A New Class of Conjugated Ionic Polyacetylene. Cyclopolymerization of Dihexyldipropargylammonium Salts by Metathesis Catalysts

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ABSTRACT: A new class of substituted ionic polyacetylene was synthesized by metathesis polymerization with transition-metal catalysts. The monomers used were dihexyldipropargylammonium salts having bromide and tosylate as counteranions. It was found that $MoCl_5$-based catalyst systems were very effective for the cyclopolymerization of the present ionic monomers. The resulting dark-red polymers exhibited good solubility in polar organic solvents such as methanol, DMSO, DMF, THF, $CHCl_3$, etc., indicative of their ionic nature. Structure of the polymers was confirmed by IR, UV–visible, and ^1H and ^{13}C NMR spectroscopy. When doped with an acceptor such as iodine, the polymers exhibited a substantial increase in electrical conductivity (10^{-3} S/cm) compared to the undoped state (10^{-9} S/cm).

Introduction

Since the discovery of the polymerization of 1,6-heptadiyne using Ziegler–Natta catalyst in 1961,[1] there have been many studies on the cyclopolymerization of nonconjugated diynes giving conjugated double bonds in the polymer backbone and a cyclic recurring unit. However, this catalyst leads to insoluble polymer films.[2] It was known that group VI metal-based catalysts exhibit a high catalytic activity for the polymerization of substituted acetylenes.[3-5] Recently, we have found that Mo- and W-based catalyst systems are very effective for the cyclopolymerization of dipropargyl derivatives.[6-12] The corresponding polymers have good solubility in organic solvents, long-term stability toward oxidation, and high electrical conductivity. In the cyclopolymerization of nonconjugated diynes as well as the polymerization of substituted acetylenes by transition-metal catalysts, the polymerization of ionic nonconjugated diynes has not been investigated so far because of its poor solubility in organic solvents and the deactivating effect of polar ionic species on the Lewis-acidic transition-metal halide catalysts.

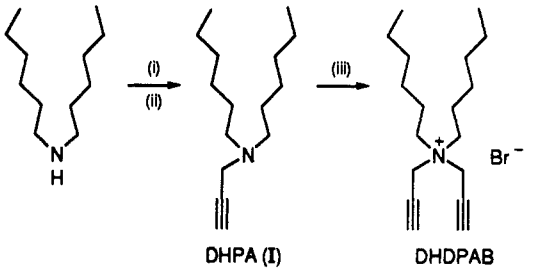
In a recent series of papers,[13-16] Blumstein et al. reported the synthesis of mono- and disubstituted ionic polyacetylene with an extensively conjugated backbone. The polymerization was achieved via activation of the acetylene bond in ethynylpyridines by introduction of strong electron-withdrawing substituents in conjugation to it.

In this paper, we introduce the first synthesis of substituted ionic polyacetylenes by methathesis catalysts. The monomers used are dihexyldipropargylammonium salts with bromide and tosylate counteranions. The physical and spectroscopic properties of the resulting polymers will be discussed.

