

# Conjugated Ionic Polyacetylenes. 5. Spontaneous Polymerization of 2-Ethynylpyridine in a Strong Acid<sup>1-5</sup>

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**ABSTRACT:** The spontaneous polymerization of the acetylenic bond in 2-ethynylpyridine in concentrated hydrochloric acid resulted in a substituted, extensively conjugated ionic polyacetylene bearing protonated pyridinium side groups. The conjugation length for the polymer was much greater than those obtained by spontaneous processes via a Menshutkin reaction or by complexation with bromine. Base-catalyzed deprotonation of the polymer resulted in a substantial decrease in backbone conjugation. The physical and spectral data prior to and after deprotonation correlate well with calculated values and provide insight into the structural and conformational characteristics of the polymer.

## Introduction

In a series of recent papers, we have reported a new family of mono- and disubstituted ionic polyacetylenes that possess extensive backbone conjugation.<sup>1-5</sup> Such conjugated structures for disubstituted polyacetylenes were hitherto unreported. The polymerization reaction involved activation of the acetylenic triple bond in ethynylpyridine and its derivatives by quaternization via a Menshutkin reaction<sup>3,4</sup> or by formation of donor-acceptor complexes with bromine.<sup>5</sup> Figure 1 shows the activated monomers obtained in these reactions. Both methods were, however, limited by relatively low molecular masses (~4000) for the product polymers. The reaction mechanism in these spontaneous processes is an ionic one, since radical inhibitors do not affect the polymerization. The overall process is similar to that observed for the spontaneous polymerization of 4-vinylpyridine upon quaternization by alkyl halides.<sup>6,7</sup>

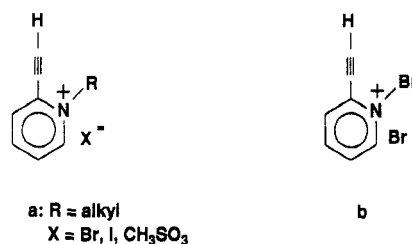
The low molar masses for these ionic polyacetylenes obtained via quaternization may be attributed to relatively slow activation of the triple bond (which results in a low concentration of the activated species) compared to rapid propagation and termination steps. Fife et al. have shown that the quaternization of 4-vinylpyridine by ethyl bromide or ethyl tosylate is a rather slow reaction with  $t_{1/2} = 1000$  min.<sup>8</sup> In view of this, an alternative method was sought for a more rapid activation of the monomer. Such methods involve use of a highly reactive quaternizing agent in high concentrations.

In this paper, we report the polymerization of 2-ethynylpyridine by a strong acid. The reaction of 2-ethynylpyridine in concentrated hydrochloric acid resulted in spontaneous polymerization of the acetylenic triple bond giving a highly conjugated, ionic polyacetylene. The proposed structure for the polymer is illustrated in Figure 2.

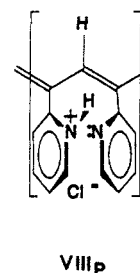
## Experimental Section

**Materials.** 2-Ethynylpyridine was obtained from Farchan Laboratories and distilled under vacuum before use. Concentrated hydrochloric acid was obtained from VWR Scientific Co. and used as received.

**Measurements.** Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform spectrometer using KBr plates. UV absorption spectra were obtained at 22 °C in DMSO and chloroform on an IBM 9420 visible-ultraviolet spectrophotometer. Thermal analyses were carried out on a Du Pont TGA 2950 thermogravimetric analyzer. X-ray diffraction patterns of unoriented samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Warrus flat-plate camera using Ni-filtered Cu K $\alpha$  radiation. Dilute-solution viscosity measure-



**Figure 1.** Activated 2-ethynylpyridine monomers obtained by (a) a Menshutkin reaction and (b) a complexation reaction with bromine.



**Figure 2.** Proposed structure for conjugated, ionic polyacetylene resulting from spontaneous polymerization of the acetylenic triple bond of 2-ethynylpyridine.

ments were made in DMSO and chloroform at 25 °C using a Cannon-Ubbelohde dilution type viscometer. Molecular weight determination by vapor pressure osmometry was made on a UIC Inc. 070 vapor pressure osmometer in chloroform at 30 °C. Calibration was done with low molecular weight polystyrene ( $M_n = 2000$ ) with an estimated error of  $\pm 5\%$ . Fluorescence spectra were obtained on a Perkin-Elmer MPF-44B fluorescence spectrophotometer equipped with a PE 150 xenon source in conjunction with a Stanford Research System Model SR440 DC 300-MHz amplifier and a SR400 two-channel gated photon counter. All spectra were recorded in DMSO at 22 °C. Excitation wavelengths of 360 and 265 nm respectively were used for the protonated and deprotonated form of polymer VIIIp. Elemental analyses were performed at Atlantic Microlabs, Atlanta, GA.

**Poly(2-pyridinium hydrochloride-2-pyridylacetylene) Copolymer VIIIp.** To neat 2-ethynylpyridine (2.06 g, 0.02 mol) stirred at 0 °C was added dropwise concentrated hydrochloric acid (0.71 g, 0.02 mol). An exothermic reaction ensued, and the reaction mixture acquired a dark color immediately accompanied by a rapid increase in viscosity. The polymer separated out as a black solid mass. It was washed repeatedly with ether and dried overnight in vacuum at 40 °C. The dry polymer was obtained as a lustrous black powder (2.0 g) that was readily soluble in water and DMSO but insoluble in chloroform.

