatures and enthalpies measured by DSC. K–K = crystal–crystal; m = melting; p = polymerization; d = decomposition. [b] Decomposition temperatures from TGA.

gether with the corresponding enthalpies for monomers 8 and 9.

The thermal reactivity of the acetylenic triple bond in 8 is not surprising. It is well known that activation of the carbon–carbon triple bond by introduction of strongly electron-withdrawing groups on the acetylenic carbons enhances their reactivity. The increased reactivity of the acetylenic bond in the quaternized ethynylpyridines is attributed to the strongly electron-withdrawing nature of the pyridinium substituents, which effectively lowers the energy of the lowest unoccupied molecular orbital (LUMO) of the acetylenic moiety.[12] A Diels–Alder reaction involving ethynylpyridinium salts was first reported by Yamashita and co-workers,[12,13] who observed that 1,2-bis(2-pyridylethynyl)- and -(4-pyridylethynyl)pyridinium salts showed substantially enhanced dienophilic character and readily underwent cycloaddition with cyclopentadiene. The corresponding unquaternized bis(pyridylethynes), however, do not undergo cycloaddition even under drastic conditions. The reactivity of the acetylenic moiety is also greatly dependent on the position of the nitrogen atom in the pyridinium group with respect to the triple bond. The acetylenic bond in 1,2-bis(2-pyridyl)ethyne, for example, was found to be most reactive in Diels–Alder reactions, followed by the corresponding 4-pyridinium derivative. The 3-pyridinium salt, in contrast, showed poor reactivity even under severe conditions since the pyridinium nitrogen is not in conjugation with the acetylenic triple bond.[13] From the present study, it is evident that such activated triple bonds are also susceptible to a free-radical attack.

**Polymerization Initiated by Nucleophiles.** The monomer triflate salts 8 and 9 polymerize readily in polar solvents such as $CH_3CN$ and DMSO in the presence of a nucleophilic initiator such as pyridine. The product polymers **8p*α*** and **9p*α*** are black, lustrous solids that are hygroscopic and soluble in polar solvents and in water. Their infrared spectra indicate the absence of the absorption bands due to the acetylenic group that occur at 3251 and 2121 cm$^{-1}$ (≡CH and C≡C stretch) for 8 and 2119 cm$^{-1}$ (C≡C stretch) for 9. They are replaced by a strong bands at 1613 and 1620 cm$^{-1}$, respectively, which arise from the backbone C═C stretch. Figure 4 shows the IR spectra for monomer 8 and polymer **8p*α***. The UV/vis spectra for polymers **8p*α*** and **9p*α*** show strong absorption bands at 598 and 610 nm, respectively, compared to the corresponding monomer salts that do not absorb beyond 330 nm. This is indicative of their extensively conjugated structures. The similarity in the absorption maxima for **8p*α*** and **9p*α*** is surprising in view of the bulky trimethylsilyl (TMS) substituents in the latter. Modeling studies performed by us on such systems using dynamic mechanical simulation methods have shown that both the *trans-transoidal* and *cis-transoidal* conformations are energetically favored.[7] Both conformers give rise to a conjugated polyene backbone due to strong electrostatic interactions between the side group pyridinium rings and the counterions. This is supported by the fact that monomers 8 and 9 when polymerized by molecular bromine resulted in conjugated polyenes of which only the polymer derived from 8 displayed excimer fluorescence.[5] Stacking of pyridinium rings along the backbone is possible only in a *trans-transoidal* conformation. This suggests that a *trans-transoidal* conformation is probably favored in the former and *cis-transoidal* one in the latter, thus obviating the steric factors that are associated with the bulky TMS groups.