Experimental Section

Monomer Synthesis. Dihexyldipropargylammonium Bromide (DHDPAB). To a flask charged with a DMF solution (150 mL) of dihexylamine (12.4 g, 0.07 mol) containing K_2CO_3 (18.4 g, 0.13 mol) was slowly added propargyl bromide (12 g, 0.10 mol) at room temperature. The reaction mixture was refluxed for 3 h with vigorous stirring. After water was added, the solution was extracted with diethyl ether, and then the extract was dired over anhydrous $MgSO_4$. The ether was removed on a rotatory evaporator and dihexylpropargylamine (I, DHPA; Scheme I) was isolated by fractional distillation [90% yield, bp 72 °C (1 mmHg)]. Using 150 mL of dried methanol as solvent, DHPA (7.85 g, 0.03 mol) was refluxed with propargyl bromide (6.25 g, 0.05 mol) for 10 h. After the solvent was removed, the crude solid product was purified by recrystallization from a mixed solvent of ether and THF. The pure DHPAB was obtained (83% yield). ^1H NMR ($CDCl_3$): δ 0.8 (t, CH_3–), 1.3–1.8 (m, –$(CH_2)_4$–), 2.9 (t, ≡CH), 3.5 (t, CH_2N), 4.7 (d, CH_2C≡). ^{13}C NMR ($CDCl_3$): δ 14.3 (C of CH_3–), 22.8, 23.1, 26.5, 31.4 (C of –$(CH_2)_4$–), 51.0 (C of CH_2N), 61.2 (CH_2 of CH_2C≡), 71.5 (≡CH), 82.0 (–CH≡). IR (KBr): 3132, 2937, 2114 cm^{-1}. Elem anal. Calcd for $C_{18}H_{32}NBr$: C, 63.15; H, 9.42; N, 4.09; Br, 23.34. Found: C, 63.08; H, 9.51; N, 4.22; Br, 23.19.

Scheme I[a]



[a] (i) K_2CO_3/DMF. (ii) $BrCH_2C$≡CH. (iii) $BrCH_2C$≡CH/CH_3OH.

Dihexyldipropargylammonium Tosylate (DHDPAT). In a 500-mL three-neck flask with a thermometer, an ice–water bath, and a 250-mL dropping funnel were placed propargyl alcohol (10.6 g, 0.19 mol) and pure *p*-toluenesulfonyl chloride (20 g, 0.10 mol). From the dropping funnel, 32 mL of a 5 N NaOH solution was added dropwise at a rate that did not cause the temperature of the reaction mixture to exceed 15 °C. Another portion of *p*-toluenesulfonyl chloride (20 g, 0.10 mol) was added and then 32 mL of a 5 N NaOH solution was slowly introduced. Stirring was continued for 4 h, and the oily layer was separated from the water layer by extraction with diethyl ether. The ether layer was washed thoroughly with 50 mL of a 10% NaOH solution and dried by stirring overnight over 20 g of anhydrous K_2CO_3. After removal of the solvent, the residue was distilled at reduced pressure. Pure propargyl tosylate (II; Scheme II) was obtained [55% yield, bp 105–110 °C (1 mmHg)]. To a stirred solution of DHPA (3 g, 0.013 mol) in 100 mL of dried methanol was added II (3.4 g, 0.016 mol) at room temperature. The reaction mixture

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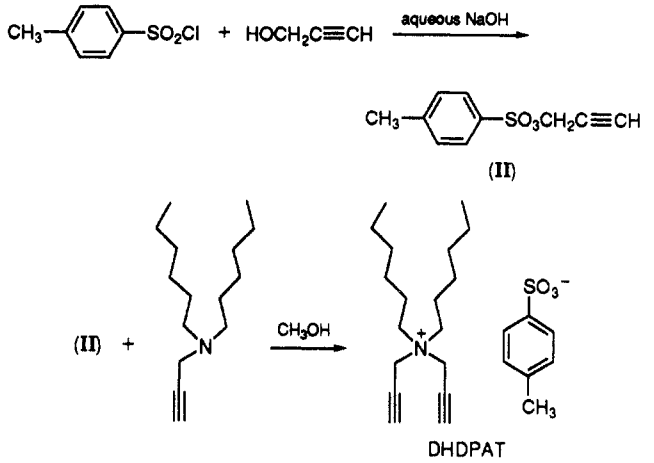
Scheme II



