Macromolecules 1991, *24*, 2668–2674

Conjugated Ionic Polyacetylenes. 3. Polymerization of Ethynylpyridinium Salts[1–3]

Sundar Subramanyam and Alexandre Blumstein*

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

Received July 27, 1990; Revised Manuscript Received November 15, 1990

ABSTRACT: A novel and simple method for polymerization of the acetylenic bond conjugated with or directly attached to a quaternizable heteroatom is described. The resulting polymers are black, amorphous solids, soluble in polar organic solvents and in water. Their solubility depends both on molecular mass and on the nature of the counterion. Unlike unsubstituted polyacetylene, they are more stable to air. The polymerization method is illustrated on examples involving polymerization of 2- and 4-ethynylpyridines and their derivatives. The acetylenic triple bond is sufficiently activated to undergo spontaneous polymerization leading to substituted, highly charged polyacetylenes with extensively conjugated backbones. Thus in contrast to previous reports, extensive substitution does not appear to affect long conjugation sequences in polyacetylenes.

Introduction

The polymerization of unsubstituted acetylene is well documented in the literature. A variety of catalysts are used in these reactions such as Ziegler-Natta,[4] ionic,[5] and free radical.[6] Most of these methods however, are not very effective for mono- and especially for disubstituted acetylenic monomers, resulting mostly in low molecular weight materials such as oligomers and cyclic trimers. Cukor et al.[7] have reported the formation of polymeric products from monosubstituted acetylenes such as propiolonitrile, 3-chloro-1-propyne, and 3,3,3-tris(trifluoromethyl)-1-propyne. While the nitrile-containing monomer gave a conjugated polyacetylene, polymerization of 1-chloro-2-propyne resulted in an insoluble product, possibly due to cross-linking. The trifluoromethyl monomer yielded only low molecular weight material. These results are indicative of steric factors resulting from the substituent that influence both the degree of polymerization and the extent of conjugation in substituted polyacetylenes. While the linear nitrile substituent and the chloromethyl group give rise to conjugated products, the bulky trifluoromethyl substituent leads to lower conjugation in the resulting oligomer.

More recently, Higashimura, Masuda, and co-workers reported in a series of papers, a family of effective catalysts based on transition-metal halides of groups V and VI of the periodic table. Catalysts such as $NbCl_5$, $MoCl_5$, or WCl_6 either in their pure form or with a cocatalyst were found to be capable of polymerizing both mono- and disubstituted acetylenic monomers to high molecular masses in good yields. This work was recently reviewed by the authors, who described the synthetic methods involved and the properties of the resulting polymers.[8] The polymers obtained by these methods are, however, not extensively conjugated due to their predominantly cis-cissoid and cis-transoid components and are thus devoid of strong absorptions in the visible range. The conjugation length (number of conjugated double bonds in the polymer backbone) n deduced from their spectral characteristics in the UV region is 2–3. The poor conjugation in substituted polyacetylenes is attributed to steric constraints introduced by substituents, which force the double bonds in the chain to twist out of coplanarity. This results in reduced effective overlap of the π orbitals, thereby disrupting extended conjugation.[6] The amorphous nature of such polymers and their enhanced solubility in organic solvents also arise from these factors.

An important property of substituted polyacetylenes is their stability to oxidation, which is in contrast to the relatively poor stability of unsubstituted polyacetylene.[6] This, coupled with their enhanced solubility in common organic solvents, makes them more suited for applications such as permselective membranes because of greater processability. Due to their short conjugation lengths however, substituted polyacetylenes are poor conductors of electricity (10^{-7} S cm^{-1}), although when heavily doped, certain monosubstituted polyacetylenes show a pronounced increase in conductivity (10^{-3} S cm^{-1}).[7] Whether the reduced conjugation length is an inherent property of the monomer structure or arises as a result of the reaction mechanism involved in the polymerization (which is dependent on the nature of the transition-metal–halide coordination catalyst) was an open question. It is apparent from the present work that it is possible to achieve fairly long conjugation sequences in highly substituted polyacetylenes. Thus it appears that it is the charged nature of the substituents that may be responsible for the extensive conjugation in these polyacetylenes. The reaction mechanism in this case involves the activation of the acetylenic bond followed by rapid, spontaneous polymerization. The resulting polymers are highly charged, thereby exhibiting enhanced solubility in organic solvents and in water.