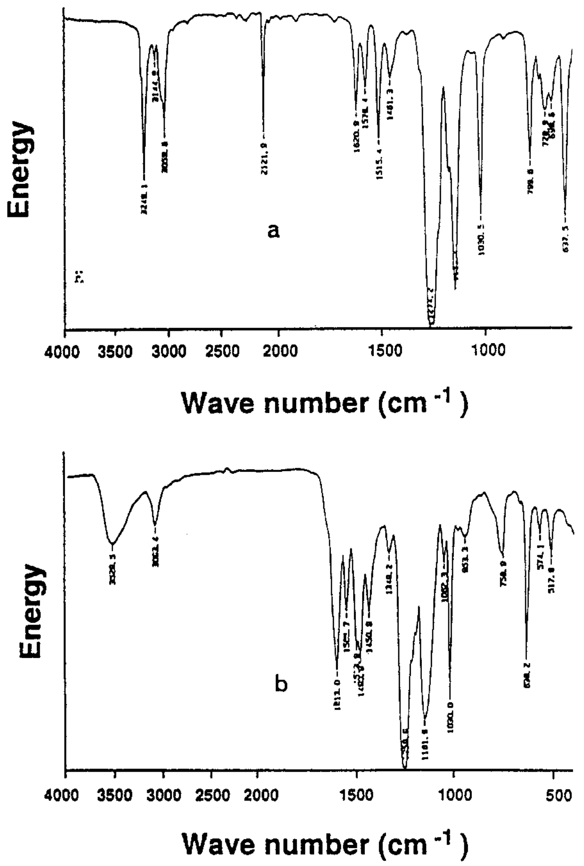
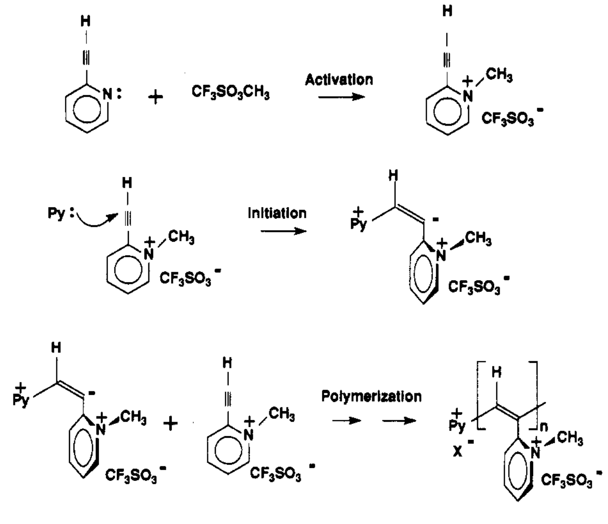


**Figure 4.** Infrared spectra of (a) monomer 8 and (b) polymer **8p*α***.

The present polymerization reactions presumably occur via a nucleophilic attack by pyridine on the acetylenic carbon of the monomer salt. It is proposed that the reaction proceeds via an initiation step that involves the formation of a macrozwitterion (Scheme I). The addition of tertiary amines such as pyridine to activated acetylenes is known to proceed vai a bimolecular nucleophilic addition that results in the formation of a zwitterion.[14] Although this intermediate ion has not been isolated for amine-initiated reactions, the vinyl anion that is formed has been

**Scheme I. Overall Reaction Pathway for Nucleophile-Initiated Polymerization**



Py = pyridine; X = from terminating species

isolated and trapped in the reaction of dimethyl acetylenedicarboxylate upon initiation with triphenylphosphine.[15] On the basis of orbital considerations, it has been suggested that an open, stereo stable "*anti*" anion is formed, resulting in the *anti* course of the 1,2 addition.[14] The nonspontaneous, nucleophile-initiated polymerization of these ethynylpyridinium triflate salts also tends to substantiate the activation and initiation steps proposed by us previously for the spontaneous polymerization of ethynylpyridines via a Menschutkin reaction.[4] An initiation step involving a nucleophilic attack on the acetylenic carbon of the activated, quaternized monomer by unquaternized species was envisaged for those reactions. The exact nature of the reaction mechanism, however, remains unclear at present. A detailed kinetic study is ongoing and will be the subject of a separate paper.

The molecular weights of the present polymers did not, however, increase substantially ($\eta_{inh}$ = 0.2–0.25 dL/g) in spite of eliminating the possibility of termination by excess quaternizing agent that posed a problem in the spontaneous polymerizations. This implies that an alternative rapid termination process is operative here. A possible explanation could lie in the macrozwitterionic nature of the propagating species proposed in Scheme I. Polymerization of vinyl monomers initiated by neutral nucleophilic initiators has been known to result in low degrees of polymerization ($D_p$).[14] This is generally attributed to two factors: (i) substantially reduced nucleophilicity of the zwitterionic species generated upon initiation and due to the proximity of opposite charges; the subsequent propagation step is, therefore, slow; and (ii) lack of stabilization for the carbanion in the growing polyene chain possibly resulting in a rapid termination. Stabilization of the carbanion in the growing polymer chain has been found to be an important factor that leads to increase in molecular weight for polymerizations via zwitterionic propagation.[14] In the case of highly stabilized carbanions, the polymerization acquires a living character at very low temperatures.[16-18] Our modeling studies reveal that the side group pyridinium rings are nearly orthogonal to the polyene backbone.[7] This suggests that the intermediate carbanion is not greatly stabilized by the pyridinium substituents thereby resulting in low molar masses. The possibility of termination by chain transfer to monomer is, therefore, an additional factor that could have an adverse effect on the $D_p$ in these reactions.