was refluxed for 10 h. After the solvent was removed, the pure DHDPAT was obtained in 71% yield by recrystallization from ether and THF. ^{1}H NMR ($CDCl_3$): δ 0.8 (t, CH_3–), 1.2–1.75 (m, –$(CH_2)_4$–), 2.29 (s, CH_3 of tosylate), 2.8 (t, ≡CH), 3.4 (t. –CH_2N), 4.5 (d, CH_2C≡), 7.0–7.7 (m, phenyl ring). ^{13}C NMR ($CDCl_3$): 14.3 (C of CH_3–), 21 (CH_3 of tosylate), 22.7, 22.8, 26.4, 31.4 (C of –$(CH_2)_4$–), 50.1 (C of CH_2N), 60.8 (CH_2 of CH_2C≡), 71.7 (≡CH), 81.6 (–C≡), 126.4, 129.0, 139.4, 144.5 (aromatic carbons). IR (KBr): 3200, 2921.1, 2121.8, 1198 cm^{-1}. Elem anal. Calcd for $C_{25}H_{39}NO_3S$: C, 69.25; H, 9.06; N, 3.23; S, 7.39. Found: C, 69.16; H, 9.21; N, 3.30; S, 7.23.

Other Materials. Commercial grades of transition-metal compounds and organometallic cocatalysts were used without further purification. Chlorobenzene and other polymerization solvents were purified by standard methods. Special care was taken to ensure complete removal of moisture and oxygen.

Polymerization. Catalyst preparation and polymerization were carried out under a dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in each solvent to make 0.2 M solutions before use. A typical polymerization procedure was as follows: Solvent, catalyst solution, and, when needed, cocatalyst solution were injected into a 20-mL ampule equipped with a rubber septum in the other given. When cocatalyst was used, the catalyst system was aged at 30 °C for 15 min. Finally, monomer dissolved in each solvent was injected into the polymerization ampule. After the reaction mixture was allowed to react at 70 °C for 24 h, the polymerization was terminated by adding a small amount of methanol. The resulting polymer was dissolved in THF and precipitated with a large excess of hexane. The polymer was filtered off and dried under vacuum at 30 °C for 24 h. The polymer yield was determined by gravimetry.

Doping. The iodine doping was performed by exposing the polymer films to iodine vapor in a vacuum desiccator (initially at 10^{-1} mmHg) at 30 °C for 24 h. The dopant concentration was estimated by the weight uptake method.

Instruments. ^{1}H and ^{13}C NMR spectra were recorded with the use of Bruker AM-300 spectrometer, and chemical shifts were reported in ppm units with TMS as internal standard. Infrared spectra were measured on a Bomen MB-100 Fourier transform spectrophotometer using KBr pellets. UV–visible absorption spectra were obtained in CH_3OH on a Shimadzu UV-3100S spectrophotometer. Thermal analyses were carried out on a Du Pont TGA 9900 thermogravimetric analyzer in a nitrogen atmosphere at 10 °C/min. X-ray diffraction patterns of unoriented samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Wahrus flat-plate camera using Ni-filtered Cu Kα radiation at a scan speed of 4°/min. Dilute-solution viscosity measurements were made in CH_3OH at 30 °C using a Lauda viscometer. Electrical conductivities were measured by the four-point probe DC method. Elemental analysis was performed with a Perkin Elmer 240DS elemental analyzer.

Results and Discussion

In the case of a neutral tertiary amine, hexyldipropargylamine, we could not obtain the polymeric products with Lewis-acidic transition-metal catalysts. This is thought to be due to the deactivating effect of a basic nitrogen atom on catalysts. Also, since the monomer with a chloride counteranion, dihexyldipropargylammonium chloride, has a poor solubility in the nonpolar polymerization solvent, we could not carry out the polymerization.

Scheme III outlines the cyclopolymerization of the monomers with transition-metal catalyst systems.

Scheme III

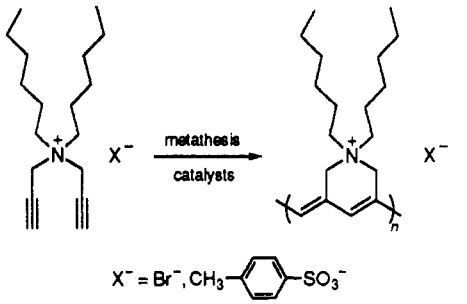


Table I. Polymerization of DHDPAB by Transition-Metal Catalysts[a]