All polymerization reactions by the present method involve quaternization of the pyridine nitrogen in ethynylpyridine precursors. The quaternizing agents used were straight-chain alkyl bromides, iodides, and methanesulfonates. Quaternization of 4-ethynylpyridine (**1**) with 1-bromododecane, for example, gave poly[(4-*N*-dodecylpyridiniumyl)acetylene bromide] (**1p**), while 2-ethynylpyridine (**2**) when reacted with the same alkylating agent gave poly[(2-*N*-dodecylpyridiniumyl)acetylene bromide] (**2p**). Dipyridylacetylenes such as 1,2-bis(4-pyridyl)acetylene (**3**) on quaternization with 1-bromododecane gave poly[1,2-bis(4-*N*-dodecylpyridiniumyl)acetylene bromide] (**3p**) in good yield and, when reacted with 1-heptylmethanesulfonate, resulted in a water-soluble polymer that is extremely hygroscopic. When the same reaction was carried out with nonane-1,9-bis(methanesulfonate), an insoluble cross-linked product was obtained. The polymerization reaction was also extended to pyridine-containing diacetylenes. The reaction of 1,4-bis(4-pyridyl)butadiyne

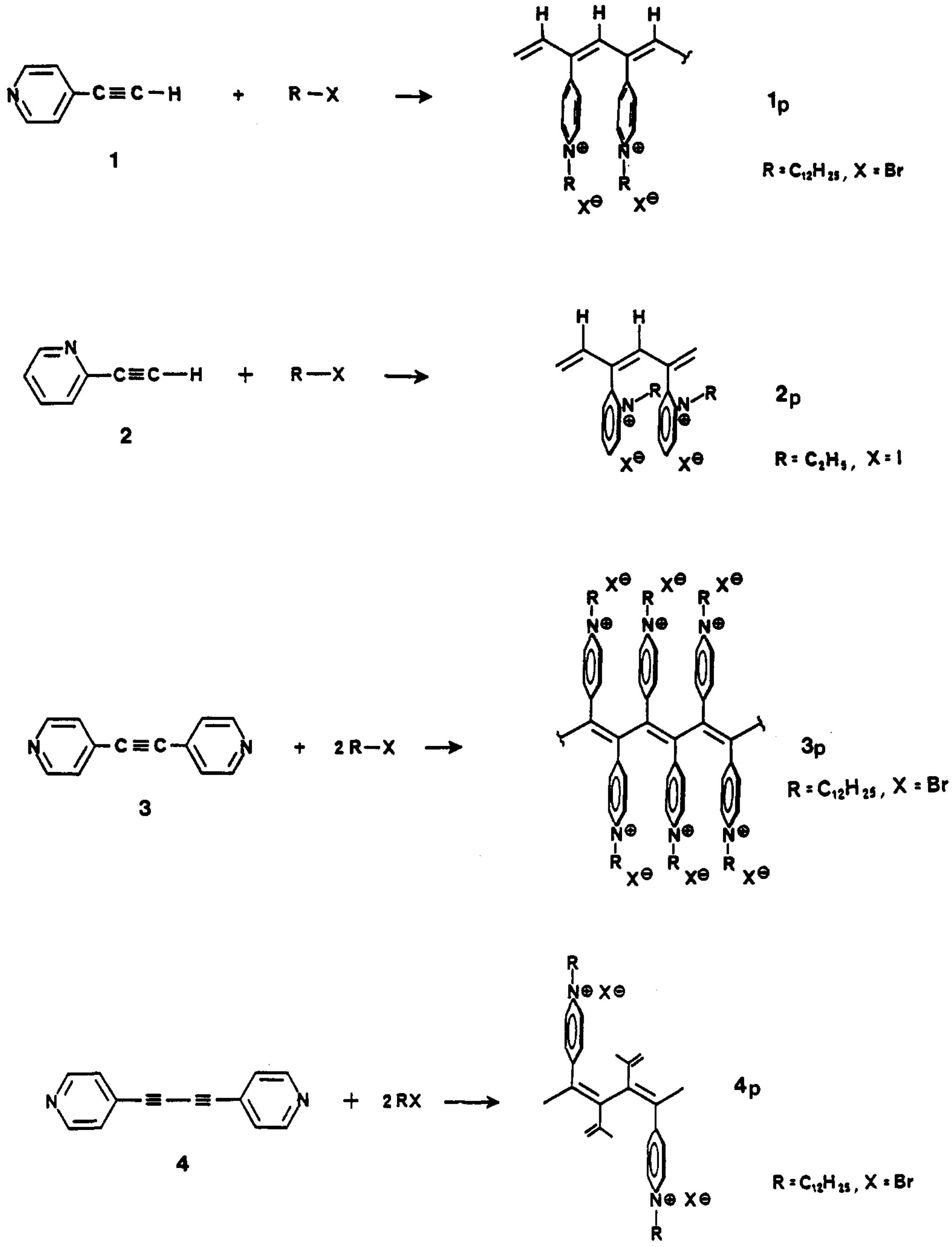

Figure 1. Synthetic scheme for polymers obtained by the quaternization method.

(4) with 1-bromododecane also resulted in a highly insoluble, cross-linked polymer 4p. Figure 1 illustrates these reactions and the polymeric products obtained.

