A New Class of Conjugated Ionic Polyacetylene. 2. Cyclopolymerization of Dihexyldipropargylammonium Salt by Metathesis Catalysts

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Introduction

Recently, we have reported that Mo- and W-based catalyst systems are very effective for the cyclopolymerization of dipropargyl derivatives giving conjugated double bonds in the polymer backbone and a cyclic recurring unit.[1-10] The corresponding polymers have good solubility in common organic solvents, long-term stability toward oxidation, and high electrical conductivity.

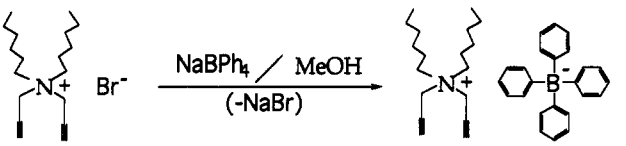
In general, transition-metal catalysts, including metathesis catalysts, possess only limited stability toward functional groups that contain heteroatoms such as O, N, and S. This has hampered their use for the polymerization of acetylene monomers that contain such functionalities. However, when the functionally substituted substrates are 1,6-heptadiyne derivatives, several catalyst systems show remarkable tolerance to a variety of functional groups. However, 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 their 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,[12-16] 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 the previous report,[11] we described the first cyclopolymerization of dipropargylammonium derivatives by metathesis catalysts to give a new type of substituted ionic polyacetylene with an extensively conjugated cyclic backbone. 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. The monomers used were dihexyldipropargylammonium salts with bromide and tosylate counterions. The nature of the counterion appeared to make an important effect on the polymerization behavior. A highly Lewis-acidic W-based catalyst, which shows excellent catalytic activity for phenylacetylene but is adversely affected by the presence of a polar functional group on the metathesizing moiety, exhibited poor catalytic activity for these monomers with polar ionic species such as bromide and tosylate anions.

In this paper, we report the cyclopolymerization of dihexyldipropargylammonium salt with tetraphenylborate counterion which has no nucleophilic or basic nonbonding electron pair in contrast to the bromide and tosylate anions,

Scheme 1



and the physical and spectroscopic properties of the resulting polymer will be discussed.

Experimental Section

Monomer Synthesis. Dihexyldipropargylammonium Bromide (DHDPAB) (Scheme 1). This compound was obtained from the reaction of dihexylpropargylamine with propargyl bromide according to the method previously reported.

Dihexyldipropargylammonium Tetraphenylborate (DHDPATB). This compound was prepared by the following ion exchange reaction. A solution of DHDPAB (7 g, 0.02 mol) in 50 mL of methanol was added to a solution of $NaBPh_4$ (8.3 g, 0.024 mol) in 100 mL of methanol with stirring, and the precipitated product was filtered, washed repeatedly with distilled water and methanol, and dried under vacuum. The product was further purified by recrystallization from a mixed solvent of chloroform and hexane (yield 98%): mp 112 °C; FT-IR (KBr) 3308 (≡CH), 3047 (aromatic CH), 2135 cm^{-1} (C≡C); ^1H NMR (acetone-d_6) δ 0.8 (t, CH_3), 1.3–1.8 (m, $-(CH_2)_4-$), 3.5 (m, ≡CH, CH_2N), 4.4 (d, $CH_2C\equiv$), 6.7–7.3 (m, aromatic H); ^{13}C NMR (acetone-d_6) δ 14.1 (C of CH_3), 22.6, 22.9, 26.5, 32.7 (C of $-(CH_2)_4-$), 50.5 (C of CH_2N), 60.6 (CH_2 of $CH_2C\equiv$), 71.5 (≡CH), 83.1 (−C≡), 122.2, 125.9, 126.1, 136.9 (aromatic C). Elem anal. Calcd: C, 86.72; H, 9.01; N, 2.41. Found: C, 86.58; H, 9.12; N, 2.50.

Other Materials. Tungsten(VI) and molybdenum(V) chloride (Aldrich Chemical Co., resublimed 99.9%) were used without further purification. Palladium(II) chloride, $NaBPh_4$, tetrabutyltin, and ethylaluminum dichloride (Aldrich Chemical Co.) were used without further purification. All solvents were used after purification according to conventional 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 prior to use. Polymerization was carried out according to the method previously reported. Solvent, catalyst solution, and, when needed, cocatalyst solution were injected into a 20-mL ampule equipped with a rubber septum in the order given. When cocatalyst was used, the catalyst system was aged at 30 °C for 15 min. Finally the 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 40 °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 line at 30 °C. The dopant concentration was estimated by the weight uptake method.