expt no.	cat. syst (mole ratio)	polymer yield (%)[b]	η_{inh} (dL/g)[c]	λ_{max} (nm)[e]
1	$MoCl_5$	64	0.10	380
2	$MoCl_5$ (M/C = 25)	78	0.12	385
3	$MoCl_5$–$EtAlCl_2$ (1:4)	93	0.30	480
4	$MoCl_5$–$EtAlCl_2$ (1:2)	85	0.25	460
5	$MoCl_5$–$SnCl_4$ (1:4)	30	0.07	
6	WCl_6	0		
7	WCl_6–$EtAlCl_2$ (1:4)	53	0.08	
8	$PdCl_2$	62	0.09	

[a] Polymerization was carried out in chlorobenzene at 70 °C for 24 h, $[M]_0 = 0.5$. [b] Hexane-insoluble polymer. [c] Inherent viscosity at 30 °C in methanol. Concentration $C = 0.1$ g/100 mL. [d] Polymerized in DMF at 90 °C for 24 h. [e] λ_{max} in a methanol solution.

Table II. Polymerization of the DHDPAT by Transition-Metal Catalysts[a]

expt no.	cat. syst (mole ratio)	polymer yield (%)[b]	η_{inh} (dL/g)[c]	λ_{max} (nm)[e]
1	$MoCl_5$	34	0.06	370
2	$MoCl_5$ (M/C = 25)	76	0.09	375
3	$MoCl_5$–$EtAlCl_2$ (1:4)	91	0.12	460
4	$MoCl_5$–$EtAlCl_2$ (1:2)	83	0.10	440
5	$MoCl_5$–$SnCl_4$ (1:4)	0		
6	WCl_6	0		
7	WCl_6–$EtAlCl_2$ (1:4)	0		
8	$PdCl_2$	58	0.07	

[a] Polymerization was carried out in chlorobenzene at 70 °C for 24 h, $[M]_0 = 0.5$. [b] Hexane-insoluble polymer. [c] Inherent viscosity at 30 °C in methanol. Concentration $C = 0.1$ g/100 mL. [d] Polymerized in DMF at 90 °C for 24 h. [e] λ_{max} in methanol solution.

Polymerization of DHDPAB and DHDPAT. The polymerizations of DHDPAB were carried out with $MoCl_5$- and WCl_6- based catalysts, and their results are summarized in Table I. The catalytic activity of $MoCl_5$ was greater than that of WCl_6. As shown in Table I, $EtAlCl_2$ exhibits excellent cocatalytic activity compared with Me_4Sn. The inherent viscosities and λ_{max} of poly(DHDPAB) are also listed in Table I. The polymeric products obtained were dark-red. The results of the polymerization of DHDPAT by Mo- and W-based catalysts are summarized in Table II. The results are similar to those obtained in the polymerization of DHDPAB. However, poly(DHDPAB) with bromide counteranion has a higher polymerization degree than poly(DHDPAT) with tosylate counterion.

Polymer Structure. The ^{1}H NMR spectra of poly(DHDPAB) and poly(DHDPAT) are shown in Figure 1.