It has been shown previously that quaternization of the pyridine nitrogen in 4-vinylpyridine leads to spontaneous polymerization of this monomer, resulting in poly(4-vinylpyridinium) salts of high molecular mass.[10-12] The polymerization was found to occur in the quaternized monomer intermediate only and is pH dependent, following different pathways leading to either poly(vinylpyridine) at low pH or ionenes for $\mathrm{pH} > 10$.[13] Kabanov et al.[14] reported the spontaneous polymerization of propargyl derivatives with tertiary amines via quaternization. The acetylenic triple bonds in these cases are not in direct conjugation to the quaternized group, and as a result of insufficient activation, polymers with low intrinsic viscosities (0.04 dL/g) were obtained. More recently, Katritzky and co-workers[15] studied the reaction of propargyl chlorides and bromides with pyridines and substituted pyridines. No polymeric products were obtained from these reactions, but only the corresponding pyridinium salts were isolated. Polymerization reactions by activation of the C≡C triple bond via quaternization of a heteroatom conjugated to it have not been previously reported. Yamashita and co-workers found that quaternization of 2-ethynyl- and 4-ethynylpyridine with hydrochloric acid and their subsequent transformation to the corresponding fluoroborate salts activated the acetylenic triple bond sufficiently for them to function as efficient dienophiles in Diels–Alder reactions with dienes.[16,17] No polymerization of the triple bond was observed under these conditions. In the present work, we report the spontaneous polymerization of 2- and 4-ethynylpyridines and related compounds that contain an acetylenic triple bond in conjugation to a quaternizable nitrogen atom in a pyridine ring. The product polymers resulting from these reactions have higher inherent viscosities (0.2–0.5 dL/g) than those involving propargyl derivatives,[14] which is indicative of higher molecular weights.