IR (cm<sup>-1</sup>): 3414 (br, hydrogen-bonded ring =NH stretch), 1617 (backbone C=C stretch), 1605 (aromatic ring C=C stretch). UV:  $\lambda_{max}$  C=C (nm) 530.  $\eta_{inh}$ : DMSO (dL/g) 0.2. Anal. Calc: C, 70.88; H, 4.61; N, 11.81; Cl, 12.70. Found: C, 70.25; H, 4.82;

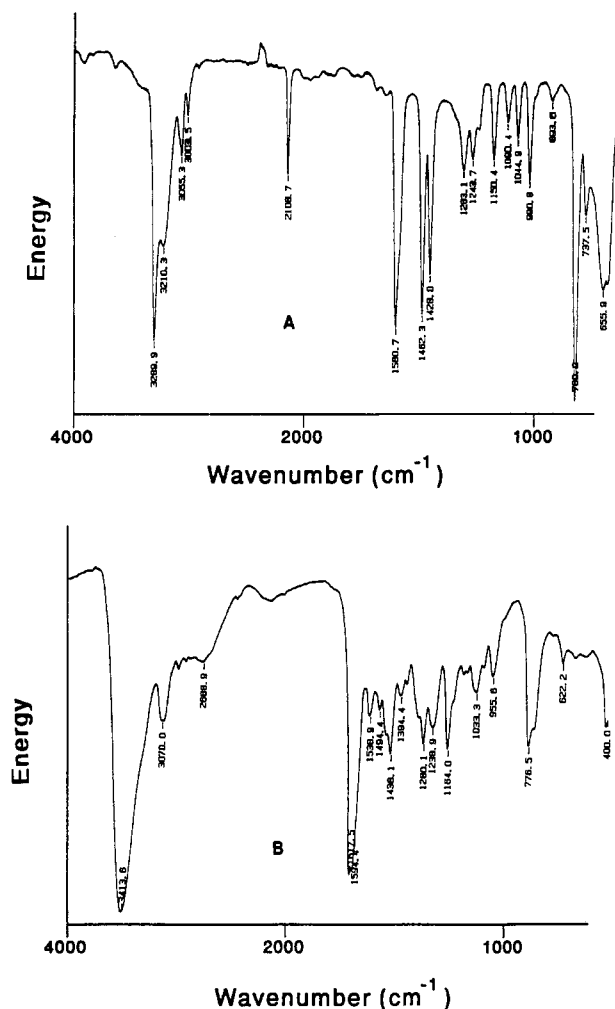


Figure 3. Infrared spectra of (A) 2-ethynylpyridine and (B) polymer VIIIp.

N, 11.80; Cl, 12.75.

**Deprotonation of Poly(2-pyridinium hydrochloride-2-pyridylacetylene) Copolymer.** The protonated polymer VI-Iip (1.0 g) was dissolved in 50 mL of deionized water, and to the stirred solution was added slowly 100 mL of 1 M KOH. Stirring was continued for 12 h, during which time the deprotonated polymer precipitated out as a dark solid. This was extracted with chloroform, and the combined organic layers were dried and the solvent evaporated under reduced pressure to yield a lustrous black solid. This was dried overnight in vacuum at 40 °C. The dry polymer (0.5 g) was soluble in chloroform and DMSO but insoluble in water.

IR (cm<sup>-1</sup>): 1634 (C=C), 1585 (aromatic C=C). UV:  $\lambda_{\text{max}}$  C=C (nm) 419.  $\eta_{\text{inh}}$ : DMSO (dL/g) 0.2. Anal. Calc: C, 79.27; H, 4.82; N, 13.20; Cl, 2.71. Found: C, 75.20; H, 4.67; N, 12.33; Cl, 3.01.

## Results and Discussion

The polymer obtained by the bulk polymerization of 2-ethynylpyridine in concentrated hydrochloric acid is a black lustrous solid indicative of the highly conjugated nature of the backbone (Figure 2). This is evident from its infrared spectrum, which reveals a strong absorption band at 1617 cm<sup>-1</sup> due to the C=C stretch from the backbone carbons. Furthermore, the =CH and C≡C stretching bands at 3290 and 2108 cm<sup>-1</sup>, respectively, that are present in the monomer are absent in the product polymer (Figure 3). The highly charged nature of the polymer is evidenced by the broad, intense band at 3400 cm<sup>-1</sup> that arises from the =NH stretch of the side-group pyridinium rings and is indicative of the strong hydrogen-bonding effect due to the charged nature of the side groups. This band is characteristic of all polymers reported by us

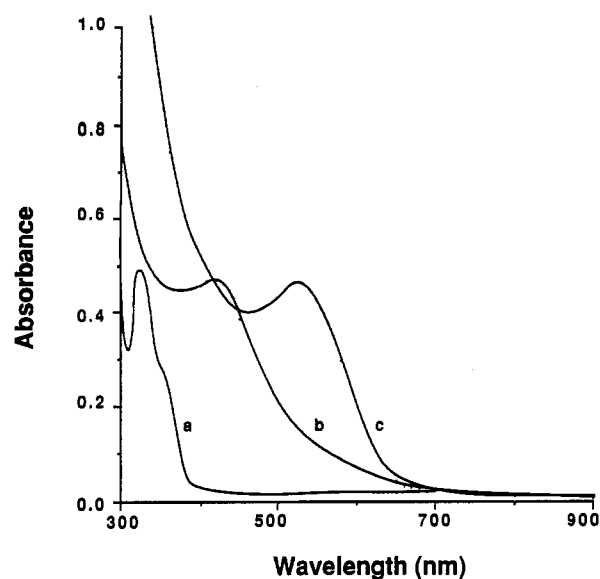


Figure 4. UV-visible spectra of (a) monomer and polymer VI-Iip in the (b) deprotonated and (c) protonated forms.

previously possessing similar structures, including disubstituted polyacetylenes.<sup>3-5</sup> The UV-visible spectrum of polymer VIIIp showed a strong absorption centered at 530 nm resulting from the  $\pi$ - $\pi^*$  transition of the conjugated polymer backbone. Figure 4 shows the UV-visible spectra of the monomer and polymer VIIIp. The polymer is soluble in DMSO and in water but not in chloroform, which is characteristic of its ionic nature.