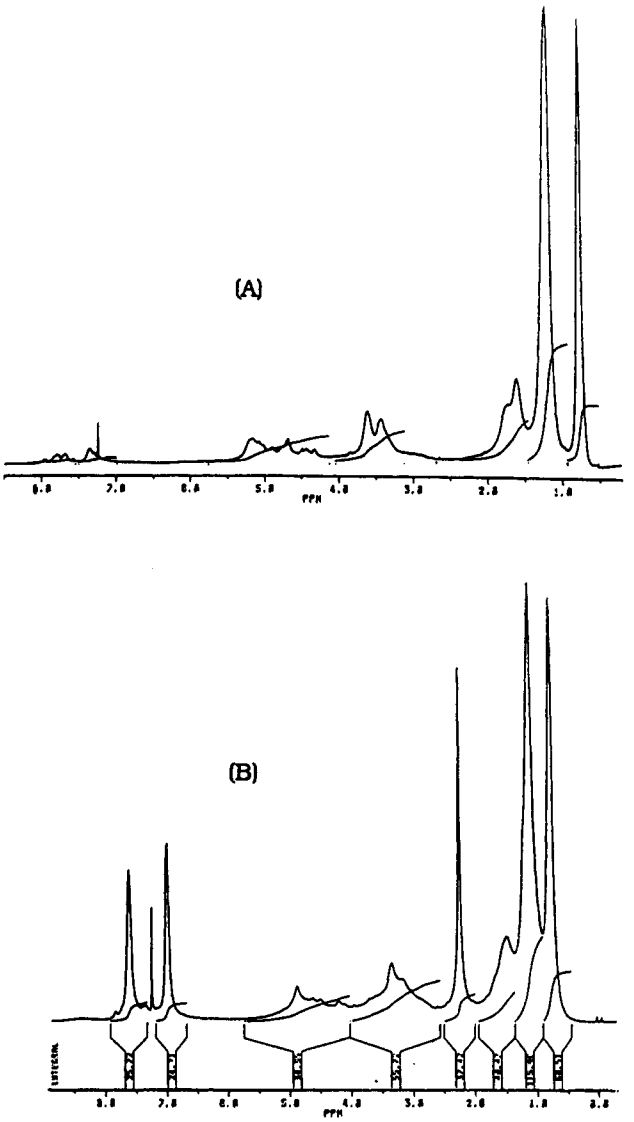


Figure 1. ^1H NMR spectra of poly(DHDPAB) (A) and poly(DHDPAT) (B) in $CDCl_3$ (sample: expt no. 3 in Table I and expt no. 3 in Table II).

As the polymerization proceeded, acetylenic proton peaks of monomers at 2.9 ppm disappeared, and new broad peaks appeared at 7–8 ppm due to protons on the conjugated double bond. Also the broad peak around 4.8 ppm is assigned to the allylic methylene protons adjacent to the nitrogen atom on the ring. Figure 2 shows the ^{13}C NMR spectra of poly(DHDPAB) and poly(DHDPAT). Acetylenic carbon peaks at 82 and 71 ppm disappeared, and new broad olefinic carbon peaks appeared at 120–140 ppm. In the case of poly(DHDPAT), a methyl carbon peak of tosylate appears at 21 ppm.

The IR spectra of monomer and poly(DHDPAB) are shown in Figure 3. The spectrum of poly(DHDPAB) shows a broad, intense absorption band at 3400 cm^{-1} which arises from associated water. This band is indicative of the highly charged nature of the polymer. The ≡CH and –C≡C– stretching bands at 3132 and 2120 cm^{-1}, respectively, that are present in the monomers are absent in the polymeric products.

The UV–visible spectra of the polymeric products provide additional evidence for the extended conjugation when compared with those of the monomer. Figure 4 shows the UV–visible spectra of polymers. The UV–visible spectra of poly(DHDPAB) and poly(DHDPAT) obtained in MeOH exhibit characteristically broad absorption bands at 400–600 nm which are due to the π-π^* transition of