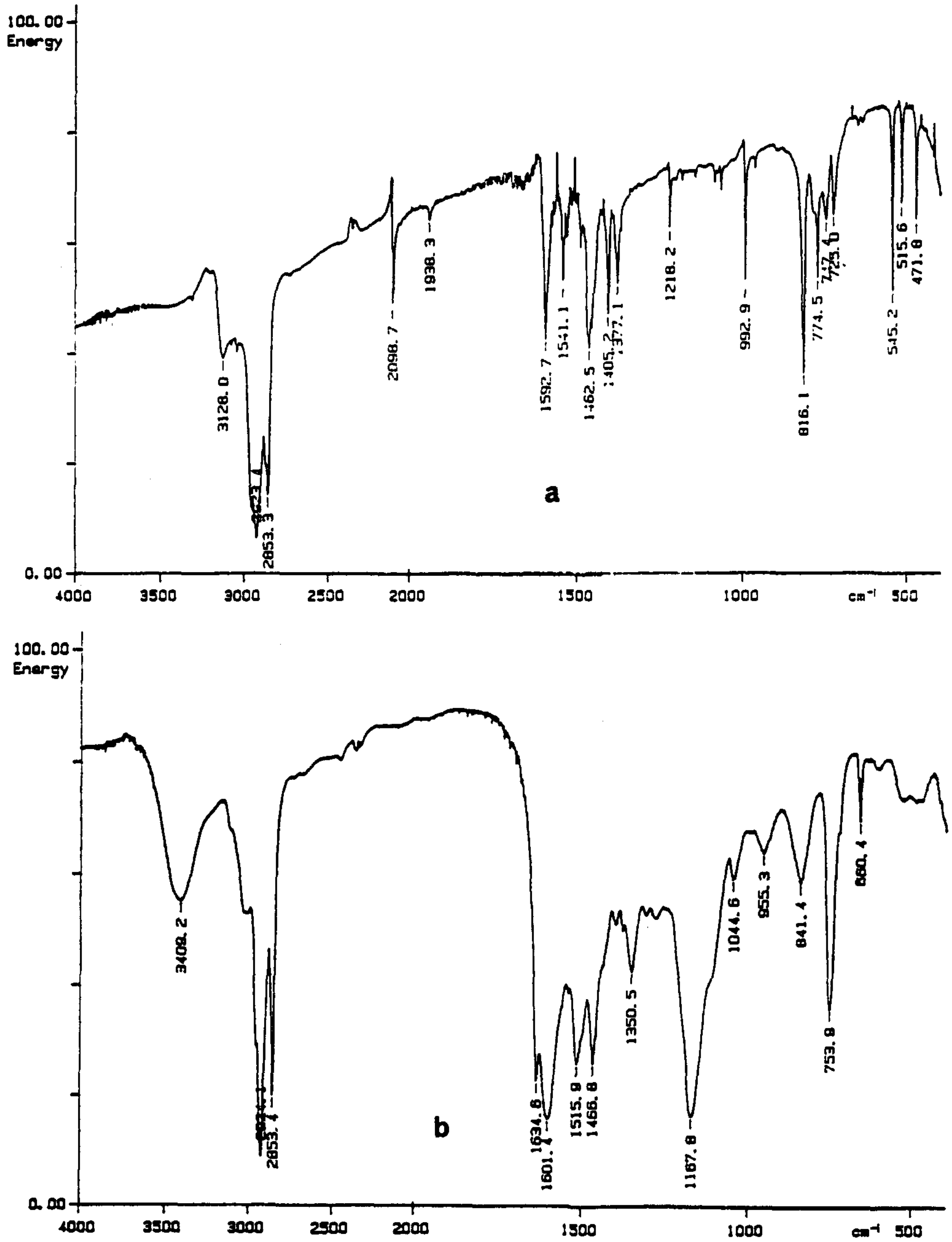

Figure 2. Infrared spectra of (a) monomer 1 and (b) polymer 1p.

Results and Discussion

All polymers obtained by the quaternization method are purple-black or black in appearance, indicative of the conjugated structures illustrated in Figure 1. Their infrared spectrum showed a broad band at 3415 cm^{-1} (C=C—H stretching), which could arise either from C=C—H stretching[7] or from OH stretching of residual hydrated water. Samples heated to 110 °C at 3 mmHg, however, did not show any significant decrease in the intensity of this band. Consequently, we attribute this absorption to C=C—H stretching. In addition, an intense band between 1630 and 1590 cm^{-1} (—C=C— stretching) was observed for all cases, indicating extended conjugation. This band was shifted to as low as 1530 cm^{-1} for some cases. The —C≡C—H and the —C≡C— stretching bands at 3130 and 2098 cm^{-1}, respectively, that are present in the monomers are absent in the product polymers. Figure 2 shows the IR spectra of starting monomer 1 and the product polymer 1p. Additional evidence for this extensive conjugation is provided by the large bathochromic shift in the UV-visible spectra when passing from monomer to polymer. The absorption maximum for the conjugated backbone (λ_{max}) occurs between 440 and 530 nm. Figure 3 illustrates the UV shift for polymer 1p. The absorption maximum for polymers obtained by quaternization of 4-vinylpyridine, which has a fully saturated backbone on the other hand, is around 270 nm.[18] Conjugated pyridinium ions do not show any UV absorption maxima above 330 nm. This has been confirmed in both monomeric and polymeric quaternized 1,2-*trans*-1,4-dipyridylethylenes.[19-21] The large bathochromic shifts in the present polymers is thus indicative of extended conjugation. Figure 4 shows a plot of the UV absorption maxima (λ_{max}) versus conjugation length for unsubstituted polyenes.[22] Assuming this relationship is valid for substituted polyenes, the conjugation lengths *n* for these polymers range from 10 to 16. Table I lists the physical data obtained for the polymers obtained by the present method.

We have found the values of λ_{max} to be essentially uninfluenced by the nature of the counterion (Br$^-$, I$^-$, and $CH_3SO_3^-$), which precludes viologen formation.[23] In

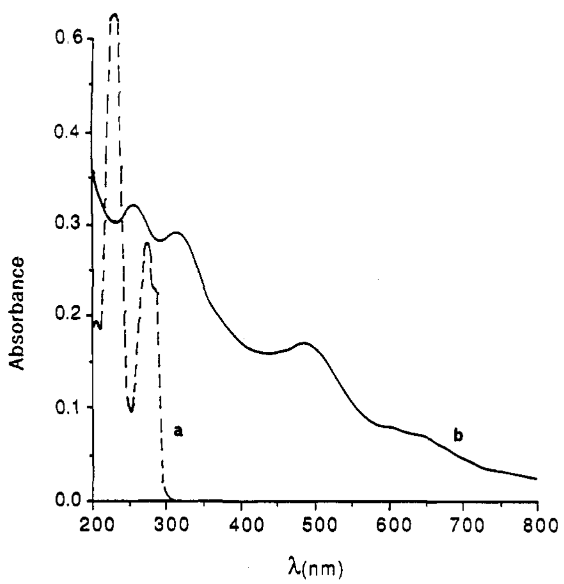

Figure 3. UV-visible spectra of (a) monomer 1 and polymer 1p in absolute ethanol at 25 °C.