The present polymerization can be compared to that of 4-vinylpyridine in concentrated acids reported by Salamone<sup>9</sup> and later by Ringsdorf.<sup>10,11</sup> The former study concluded that an ionic mechanism is unlikely in such strongly protic media and that the polymerization probably proceeds by a step-growth process. The latter study proposed a mechanism wherein the polymerization of the protonated vinylpyridine occurs in an ordered array of the pyridinium halide molecules. The polymerization of 2-ethynylpyridine also occurs in the protonated monomer which activates the acetylenic triple bond. Since the spontaneous polymerization occurs only in the presence of excess unquaternized monomer (no polymerization was observed when monomer was added to excess acid), we conclude that the initiation step occurs via the nucleophilic addition of unquaternized monomer to the triple bond of the quaternized activated species. This is also supported by the fact that the isolated monomer salt failed to undergo polymerization in concentrated HCl. The propagation step, therefore, appears to proceed in a manner analogous to that suggested by Ringsdorf et al., wherein immediate termination via protonation does not occur. The molecular mass of polymer VIIIp is, however, low ( $\eta_{\text{inh}}$  = 0.2 dL/g) suggesting that termination step(s) compete effectively with chain propagation.

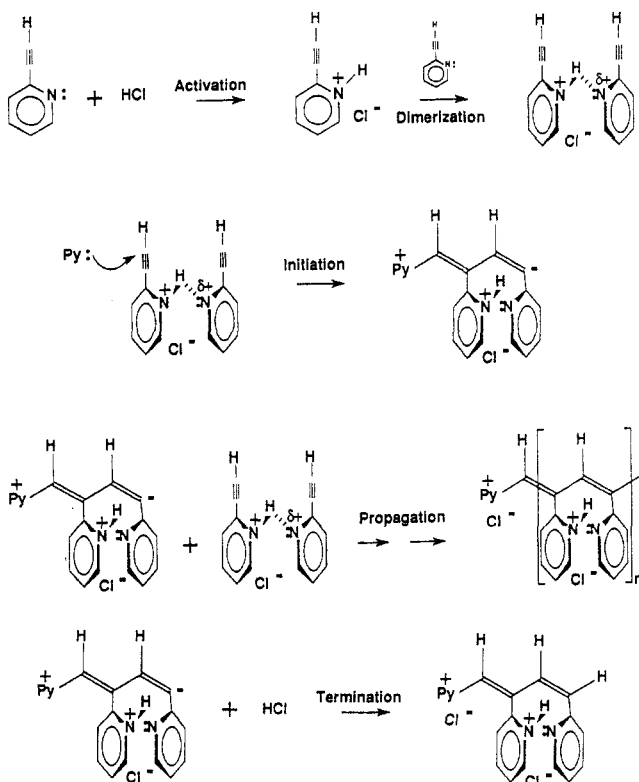
A unique characteristic that distinguishes the present polyacetylene from the ones obtained by us via the Menschutkin reaction or complexation with bromine is that, unlike the previously described systems wherein the charged side groups consist of either alkylpyridinium or bromopyridinium moieties, it has protonated pyridinium ring substituents. This allows for relatively easy deprotonation of the ionic polyene in basic media, giving rise to a largely neutral species. Such a transformation in the previously reported materials would involve drastic conditions and elevated temperatures at which polymer degradation becomes a serious problem.

**Table I**  
**Elemental Composition (%) of Poly(2-pyridinium**  
**hydrochloride-2-pyridylacetylene) Copolymer before and**  
**after Deprotonation by Base**

	mol formula		C	H	N	Cl
prior to deprotonation	$[C_{14}H_{11}ClN]_n$	calc	70.88	4.61	11.81	12.70
		found	70.25	4.82	11.80	12.75
treated with KOH	$[C_{14}H_5(0.1)-ClN]_n^a$	calc	79.27	4.82	13.20	2.71
		found	75.20	4.67	12.33	3.01

<sup>a</sup> Assuming 10% residual chloride ions.

**Scheme I**



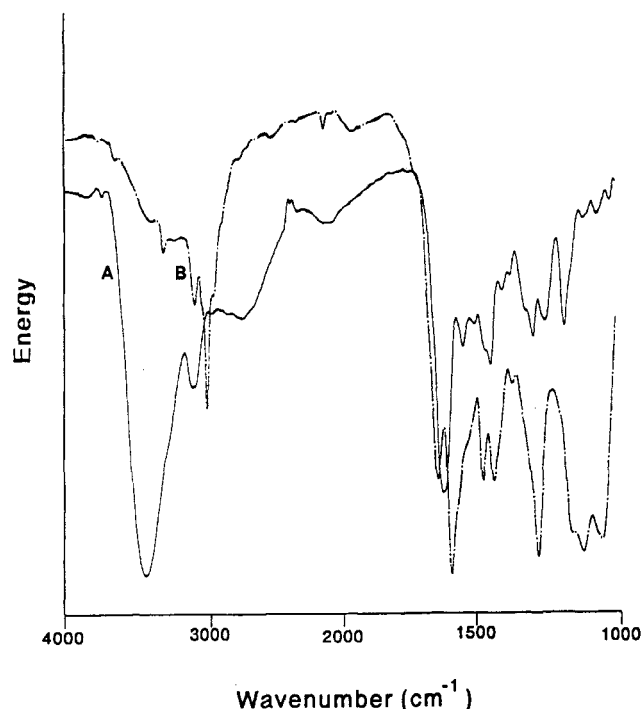
Py := unquaternized monomer

The analytical data of polymer VIIIp fit remarkably well with a structure wherein only 50% of pyridine rings in the polymer contain quaternary nitrogens (Table I). These results imply the incorporation of unquaternized monomeric units in the polymer chain even prior to deprotonation of the pyridinium ring side groups. A possible explanation for this could be the formation a dimeric complex between a protonated and an unprotonated monomeric species via intermolecular hydrogen bonding. This would then provide sufficient activation for the triple bond in the unquaternized molecule for it to undergo polymerization. Scheme I illustrates the proposed reaction mechanism for the polymerization. Such dimer formation has also been reported in partially protonated poly(2-vinylpyridine) between two adjacent pyridine side groups, one of which is protonated.<sup>12</sup> A charge-transfer complex polymerization mechanism is also possible via the formation of a weakly reactive charge-transfer complex biradical between the protonated and unprotonated ethynylpyridine molecules. The low molecular weight of the polymer and lack of temperature dependence of  $M$ , however, suggest that the latter mechanism is unlikely.