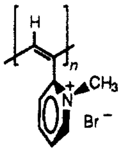
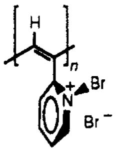
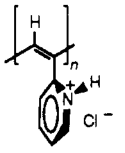
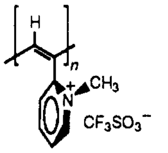
The formation of cyclic side products during polymerization of the monomer triflate salts 8 and 9 was also examined. In a recent paper, Fife et al.[9] reported that in the reaction of 1-methyl-4-ethynylpyridinium triflate in aqueous DMSO upon heating to 100 °C for 2 h cyclotrimerization of the monomer salt occurred to form 1,3,5-tris(1-methyl-4-pyridinio)benzene triflate in addition to a polymeric product. The corresponding N-protonated triflate, however, did not result in a cyclic compound.[9] Attempts to isolate such cyclic trimerization products by precipitation methods used in the above study were unsuccessful for monomer salts 8 and 9 polymerized under the reaction conditions outlined in the present study. We believe that the formation of cyclic products is highly unlikely in the present case due to the followng; (i) the steric factors involved with the alkyl substituent on the pyridinium nitrogen in the 2-position, especially in the case of monomer 9, wherein the formation of a cyclic trimer would be severely hindered by the bulky trimethylsilyl group; (ii) substantially lower reaction temperatures (reactions were run at 0 and 20 °C) in non aqueous solvents; both 2- and 4-ethynylpyridinium triflate salts are stable in solutions of water and DMSO at these temperatures; and (iii) low concentration of the nucleophilic initiator (1-2 mol %).

The conjugation lengths based on spectral data for the ionic polyacetylenes obtained by the presently described nonspontaneous method is greater compared to those obtained by methods involving spontaneous processes[4-6] and is, by far, the highest reported for substituted polyacetylenes. Table II lists the spectral data and the calculated conjugation number $n$ for ionic polyacetylenes synthesized by different methods. The strong absorption in the visible may be due to backbone conjugation coupled with the ionic side groups since no substantial shift is observed in the absorption maxima of poly(4-vinylpyridinium bromide) compared to the corresponding uncharged poly(4-vinylpyridine) (260 and 250 nm, respectively).[19]

We have previously determined that the conjugated number ($n$) obtained from the absorption maxima for such ionic polyenes (using the Lewis Calvin equation[20,21]) may be correlated to their degree of polymerization ($D_p$), assuming fully conjugated backbone. This was substantiated by comparing the calculated $D_p$ with the experimental one determined from $M_n$ measured by vapor pressure osmometry.[6] It was found that $n$ can be related to $D_p$ (within the experimental error of 20%) for up to $n = 16$.[6] On the basis of these results polymers **8p**$\alpha$ and **9p**$\alpha$ should have $D_p$ values of $\geq 16$. It must be emphasized, however, that the calculated values of $n$ are only an approximate, since the relation $\lambda^2 = kn$ becomes increasingly nonlinear and saturates at about 30 for conjugated polyenes.[22] On the basis of a band gap energy of 2.4 eV for fully *trans*-polyacetylene, the $\lambda_{max}$ (C=C) saturates at ~630 nm.[22] Hence, the C=C absorption maximum is no longer sensitive to the conjugation number of the polyene chain.

**Polymerization with Free-Radical Initiator.** Polymerization of monomer salt 8 with azobis(isobutyronitrile) (AIBN) in acetonitrile resulted in a black solid (**8p**$\beta$) whose infrared spectrum resembled those of the ionic polyacetylenes obtained by using a nucleophile initiator. The acetylenic ≡CH and C≡C bands of the monomer are replaced by a strong band at 1620 cm$^{-1}$ from the backbone C=C stretch. The molecular weight of the resulting polymer is very low ($\eta_{inh}$ = 0.05 dL/g), i.e., in the oligomeric range. This is also supported by the C=C absorption band at 384 nm which is in contrast to the corresponding polymer obtained by nucleophilic initiation that occurs at 598 nm. The UV/vis/NIR spectrum of **8p**$\beta$, however, shows a long-wavelength absorption band at 908 nm that

**Table II. Absorption Maxima and Conjugation Lengths (*n*) of Ionic Polyacetylenes Obtained by Nucleophilic Initiation**

| method | structure | $\lambda_{max}$ (C=C)$^a$ (nm) | $n^b$ (calcd) | $(\eta)_{inh}{}^c$ (dL/g) | ref |
|---|---|---|---|---|---|
| Menschutkin reaction |  | 370–480 | 8–12 | 0.1–0.2 | 3, 4 |
| halogen complex |  | 450 | 11 | 0.1 | 5 |
| protonation |  | 530 | 15 | 0.2 | 6 |
| triflate salts |  | 600 | >16 | 0.2–0.25 | this work |

[a] From UV/vis spectra. [b] From Lewis Calvin equation (ref 20). [c] At 28 °C, concentration = 0.5 g/dL.