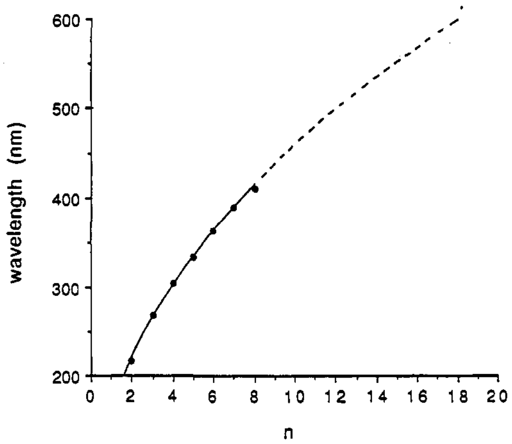

Figure 4. Plot of absorption maxima for unsubstituted polyenes versus conjugation length.

addition, most viologens with similar pyridinium units exhibit UV absorptions under 400 nm in their nonreduced state. These factors suggest that the possibility of viologen formation is remote in the present polyacetylenes.

Thermal investigations were carried out on polymers 1p and 3p. TGA curves were generated both in air and in nitrogen to assess their stability to oxygen. For polymer 1p, the TGA run in nitrogen (Figure 5a) showed one sharp, continuous weight loss starting at 250 °C and continuing to 440 °C. No further loss was detected thereafter up to 800 °C. The sample degraded to 20% of the original weight, and a grey residue with a metallic luster was obtained. The TGA curve for polymer 3p run in nitrogen (Figure 5b) showed a two-step weight loss, the first starting at 240 °C and continuing to 430 °C, and a second one between 510 and 680 °C. In this case, the material degraded almost completely. No significant differences were observed between heating runs in air and in nitrogen for both polymers, indicating their greater stability to oxidation compared to unsubstituted polyacetylene.

DSC thermograms for polymer 3p (Figure 6) show a distinct transition at 342 K (69 °C) during the first heating, but no significant heat evolution is associated with it. These changes are reversible, but can be "locked in" by rapid cooling. The original conformer appears to be restituted by annealing the material as is evident from Figure 6. This phenomenon may be attributed to a reversible conformational change, although a reversible absorption-desorption of ionic hydration water cannot be excluded. This aspect is being currently investigated. On the basis of FTIR and TGA studies, decomposition of the polymer at these low temperatures may be precluded.

Due to their ionic nature, the present polymers are highly soluble in common polar solvents and in water. They are among the few known examples of water-soluble polyacetylenes. Polymers with I^- and $CH_3SO_3^-$ counterions were soluble in water, methanol, and ethanol but insoluble in THF, acetonitrile, and chlorinated hydrocarbons, while those with Br^- counterions were insoluble in water, but soluble in ethanol, THF, chloroform, and acetone. The solubility is also greatly influenced by the molecular mass and the extent of quaternization. In most cases, comparisons were made between samples with η_{inh} varying between 0.2 and 0.5 dL/g and the degree of quaternization from 80 to 95% (based on the elemental analysis of halide content). The nature of the counterion, however, appears to play an important role in the solubility characteristics of these systems. Polymers containing methanesulfonate counterions for example, were found to be more hygroscopic than those containing halides. X-ray diffractograms indicate that the "in situ" polymers are amorphous and DSC thermograms confirm the absence of crystallinity.

A free-radical mechanism for the formation of these polyacetylenes may be ruled out on the basis of following observations: (1) Inhibitors of free-radical polymerization (such as oxygen) do not interfere with the polymerization process. (2) Only quaternized monomeric species are found to participate in the polymerization process. A catalytic amount of quaternizing agent did not yield polymeric products (a 10% mol equiv of the quaternizing species resulted in an oligomer in the form of an orange-brown oil). (3) Cocatalysts are not required for the reaction. Strong acids do not favor polymerization, but result in quaternized ammonium salts, which precipitate out.[16,17]

Two different mechanisms can be invoked to explain the formation of the present polyacetylenes. One, described by Kabanov and co-workers[24,25] for the polymerization of quaternized vinylpyridines, involves initiation by the counterion followed by propagation by the created anionic species (Figure 7a). The alternate mechanism involves an initiation step involving a nucleophilic attack by the unquaternized amine on the electrophilic triple bond of the quaternized acetylenic monomer. This is followed by an identical propagation step that involves the created macroanion and the quaternized monomeric species (Figure 7b). The latter mechanism appears more favorable based on recent findings by Katritzky et al.[26] These authors succeeded in isolating the quaternized monomeric pyridinium salt in reactions of propargyl chlorides and bromides with pyridine. Polymerization could be initiated in these species by addition of nucleophiles such as pyridines and tertiary amines.