Treatment of VIIIp with aqueous potassium hydroxide solution gave a compound that possesses approximately 20% of the original charges (based on halide ion content). Table I lists the analytical data before and after deprotonation. Assuming that these residual charges are due

to charged end groups that cannot undergo neutralization, the DP of the polymer is approximately 12 ethynylpyridine units. Although the deprotonated polyacetylene retained its black color, remarkable changes were observed in its spectral properties. The UV-visible spectrum showed a large blue shift for the  $\pi-\pi^*$  transition of the conjugated polymer backbone compared to the protonated form. The absorption maximum shifted from 530 nm for the protonated form to 419 nm for the deprotonated one. Figure 4 shows the change in the absorption maxima of polymer VIIIp before and after treatment with base. The large hypsochromic shift observed in the present polymer on deprotonation results from reduced conjugation presumably from backbone twist introduced upon deprotonation and is not due to a change in the pyridinium chromophore. This is substantiated by the fact that the UV-visible spectra of protonated poly(2-vinylpyridine) and neutral poly(2-vinylpyridine) do not differ much, displaying absorption maxima at 260 and 250 nm, respectively.<sup>12</sup> The backbone twist may be attributed to the absence of electrostatic interactions between the counterions and the pyridinium rings that were present in the protonated form, thereby resulting in the steric interaction between the side groups becoming a dominating factor. This view is also supported by the fact that the  $\lambda_{\max}(C=C)$  for the backbone undergoes a bathochromic shift on reprotonation from 419 to 460 nm, trailing to  $\sim 800$  nm. The deprotonated polymer is no longer water soluble but is readily soluble in chloroform due to its considerably diminished ionic character.

The reduced backbone conjugation in the deprotonated form of VIIIp is also supported by its IR spectrum, which shows a corresponding high-frequency shift of the backbone  $C=C$  stretch from 1617 to 1634  $cm^{-1}$ . The aromatic ring  $C=C$  band shifted from 1605  $cm^{-1}$  for the protonated form to 1585  $cm^{-1}$  for the deprotonated one, which is identical to that observed for 2-vinylpyridine (1586  $cm^{-1}$ ).<sup>13</sup> The  $C=N$  stretch of the pyridine ring occurring at 1458  $cm^{-1}$  for the ionic form is shifted to 1467  $cm^{-1}$  upon deprotonation, again being similar to that of 2-vinylpyridine (1472  $cm^{-1}$ ).<sup>13</sup> The intense band at 3400  $cm^{-1}$  due to the hydrogen-bonded pyridinium ring  $=NH$  stretch in the protonated form disappeared almost completely on deprotonation. Figure 5 shows the IR spectra of polymer VIIIp in its protonated and deprotonated forms. The latter spectrum contains weak but distinct bands at 3292 and 2102  $cm^{-1}$  from the acetylenic  $\equiv CH$  and  $C\equiv C$  stretching in the monomer. From the mechanism depicted in Scheme I, the initiating chain end of polymer VIIIp is an ethynylpyridinium unit linked through the quaternary pyridinium nitrogen. The residual bands may, therefore, be attributed to the end groups in the polymer. This was confirmed by performing an end-group analysis based on the acetylenic  $\equiv CH$  stretching band. The relative intensity of this band at 3290  $cm^{-1}$  for the starting monomer was compared with that for polymer VIIIp after deprotonation. The intensities were normalized using the  $\beta$ -ring bending band of the pyridine ring. This band occurs at 738 and 749  $cm^{-1}$  for the monomer and polymer, respectively, and its intensity is unaffected by the nature of the substituent on the ring, i.e., alkynyl or alkenyl ( $\beta$ -ring bending for 2-vinylpyridine occurs at 745  $cm^{-1}$ ). Comparison of the infrared absorption ratio  $Abs_{\equiv CH}/Abs_{\beta\text{-ring}}$  for the monomer and deprotonated polymer (2.30 and 0.24, respectively) yields a value of 9.1% for the end-group content, which is in excellent agreement with the value calculated from analytical data (10%), (see Table I).