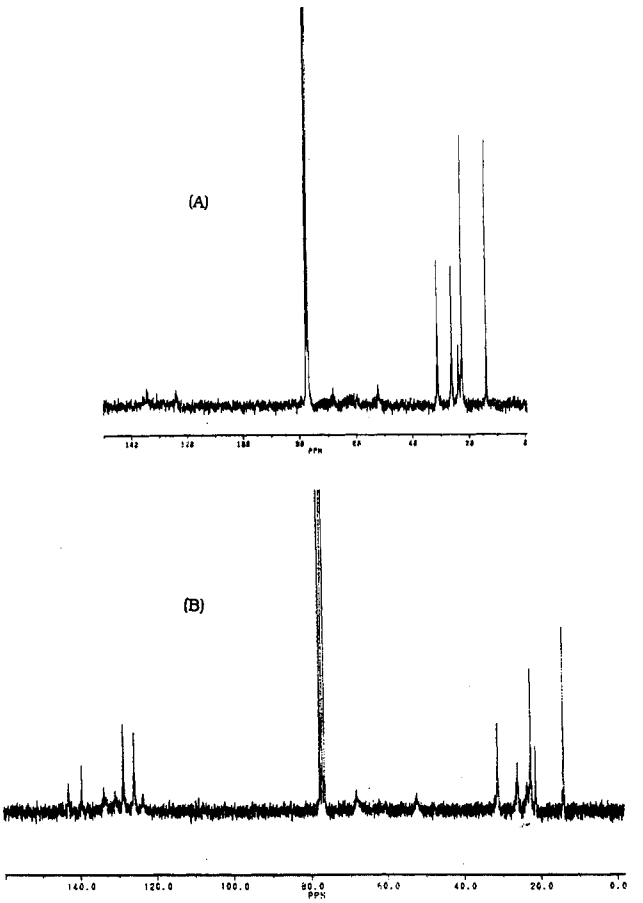


Figure 2. ^{13}C NMR spectra of poly(DHDPAB) (A) and poly(DHDPAT) (B) in $CDCl_3$ (sample: expt no. 3 in Table I and expt no. 3 in Table II).

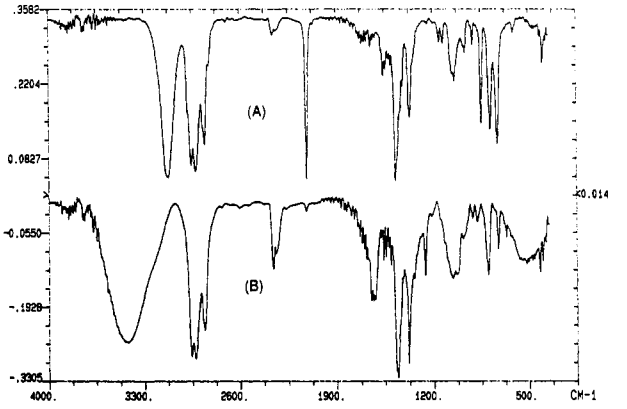


Figure 3. IR spectra of monomer DHDPAB (A) and poly(DHDPAB) (B) in KBr pellet (sample: expt no. 3 in Table I).

conjugated polyene. The polymer prepared by the $MoCl_5$–$EtAlCl_2$ catalyst system, having the largest inherent viscosity (in Tables I and II), has more extensively conjugated systems than that prepared by $MoCl_5$ alone. Extensive conjugation shifts its electronic spectrum to longer wavelength.

The absolute values of molecular weight and polydispersity were difficult to determine for these systems because of their polyelectrolyte nature and the intense color of their solutions. Therefore, relative values were estimated by inherent viscosity and UV–visible spectral data (Tables I and II). A literature survey[17] shows that the conjugation number n for a polyene may be estimated from the UV–visible spectra of the conjugated segment in the polymer. Assuming the relationship of the UV absorption maxima versus conjugation length for unsub-