Although the present polymers are of the "self-doped" type, they showed very low conductivities in their undoped state ($<10^{-9}$ S cm^{-1}). Their electrical conductivity increased significantly upon introduction of dopants, with the magnitude being dependent on the nature of the dopant. Acceptor-type dopants such as iodine resulted in conductivies of $\sim 10^{-4}$ S cm^{-1}, which is in the typical semiconductor range. No photocurrent was detected for the iodine-doped polymers. Polymer films subjected to vapor-phase iodine doping showed large, irreversible iodine uptakes with no significant decrease in iodine content after

Table I
Physical Properties of Polymer —(C(R)=C(R'))$_n$—[a]

	R[b]	R'[b]	color	λ_{max}, nm	ϵ_{max}	η_{inh}, dL/g	ref
	H	*t*-Bu	colorless	283	1500	0.97[c]	8
	Me	Ph	colorless	283	2500	2.7[c]	8
1p	H	a	black	450	22000	0.2	this work
2p	H	b	black	447	31300	0.2	this work
3p	a	a	black	499	82000	0.5	this work

[a] In methanol at 28 °C with c = 1 g/L. [b] a = *N*-dodecylpyridinium-4-yl bromide; b = *N*-dodecylpyridinium-2-yl bromide. [c] Intrinsic viscosity.

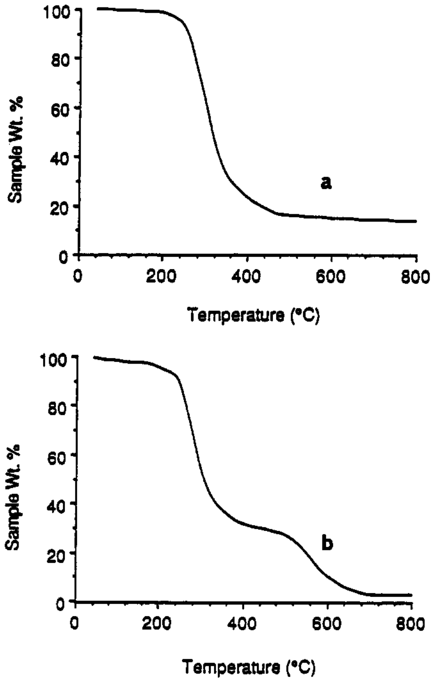

Figure 5. TGA thermograms of polymers (a) 1p and (b) 3p run in a nitrogen atmosphere (heating rate 10 °C/min).

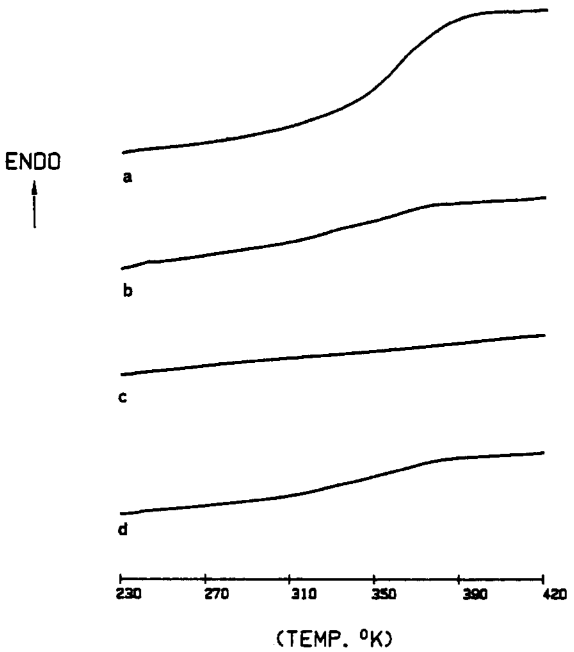

Figure 6. DSC of polymer 3p. (a) First heating, (b) second heating, (c) third heating, and (d) annealed at 23 °C for 172 h.

prolonged vacuum pumping (12 h). When exposed to iodine vapor, the films increased rapidly in weight, eventually turning into a lustrous, soft, pasty material. Polymer films doped with donors such as TTF displayed markedly higher conductivities (10^{-2} S cm^{-1}) compared to iodine-doped samples for similar concentration of dopant.

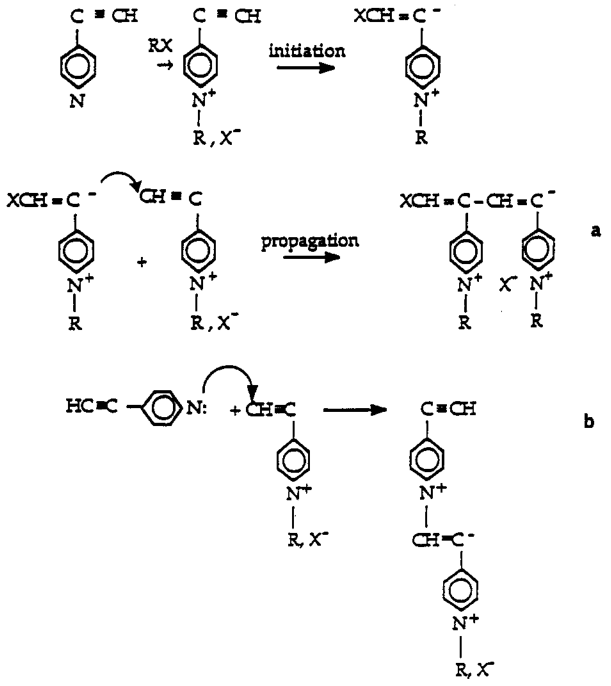

Figure 7. Reaction mechanisms for polyacetylene formation via initiation by (a) counterion and (b) unquaternized amine.