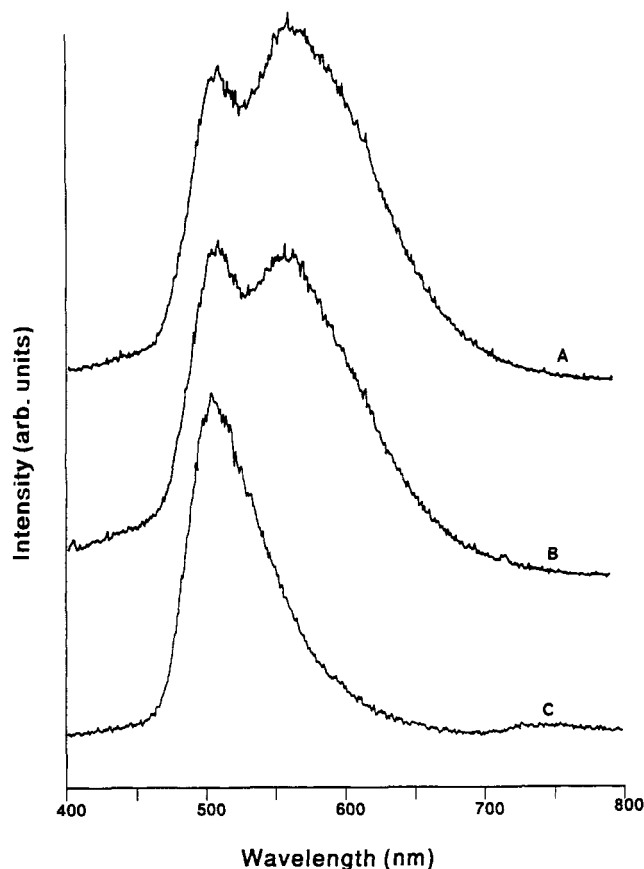


**Figure 5.** Infrared spectra of polymer VIIp in its (A) protonated and (B) deprotonated forms.

TGA analysis of polymer VIIp in a nitrogen atmosphere showed a small, gradual weight loss ( $\sim 9\%$ ) occurring at  $150^\circ\text{C}$ , followed by a rapid decomposition at  $230^\circ\text{C}$ . The deprotonated form showed an essentially similar behavior, suggesting that the ionic nature of the polymer prior to deprotonation does not contribute significantly to its thermal stability. The decomposition temperatures are similar to those for the ionic polyacetylenes obtained by us via the quaternization method ( $240^\circ\text{C}$ )<sup>3,4</sup> and considerably higher than the ones synthesized by the formation of donor-acceptor complexes with bromine.<sup>5</sup>

A characteristic feature exhibited by these ionic polyacetylenes is a broad low-energy band (560 nm) in their fluorescence emission spectra. The phenomenon is attributed to intramolecular excimer formation between the aromatic side-group chromophores. It appears to be independent of the polymerization method, since the band was observed for polyacetylenes obtained via both the quaternization and complexation methods.<sup>5</sup> It has also been reported for protonated poly(4-vinylpyridines)<sup>12</sup> and isotactic polystyrene.<sup>14,15</sup> In these ionic polyacetylenes, such excimer formation is indicative of a highly conjugated backbone with minimal twist, which is a prerequisite for efficient stacking of the pyridine rings. Such stacking seems to be largely due to a strong electrostatic interaction of each counterion with two adjacent pyridinium rings.

The fluorescence emission spectrum of polymer VIIp in DMSO, however, displayed two bands centered at 500 and 560 nm, whose intensities are similar. The intensity of the band at 500 nm was independent of polymer concentration, while that of the latter decreased slightly with increasing dilution (Figure 6a,b). This phenomenon is attributed to intramolecular excimer formation by the side-group chromophores. It is evident that two distinctly different chromophoric groups of approximately equal number (protonated pyridinium and neutral pyridine rings) are present in the polymer, substantiating the proposed structure (Figure 2) which is based on its analytical data. The band at 560 nm is assigned to the pyridinium chromophores, since it was also observed for the ionic polyacetylenes obtained by previous methods<sup>5</sup>



**Figure 6.** Fluorescence emission spectra of VIIp: (A)  $6.5 \times 10^{-3}$  g/L, (B)  $1.3 \times 10^{-4}$  g/L, and (C) deprotonated form ( $6.5 \times 10^{-3}$  g/L).

wherein more than 98% of the side-group pyridine rings were in the quaternized form. The emission at 500 nm is attributed to the unquaternized pyridine rings which is expected to occur at a higher frequency. This was verified by the fluorescence spectrum of the deprotonated form, which showed a single emission at 500 nm (Figure 6C). The fluorescence emission due to intramolecular excimer formation of polymer VIIp was also confirmed by the fact that its emission spectrum at 560 nm is essentially the same as its absorbance spectrum. We believe that, unlike flexible polymers, these polyacetylenes would not lose their excimer emission at very low temperatures due to their strongly conjugated and rigid backbones that predetermine the conformation of the side-group chromophore. The configuration required for energy transfer is, therefore, built up in the polymer chains prior to excitation. Similar observations were made by Handa et al.<sup>12</sup> for protonated poly(2-vinylpyridine), which exhibits a "dimer-like excimer" due to interaction between protonated pyridine rings adjacent to one another. Direct measurements of fluorescence at 77 K were, however, not carried out due to instrument limitation.