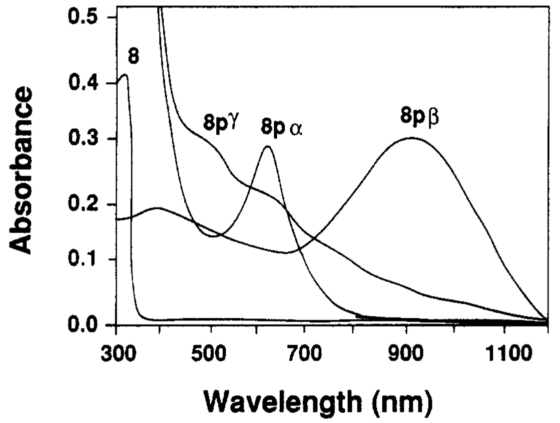


**Figure 5.** UV/vis/NIR spectra of monomer 8 and polymers 8p in $CH_3CN$ at 22 °C (concentration = $10^{-6}$ g/L).

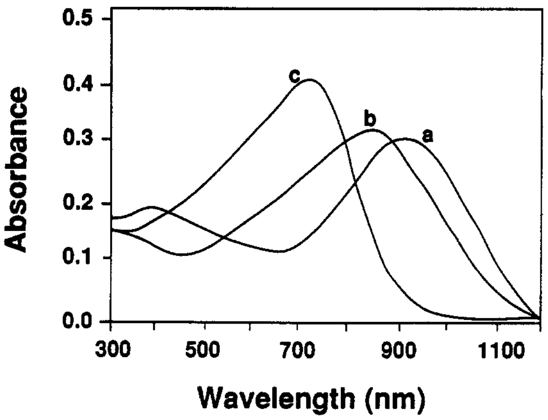


**Figure 6.** UV/vis/NIR spectra of polymer 8pβ: (a) instantaneous spectrum in $CH_3CN$; (b) after equilibration for 120 min in $CH_3CN$; (c) in $H_2O$ (all concentrations = $10^{-6}$ g/L).

was not displayed by corresponding polyenes obtained by other methods. Figure 5 shows the UV/vis/NIR spectra of monomer 8 and polymers 8pα, -β, and -γ.

The low value of $\eta_{inh}$ oligomer 8pβ is similar to those obtained by Gal et al.[23] in the attempted polymerization of 2- and 4-ethynylpyridine using transition metal catalysts. This is in contrast to the polymerization of phenylacetylene by coordination catalysts which yield high molecular weight polyacetylenes.[24] An unfavorable chain-transfer termination process that competes effectively with propagation might possibly account for the low molar masses for ethynylpyridine and its derivatives.

Unlike 8, monomer 9 did not undergo a polymerization reaction by free-radical initiation; the starting monomer was recovered after reaction with AIBN for 30 h. Introduction of a trimethylsilyl group on the acetylenic carbon in *N*-methyl-2-ethynylpyridinium triflate drastically affects the susceptibility of the acetylenic bond to free radically initiated polymerization. This is also evidenced by the reluctance of 9 to undergo thermal polymerization upon melting. This is not surprising, since it is well-known that free-radical initiation of monomers containing 1,2-disubstituted multiple bonds is difficult.

The UV/vis/NIR spectra of 8pβ show some remarkable solvent-dependent properties that were not observed for the corresponding polyacetylenes obtained by other methods. The spectrum recorded immediately upon dissolution in acetonitrile showed an absorption band at 908 nm trailing to 1050 nm (near IR) and another at 384 nm. The longer wavelength band underwent a hypsochromic shift with time, reaching an equilibrium value at 854 nm. When the polymer was dissolved in water, a large hypsochromic shift of this band to 710nm occurs, together with a decrease in intensity of the shorter wavelength absorption. The color of the polymer solution changes from red-brown in acetonitrile to blue in water. Figure 6 shows the UV/vis/NIR spectra of the polymer in the two solvents. Addition of water to an acetonitrile solution also produces the hypsochromic shift. The progressive shift in the absorption maximum of the long wavelength band as a function of time in an acetonitrile–water solution of fixed composition is shown in Figure 7. The spectra pass through an isosbestic point at 765 nm, which suggests that the conformational change giving rise to this solvatochromic shift is an equilibrium process. This is also supported by the fact that complete evaporation of solvent from an aqueous solution of the polymer followed by its redissolution in acetonitrile produces a bathochromic shift of the long wavelength band in the absorption spectrum, which resembles the one originally recorded in this solvent.