This is indicative of the present polymers being better acceptors than donors due to the positively charged side groups attached to the backbone. Table II lists the dopant type, concentrations, and measured conductivities for the present polymers. The infrared spectra of the doped polymers showed a broad absorption from 3800 to ~2000 cm^{-1}, which arises due to electronic transitions from the valence to the conduction bands in conducting polymers.

Conclusion

The quaternization of pyridylacetylenes provides a novel and simple route to highly substituted polyacetylenes with extensively conjugated backbones. The ionic nature of the resulting polymers makes them soluble in polar solvents including water. The solubility is dependent on the nature of both the quaternizing species and the molecular mass. The present polymers are among the rare examples of water-soluble polyacetylenes. The combination of extensive conjugation and substitution in these polyacetylenes obtained by us makes the present method quite unique and provides the first known examples of conjugated, disubstituted polyacetylenes. Conjugation lengths of n ~ 10–16 bonds were hitherto unreported for disubstituted polyacetylenes (n is usually 2–3). The structural and mechanistic factors promoting conjugation in these systems are of considerable interest since certain polymers obtained by this method[2] are structurally similar to a model proposed for an organic polymeric superconductor.[27] Doped materials display enhanced conductivities. They are among the rare examples of substituted polyacetylenes displaying electrical conductivities of the order of 10^{-1}–10^{-2} S cm^{-1}.

Table II
Electrical Properties of Polymers —(C(R)=(R′))$_n$—

polymer	R[a]	R′[a]	X⁻	dopant	concn, wt %	conductivity, S cm^{-1}	
						undoped	doped
1p	H	a	I⁻	I_2	125	$<10^{-9}$	2×10^{-4}
2p	a	a	I⁻	I_2	200	$<10^{-9}$	1×10^{-4}
3p	b	b	$CH_3SO_3^-$	I_2	125	$<10^{-9}$	3×10^{-4}
4p	a	a	I⁻	TTF	100	$<10^{-9}$	1.1×10^{-2}

[a] a = *N*-dodecylpyridinium-4-yl; b = *N*-dodecylpyridinium-2-yl.

Due to their extensive conjugation and ionic nature, these polymers have potential as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, and permselective membranes. Studies to assess these applications are in progress.

Experimental Section

2-Ethynylpyridine was obtained from Farchan Laboratories. 4-Ethynylpyridine and 1,3-bis(4-pyridyl)butadiyne were prepared by the method described by Ciana and Haim.[28] 1,2-Bis(4-pyridyl)acetylene was synthesized by the procedure outlined by Tanner and Ludi.[29] 1-Heptylmethanesulfonate and nonane-1,9-bis(methanesulfonate) were obtained by reacting 1-heptanol and nonane-1,9-diol, respectively, with methanesulfonyl chloride and pyridine by standard methods,[30] followed by recrystallization from absolute ethanol. Iodoethane and 1-bromododecane were obtained from Aldrich Chemical Co. Acetonitrile (HPLC grade) was obtained from VWR Scientific and distilled under nitrogen before use. Iodine doping was carried out by passing iodine vapor at 2 mmHg over polymer films. Doping with TTF was done in solution using DMSO as solvent. The substrates were laid on glass plates with aluminum contacts.

Measurements. Infrared spectra were recorded on a Perkin-Elmer 1600 series Fourier transform infrared spectrophotometer using KBr plates. UV absorption spectra were obtained in absolute ethanol on an IBM 9420 visible–ultraviolet spectrophotometer. Thermal analyses were carried out on a Perkin-Elmer DSC 2C differential scanning calorimeter and a Perkin-Elmer TMS-2 thermomechanical analyzer. X-ray diffraction patterns of unoriented samples were obtained with a Warhus flat plate camera using Ni-filtered Cuα radiation. Dilute solution viscosity measurements were made in absolute methanol at 28 °C using a Canon Ubbelohde dilution-type viscometer. Film dimensions were measured with an Olympus BH-2 optical microscope. AC and DC conductivities were measured by use of a Tektronics 576 curve tracer.