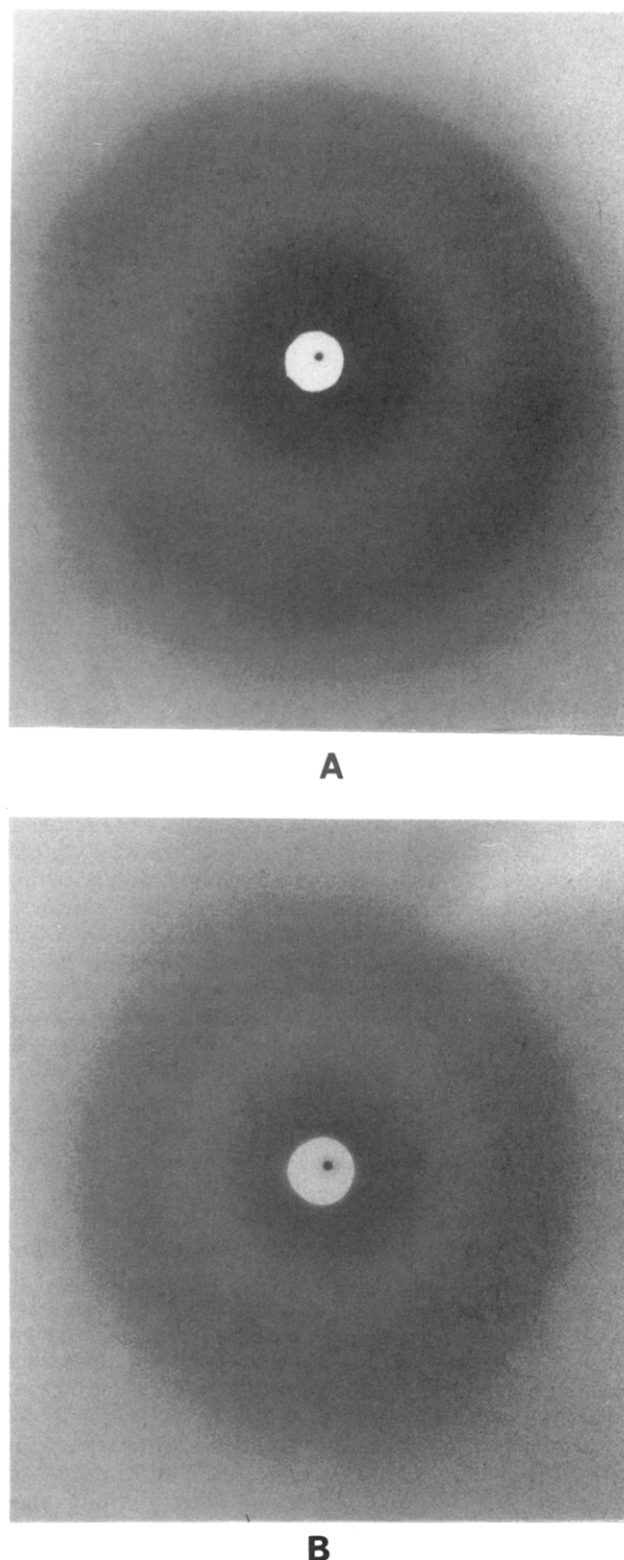
The X-ray diffractogram of an unoriented sample of VIIp indicates an amorphous scattering with a broad ring centered at  $d = 11.8 \text{ \AA}$ , possibly due to a layered structure. Similar diffraction patterns were also displayed by poly-(2-ethylpyridinium-acetylene iodide) obtained via the quaternization method and by poly[(2-bromopyridinium)-acetylene bromide] synthesized by the complexation method.<sup>5</sup> In both cases, the broad small-angle ring occurred at  $d = 11.8 \text{ \AA}$ , which suggests that this layered structure is not dependent on the nature of the atom/group attached to the pyridine nitrogen located in the 2-position with respect to the polymer backbone. This reflection may be related to the ordering of the side-group

pyridinium rings which would be the case if the polymer chain adopted a trans-transoidal conformation. The effect of cis-trans stereoregularity in substituted polyacetylenes on the X-ray diffraction patterns has been reported in a recent study.<sup>16</sup> It was found that, for poly(*tert*-butylacetylene), the *d*-spacing increases with increasing trans content from 8.5 to 10.5 Å. The diffraction pattern of deprotonated VIIIp, however, does not exhibit this characteristic ring. This is probably due to destruction of the layered arrangement caused by the increased backbone twist resulting from deprotonation. Figure 7 shows the X-ray diffractograms of the polymer prior to and after deprotonation.

The conjugation lengths based on both IR and UV-visible spectra for VIIIp are, by far, the highest observed for these ionic polyacetylenes; the spontaneous polymerization of 2-ethynylpyridine via quaternization and halogen complexation methods resulted in polymers with absorption maxima between 370 and 490 nm for the former method<sup>3,4</sup> and 470 nm for the latter.<sup>5</sup> The extended conjugation observed in these systems in spite of their substituted backbones is surprising and is in contrast to substituted polyacetylenes synthesized using coordination catalysts. Results obtained by us recently from modeling studies on these ionic systems using dynamic simulation methods<sup>17</sup> indicate that both the trans-transoidal and the cis-transoidal conformations possess similar energetics and are, therefore, equally probable. The energy-minimized conformers for 10 repeat units are shown in Figure 8. The trans-cisoidal and the cis-cisoidal conformers are substantially higher in energy. It is also evident from the study that the counterions in these charged polyacetylenes interact strongly with adjacent pyridinium rings, thereby preventing backbone twisting. This is reflected by a large electrostatic energy contribution that is responsible for the stability of such conjugated conformers in these systems. This unique feature also distinguishes them from other substituted, uncharged polyacetylenes that do not possess such extended conjugation of the backbone. Our modeling study also predicts that the removal of counterions in these polymers (i.e., the uncharged state) would result in a greater backbone twist due to steric factors introduced by the substituents in the absence of the ionic interactions, leading to reduced conjugation.

A literature survey shows that the conjugation number *n* for a polyene may be estimated from the UV-visible spectra of the conjugated segment present in the polymer. This method has been applied by Dai and White,<sup>18</sup> who have correlated the absorption maxima of conjugated segments obtained by dehydrohalogenation of iodine-doped 1,4-polyisoprene with the conjugation number *n*. Plotting *n* versus the square of the wavelength for each absorption, they obtained a straight line, indicating that the Lewis-Calvin equation,  $\lambda_{\max}^2 = kn$ , is obeyed fairly well.<sup>19</sup> This relation, which has been verified for low molecular polyenes (*n* = 3–10),<sup>20</sup> was shown by these authors to be valid for *n* ranging from 4 to 11. The conjugated sequences calculated from a single value of *k* (*k* was calculated to be 17 532) gave a good correlation of expected and found values.<sup>18</sup> The study also concluded that it was possible to predict the distribution of conjugated sequences insulated from one another from their characteristic absorption maxima for *n* values of up to 11.