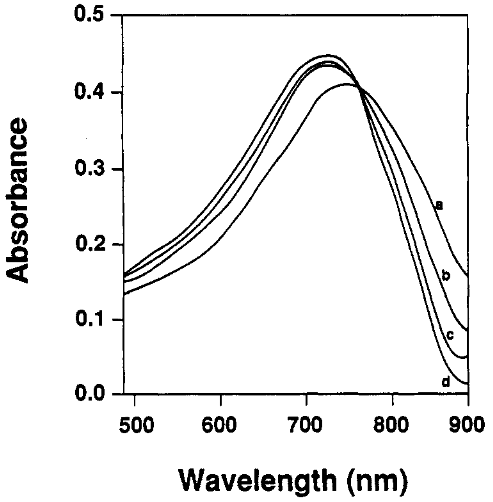


**Figure 7.** Shift in absorption maximum of polymer **8p**$\beta$ in $CH_3CN$ after addition of 95% water at 22 °C with time of (a) 45 min, (b) 90 min, (c) 120 min, (d) 150 min (all concentrations = $10^{-6}$ g/L).

Such solvatochromic behavior, which is more commonly observed for soluble polydiacetylenes and is attributed to backbone conformational changes in solution,[25,26] is unusual for polyacetylenes due to their rigid backbones. The present example provides, what we believe, to be the first known example of solvatochromism in polyacetylenes. Additionally, both the wavelengths of the absorption maxima and the magnitude of the shift is substantially larger than those reported for polydiacetylenes.

The factors responsible for the solvatochromic effect in the present polyene are not completely understood in view of its rigid structural characteristics that does not allow for conformational changes in the backbone. A tentative explanation of this most interesting effect is that it may be due to the presence of structural defects in the polyene backbone that are introduced by free-radical polymerization such as a more frequent "tail to tail" sequencing than in the corresponding polyene prepared by nucleophile initiation. Such defects would increase the distance between adjacent pyridinium rings, which would now require a near coplanar arrangement of the rings with respect to the backbone for efficient interaction with the triflate counterions. This is in contrast to the regular "head to tail" arrangement wherein the rings are close to orthogonal for such an interaction. Such a coplanar conformation would result in a substantial reduction in the band gap energy that, in turn, would cause the absorption band in the electronic spectrum to shift to the near infrared region. Modeling studies by Orchard and Tripathy[27] on the effect of substituent conformation on the electronic properties of substituted polydiacetylenes using dynamic mechanical simulations is in support of this view. Their study showed that a coplanar conformation of an electron-withdrawing substituent with the polyene backbone results in a substantial decrease in the band gap energy compared to a noncoplanar arrangement. This is reflected by a large red shift in the absorption spectrum for the coplanar arrangement with respect to the noncoplanar one. The instantaneous spectrum of polymer **8p**$\beta$ in acetonitrile may be approximated to that in the solid state wherein pyridinium rings at defect sites are in a coplanar arrangement, with adjacent rings interacting with the triflate counterions. Solvation of the pyridinium groups (and of the counterions) at defect sites would considerably reduce this interaction, thus allowing for rotation to a nonplanar conformation. This would explain the progressive blue shift in the absorption spectrum with increasing solvation. The high degree of solvation in water compared to acetonitrile could account for the larger hypsochromic effect in an aqueous solution. This aspect is being currently investigated in detail and will be the subject of a separate paper.

## Summary

The preparation of activated ethynylpyridinium monomers enables the separation of the quaternization (activation) step from their polymerization. The activated monomers can be polymerized in a controlled manner with appropriate initiators. The presently described nonspontaneous method for polymerization of activated acetylenic monomers provides a relatively simple route for the synthesis of substituted ionic polyacetylenes with backbone conjugation lengths that are relatively higher than those obtained by spontaneous processes. These activated monomers also allow polymerization of the acetylenic triple bond via free-radical initiation; the process is most unusual, since the acetylenic bond is not very susceptible to free-radical initiation. The oligomer obtained by radical initiation displays a most interesting solvatochromic effect which is uncommon for polyacetylenes. This could be of considerable interest especially in terms of its possible high third-order nonlinear optical susceptibility ($\chi_3$).

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