Poly[(4-*N*-dodecylpyridiniumyl)acetylene bromide] (1p). 4-Ethynylpyridine (0.5 g, 4.85×10^{-3} mol) was dissolved in freshly distilled acetonitrile (30 mL) and 1.21 g (4.85×10^{-3} mol) of 1-bromododecane was added rapidly to the stirred solution. The reaction mixture was warmed to 50 °C and stirring was continued at this temperature for 72 h. During this time the solution acquired a deep blue-black color and the polymeric product separated out as a black solid. It was filtered, reprecipitated from methanol with ethyl ether, and dried at 30 °C under vacuum. The yield of poly[(4-*N*-dodecylpyridiniumyl)acetylene bromide] was 1.21 g. The product was a black powder and was readily soluble in ethanol, methanol, and other polar organic solvents: IR (cm^{-1}) 3415 (C=C—H stretching), 1634 (C=C stretching), 660, 754 (C—H stretching in pyridine ring); UV, λ_{max} (nm) 499, ϵ_{max} (L mol^{-1} cm^{-1}) 8.2×10^4; η_{inh} (dL/g) 0.2. Anal. Calcd: C, 64.76; H, 8.58; N, 3.98; Br, 22.68. Found: C, 64.49; H, 8.21; N, 4.93; Br, 22.04.

Poly[(2-*N*-dodecylpyridiniumyl)acetylene bromide] (2p). 2-Ethynylpyridine (0.5 g, 4.85×10^{-3} mol) was dissolved in freshly distilled acetonitrile and 0.76 g (4.85×10^{-3} mol) of 1-bromododecane was added rapidly to the stirred solution. The reaction was run in a manner identical with that described for Ip. The deep purple-black solid product was dried at 30 °C under vacuum. The yield of poly[(2-*N*-ethylpyridiniumyl)acetylene iodide] was 0.68 g. The product was readily soluble in ethanol, methanol, and other polar organic solvents: IR (cm^{-1}) 1621 (C=C stretching), 641, 746 (C—H stretching in pyridine ring); UV, λ_{max} (nm) 443, ϵ_{max} (L mol^{-1} cm^{-1}) 1.4×10^5; η_{inh} (dL/g) 0.2. Anal. Calcd: C, 64.76; H, 8.58; N, 3.98; Br, 22.68. Found: C, 65.84; H, 8.12; N, 5.42; Br, 20.44.

Poly[1,2-bis(4-*N*-dodecylpyridiniumyl)acetylene bromide] (3p). 1,2-Bis(4-pyridyl)acetylene (0.5 g, 2.8×10^{-3} mol) was dissolved in freshly distilled acetonitrile (30 mL) and 0.69 g (5.6×10^{-3} mol) of 1-bromododecane was added rapidly to the stirred solution. The reaction was carried out in a manner identical with that described for Ip. The black solid obtained after workup was dried at 30 °C under vacuum. The yield was 1.12 g. The product was readily soluble in ethanol, methanol, and polar organic solvents: IR (cm^{-1}) 1635 (C=C stretching), 660, 755 (C—H stretching in pyridine ring); UV, λ_{max} (nm) 450, ϵ_{max} (L mol^{-1} cm^{-1}) 2.2×10^5; η_{inh} (dL/g) 0.5. Anal. Calcd: C, 63.71; H, 8.61; N, 4.13; Br, 23.55. Found: C, 64.62; H, 7.92; N, 6.34; Br, 18.84.

Poly[1,2-bis(4-*N*-heptylpyridiniumyl)acetylene methanesulfonate]. 1,2-Bis(4-pyridyl)acetylene (0.5 g, 2.8×10^{-3} mol) was dissolved in freshly distilled acetonitrile (30 mL) and 1.09 g (5.6×10^{-3} mol) of heptane-1-methanesulfonate was added rapidly to the stirred solution. The reaction was carried out in a manner identical with that described for Ip. The black solid obtained after workup as dried at 30 °C under vacuum. The yield was 1.1 g. The product was readily soluble in ethanol, methanol, and polar organic solvents: IR, (cm^{-1}) 1635 (C=C stretching) 660, 755 (aromatic C=C stretching); UV, λ_{max} (nm) 450 ϵ_{max} (L mol^{-1} cm^{-1}) 2.2×10^5; η_{inh} (dL/g) 0.2.

Poly[1,3-bis(4-*N*-dodecylpyridiniumyl)acetylene bromide] (4p). 1,3-Bis(4-pyridyl)butadiyne (0.1 g, 4.9×10^{-4} mol) was dissolved in freshly distilled acetonitrile (30 mL) and 0.24 g (9.8×10^{-4} mol) of 1-bromododecane was added rapidly to the stirred solution. The reaction was carried out in a manner identical with that described for Ip. The product obtained as a black powder was dried at 30 °C under vacuum. The yield was 0.22 g. The polymer was found to be highly insoluble, indicating extensive cross-linking.

Acknowledgment. We acknowledge the support of the National Science Foundation's Polymers Program Grant DMR-8823084. Thanks are expressed to Professor S. Mil'shtein of the Department of Electrical Engineering for useful discussions and help in the measurements of conductivity.

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