In an attempt to verify the applicability of the Lewis-Calvin equation for these ionic polyacetylenes, the UV-visible absorption maxima of their conjugated backbones were correlated with the conjugation number *n*. Figure



**Figure 7.** X-ray diffractograms of VIIIp in the (A) protonated and (B) deprotonated forms.

9 shows a plot of  $\lambda_{\max}^2(\text{C}=\text{C})$  versus *n* obtained for polyenes with *n* = 3–10 that were obtained in the previous study.<sup>20</sup> Extrapolation from this plot for polymer VIIIp using its  $\lambda_{\max}(\text{C}=\text{C})$  absorption maximum gave a conjugation length *n* of 16. If the proposed reaction mechanism for the polymerization that involves a nucleophilic addition to the acetylenic bond in the propagation step occurs in a trans fashion (which is commonly observed for additions across carbon-carbon multiple bonds), the product polymer would possess a fully extended, trans-transoidal conformation through the entire length of the

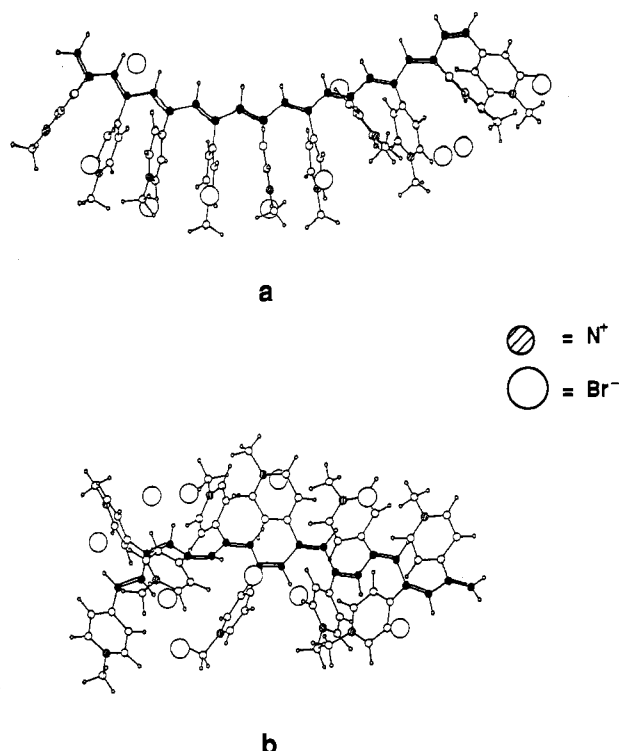


Figure 8. Energy-minimized conformers of poly(4-methylpyridinium-acetylene bromide) in the (a) trans-transoidal and (b) cis-transoidal conformations (from ref 17).

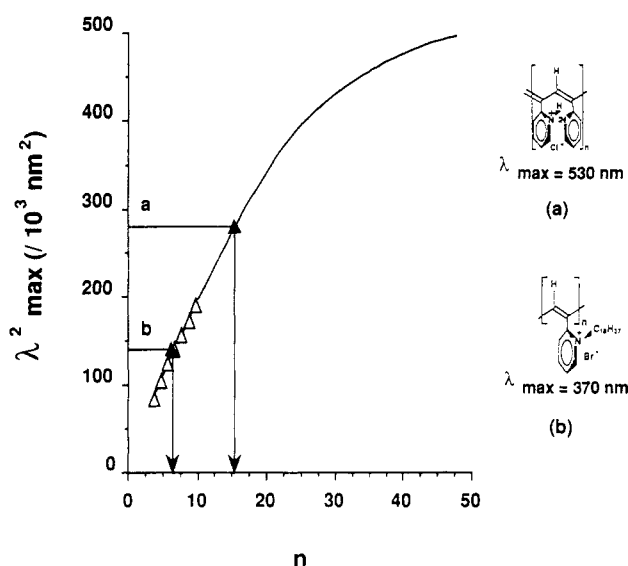


Figure 9. Plot of  $\lambda_{\max}^2(\text{C}=\text{C})$  absorption maxima versus conjugation number  $n$  for polyenes: ( $\Delta$ ) from ref 18; ( $\blacktriangle$ ) this work.

chain. Such a conformation is also predicted to be a highly stable one for these systems by our modeling studies.<sup>17</sup> If this is true, the conjugation number  $n$  for these polymers should be equal to their degree of polymerization, DP. The validity of this assumption was verified for polymer VIIIp by comparing its calculated molecular weight (assuming  $n = \text{DP}$ ) from the UV-visible spectra with the experimentally determined number-average molecular weight ( $M_n$ ) for the deprotonated form obtained by vapor pressure osmometry (Figure 10a). The agreement between the calculated and experimental values within the error of the experiment ( $\pm 5\%$ ) is particularly good. This suggests that these ionic systems do possess a fully extended, trans-transoidal conformation through almost the entire length of the polymer chain. The equation was also found to be applicable for poly(2-*n*-octadecylpyridi-

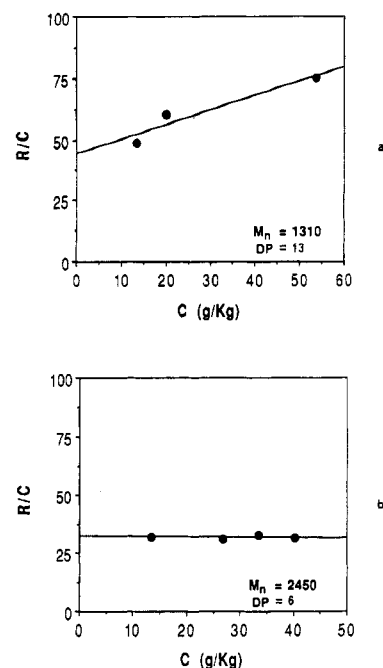


Figure 10. Plot of VPO data for (a) deprotonated VIIIp and (b) poly(2-*n*-octadecylpyridinium-acetylene bromide).