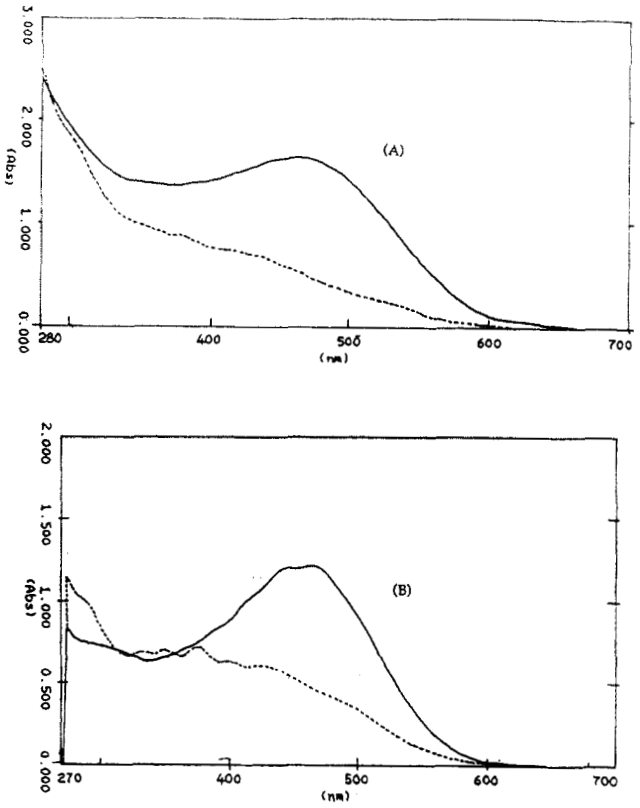


Figure 4. UV–visible spectra of poly(DHDPAB) (A) and poly(DHDPAT) (B) in a methanol solution [—, $MoCl_5$–$EtAlCl_2$ (1:4); - - -, $MoCl_5$] (sample: expt no 3 in Table I and expt no. 3 in Table II).

stituted polyene is valid for these ionic polyacetylenes, the conjugation lengths n for these polymers range from 10 to 14.

Polymer Properties. Due to their ionic nature, the present polymers are soluble in common polar organic solvents such as methanol, ethanol, DMF, DMSO, THF, methylene chloride, chloroform, etc., but insoluble in water as well as nonpolar ones such as hexane and ether. The polymers exhibit polyelectrolyte behavior in polar organic solvents such as methanol; i.e., the reduced viscosity in the absence of simple electrolytes increases sharply with decreasing polymer concentration. On addition of KBr, the viscosity decreased due to the contraction of polymer chains resulting from the screening of ionic charges along the chain.

DSC thermograms for poly(DHDPAB) and poly(DHDPAT) showed broad endothermic peaks at 140 °C which are believed to be due to the evaporation of the associated water. Figure 5 shows the TGA thermograms of poly(DHDPAB) and poly(DHDPAT). For the polymer with a bromide counteranion, TGA run in N_2 (Figure 5A), the weight loss started at 172.6 °C and 81.7% by weight was lost below 519 °C. The TGA curve for the polymer with a tosylate counteranion run in N_2 (Figure 5B) shows a two-step weight loss, the first starting at 210.3 °C and the second one at 369 °C. The small amount of weight loss exhibited at 140 °C is due to the evaporation of the associated water, consistent with the DSC experiments.

We also investigated the morphology of the two polymers by X-ray diffraction (Figure 6). The data of X-ray diffraction analysis are as follows: poly(DHDPAB), 2θ, $(\Delta 2\theta/2\theta)$ = 19.82, (0.44); poly(DHDPAT), 2θ, $(\Delta 2\theta/2\theta)$ = 19.95, (0.40). In general, the X-ray diffraction pattern of the amorphous polymer is broad, the ratio of the half-height width to the diffraction angle $(\Delta 2\theta/2\theta)$ is greater than 0.35, and the crystalline diffraction peaks are sharp;

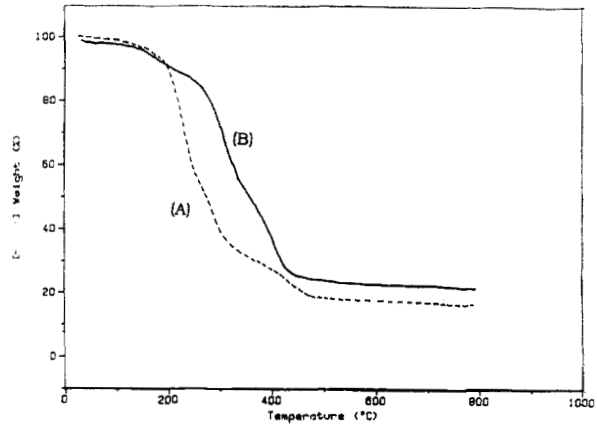


Figure 5. TGA thermograms of poly(DHDPAB) (A) and poly(DHDPAT) (B) in N_2(scanning rate = 10°/min).