Table II  
Calculated and Experimentally Determined Conjugation Numbers  $n$  and DP for Ionic Polyacetylenes

polymer	$\lambda_{\max}(\text{C}=\text{C})$ (nm)	$n, \text{DP}$	
		calc	exptl
	530	16 <sup>a</sup> 12 <sup>b</sup>	13 <sup>c</sup>
	370	8 <sup>a</sup>	6 <sup>c</sup>

<sup>a</sup> From Lewis-Calvin equation  $\lambda_{\max}^2 = kn$  (Figure 9). <sup>b</sup> From end-group analysis, assuming  $n = \text{DP}$ . <sup>c</sup> From VPO measurement.

nium-acetylene bromide) which was obtained by the quaternization method by making a similar comparison with its molecular weight obtained by direct determination using VPO (Figure 10b). The degree of polymerization, DP, of 12 and the molecular weight ( $M$ ) of 1240 calculated from the end-group analysis for deprotonated VIIIp (based on its analytical data and IR spectrum) are also in excellent agreement with experimentally determined ones (DP = 13,  $M_n$  = 1310 by VPO). This is shown in Table II.

The validity of the Lewis-Calvin relation for the ionic polyacetylenes implies that the properties of the conjugated polymer backbones in these systems resemble those of the corresponding dimethylpolyenes for which the equation was deduced. Furthermore, it is evident from this study that the range of  $n$  over which it is applicable may be extended to an  $n$  value of up to 16. Obviously, the expression cannot be expected to be valid for high values of  $n$ , since it is known that bond alternation effects in long polyenes cause the band gap [and  $\lambda_{\max}(\text{C}=\text{C})$ ] to asymptotically approach a constant value. Based on a band-gap energy of 2.4 eV for fully *trans*-polyacetylene, the  $\lambda_{\max}(\text{C}=\text{C})$  saturates at  $\sim 625 \text{ nm}$ .<sup>21</sup> A recent study of the



nonlinear optical (NLO) susceptibility of the third-harmonic generation (THG) of *trans*-polyacetylene indicates a finite conjugation length comprised of <120 carbon atoms ( $n \sim 60$ ).<sup>22</sup> Hence, the plot of  $\lambda_{\max}$  (or  $\lambda_{\max}^2$ ) versus  $n$  results in marked deviation from linearity at high values of  $n$ , eventually saturating around  $\lambda_{\max} \sim 625$  nm, as is evident from Figure 9.

Since the molecular weight calculated for polymer VI-Ip based on its extrapolated  $n$  value agrees well with the experimentally determined one, any deviation from linearity for up to  $n = 16$  should be minimal. The most significant point that emerges from this correlation for the present systems is that the conjugation number  $n$  is close to the degree of polymerization, DP, within the limits of  $n$  for which it is valid. It provides an effective method for estimating their molecular mass from the UV-visible absorption maxima of their conjugated backbones, which is particularly helpful in view of their charged nature and strongly colored solutions which make determination of  $M$  by standard methods difficult. It must be emphasized, however, that this method may not be applicable for higher values of  $n$  due to the nonlinearity of the curve in Figure 9.

In summary, a novel method for the synthesis of substituted, extensively conjugated ionic polyacetylenes has been described. This synthetic route complements the previously described methods for generating such structures by activation of the acetylenic bond in ethynylpyridines via quaternization with alkyl halides and sulfonates and by complex formation with bromine. A comparison of the UV-visible spectral properties of the polymers obtained by the various routes indicates that the present method involving protonation of the pyridine nitrogen results in greater conjugation in the polymer backbone (also indicating a higher degree of polymerization, DP) and a narrower distribution of molecular masses. We attribute this to the activation step (via protonation) being relatively fast compared to those via quaternization by alkyl halides or methanesulfonates and by complex formation with bromine.

All three methods are superior for polymerization of ethynylpyridine (and its derivatives) compared to polymers obtained by use of coordination catalysts. The polymerization of 2-ethynylpyridine with  $WCl_6$  and  $MoCl_5$  were found to yield low molecular weight products ( $\eta_{inh} = 0.04$ – $0.1$  dL/g) and considerably lower backbone conjugation.<sup>23</sup> The absorption maxima for the unsaturated backbone for these compounds exhibited only broad shoulders around 350 nm, which is indicative of a greater backbone twist in these systems due to the pyridine ring substituents. This phenomenon is characteristic of most substituted polyacetylenes synthesized by using coordination catalysts,<sup>24</sup> wherein a *trans*-*transoidal* conformation is precluded by steric factors. The extraordinary structural features of the ionic polyacetylenes obtained by us may be largely attributed to the mechanism of polymerization and the charged nature of the side groups in the resulting polymers. Confirmation of these structural characteristics by solution NMR was complicated by considerable line-broadening effects arising from aggregation of the higher charged polymer. Solid-state NMR using CPMAS methods on both the protonated and deprotonated polymers is being investigated to substantiate the proposed structures arrived at from spectral data.

The family of ionic polyacetylenes provide, what we believe, the first reported examples of substituted analogs of fully *trans*-polyacetylene. The preparative methods outlined by us for these ionic systems provide a novel approach for the synthesis of all-*trans*-substituted ionic polyacetylenes which has, to our knowledge, not been

achieved. These results may be particularly important in synthetic polyene chemistry since they offer the possibility of obtaining polyacetylenes possessing the stability and processability that is characteristic of substitution, combined with electrical properties of unsubstituted polyacetylene due to their extended conjugation. The significant increase in electrical conductivity of these ionic polyenes on introduction of dopants is indicative of this.<sup>4,25,26</sup> Furthermore, their highly charged nature confers on them the unique properties of polyelectrolytes that may have potential for applications. The inherent limitation in these reactions that preclude the formation of high molar masses is, however, an important factor that must be overcome in order for these materials to be suited for such applications. Modification of the synthetic approach is, therefore, necessary in order to circumvent this limitation. This aspect is currently under investigation.

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