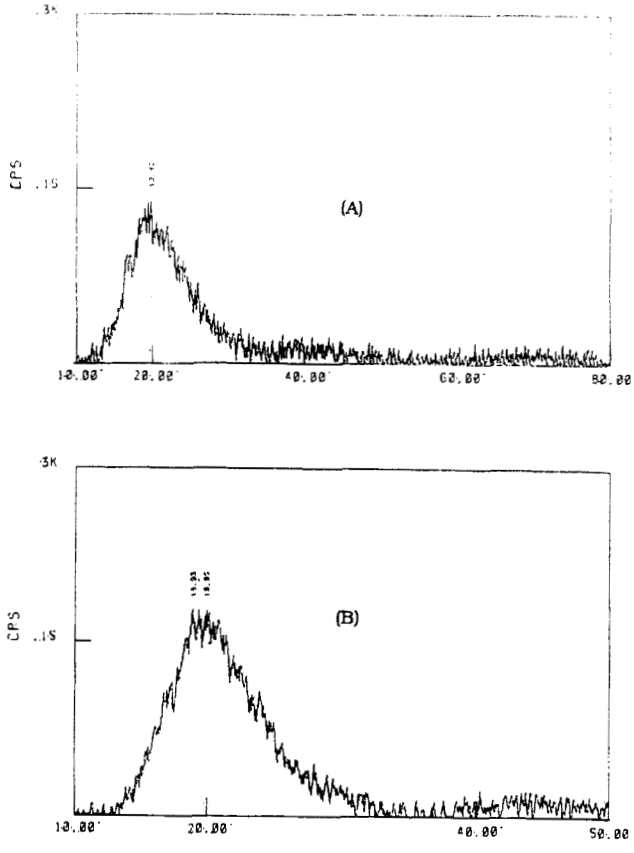


Figure 6. X-ray diffractograms of poly(DHDPAB) (A) and poly(DHDPAT) (B) (sample: expt no. 3 in Table I and expt no. 3 in Table II) (scanning rate = 4°/min).

Table III. Electrical Conductivity of Poly(DHDPAB) and Poly(DHDPAT)[a]

polymer	comp. of polymer[c]	conductivity (S cm^{-1})[c]
poly(DHDPAB)	$(C_{18}H_{32}NBr)_1(I_2)_0$	2.8×10^{-10}
poly(DHDPAB)	$(C_{18}H_{32}NBr)_1(I_2)_{0.55}$	1.5×10^{-3}
poly(DHDPAT)	$(C_{18}H_{32}NTos)_1(I_2)_0$	5.5×10^{-10}
poly(DHDPAT)	$(C_{18}H_{32}NTos)_1(I_2)_{0.37}$	0.7×10^{-3}

[a] These polymers were doped by exposure to iodine vapor under vacuum (0.1 mmHg) for 24 h. [b] Extent of doping was obtained by the weight uptake method. [c] Measured with the four-point probe DC method.

their values of $\Delta 2\theta/2\theta$ are smaller than 0.05. On this basis, it is concluded that both polymers are amorphous.

The polymer films cast from a $CHCl_3$ solution are brittle and could not be used to measure electrical conductivity. We prepared tough, free-standing films by blending the polymers with poly(vinyl chloride) (PVC) in acetone and

THF cosolvent (weight ratio 50:50).[18] The blended polymer films exhibited poor electrical conductivity in their undoped state ($<10^{-9}$ S/cm). When doped with an acceptor such as iodine, the polymers showed a substantial increase in electrical conductivity, and highly doped polymer films exhibited conductivities of 10^{-3} S/cm. The present polymers form a novel class of substituted, extensively conjugated polyelectrolytes that have potential for applications in the areas of energy storage, conductive polymer devices, and permselective membrane technology.[13] Table III lists the electrical conductivities of I_2-doped and undoped polymers.

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