Instruments. ^1H and ^{13}C NMR spectra were recorded with the use of a Bruker AM-200 spectrometer, and chemical shifts were reported in ppm units with TMS as the internal standard. IR spectra were obtained on a Bomem MB-100 Fourier transform spectrophotometer using KBr pellets. UV–visible absorption spectra were obtained in THF on a Shimadzu UV-3100S spectrophotometer. Thermal analyses were carried out on a DuPont TGA 9900 thermogravimetric analyzer in a nitrogen atmosphere at 10 °C/min. The X-ray diffraction pattern of the unoriented sample was obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Wahrus flatplate camera using Ni-filtered Cu Kα radiation at a scan speed of 4 °C/min. Dilute solution viscosity measurements were made in THF at 30 °C using a Lauda viscometer. Electrical conductivity was measured

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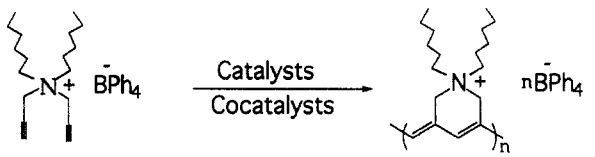
Scheme 2



Catalysts : $MoCl_5$, WCl_6, $PdCl_2$

Cocatalysts : $EtAlCl_2$, $(n\text{-}Bu)_4Sn$

Table 1. Polymerization of the Monomer by Various Transition-Metal Catalysts[a]

exp no.	cat. syst (mole ratio)	polymer yield (%)[b]	η_{inh} (dL/g)[c]	λ_{max} (nm)[e]
1	$MoCl_5$	78	0.15	475
2	$MoCl_5$ (M/C = 25)	86	0.16	480
3	$MoCl_5$ (dioxane)	88	0.19	490
4	$MoCl_5$–$EtAlCl_2$ (1:4)	94	0.18	480
5	$MoCl_5$–$EtAlCl_2$ (dioxane)	92	0.18	480
6	$MoCl_5$–$SnBu_4$ (1:4)	72	0.12	
7	WCl_6	58	0.11	455
8	WCl_6 (M/C = 25)	67	0.14	470
9	WCl_6–$EtAlCl_2$ (1:4)	82	0.16	530
10	$PdCl_2$[d]	64	0.08	

[a] Polymerization was carried out in chlorobenzene at 70 °C for 24 h. $[M]_0$ = 0.2. [b] Hexane-insoluble polymer. [c] Inherent viscosity at 30 °C in THF; concentration C = 0.1 g/100 mL. [d] Polymerized in DMF at 90 °C for 24 h. [e] λ_{max} in THF solution.

by the four-point probe dc method. Elemental analysis was performed with a Perkin-Elmer 240DS elemental analyzer.

Results and Discussion

Scheme 2 outlines the cyclopolymerization of the present ionic monomer with transition-metal catalysts.

The polymerization of DHDPATB was carried out with $MoCl_5$- and WCl_6-based catalysts and a $PdCl_2$ catalyst, and its results are summarized in Table 1. As shown in Table 1, the $MoCl_5$-based catalyst system exhibits the most effective catalytic activity for the polymerization of this monomer. $EtAlCl_2$ cocatalyst is more effective than $(n\text{-}Bu)_4Sn$. The WCl_6 catalyst, which exhibited poor catalytic for the monomers with polar functional groups such as alcohol,[3] nitrile,[10] ester,[5] and bromide and tosylate anions,[11] gives a moderate yield of polymer by itself, and the WCl_6–$EtAlCl_2$ catalyst system gives the polymer with the most extensive conjugation length based on UV–visible spectral data. Such an increased catalytic activity of WCl_6 is believed to be due to the nature of the counterion, tetraphenylborate. This bulky anion has no nucleophilic or basic nonbonding electron pair capable of adversely affecting the catalytic activity by coordinating to the Lewis-acidic transition-metal halide catalysts. The inherent viscosities and λ_{max} of poly(DHDPATB) are also listed in Table 1. The polymeric products obtained were dark red.

Polymer Structure. The ^1H NMR spectrum of poly(DHDPATB) is shown in Figure 1. As the polymerization proceeded, the acetylenic proton peak of the monomer at 3.5 ppm disappeared and a new broad peak due to protons on the conjugated double bond appeared at 7–8 ppm together with aromatic protons. Also the broad peak around 4.6 ppm is assigned to the allylic methylene protons adjacent to the nitrogen atom on the ring. Due to the positive charge on nitrogen, all the peaks shifted downfield relative to neutral amine compounds. In the ^{13}C NMR spectrum of poly(DHDPATB), acetylenic carbon peaks at 82 and 71 ppm disappeared, and new broad olefinic carbon peaks appeared at 120–140 ppm. In the IR spectrum of the polymer (Figure 2), the ≡CH and –C≡C–

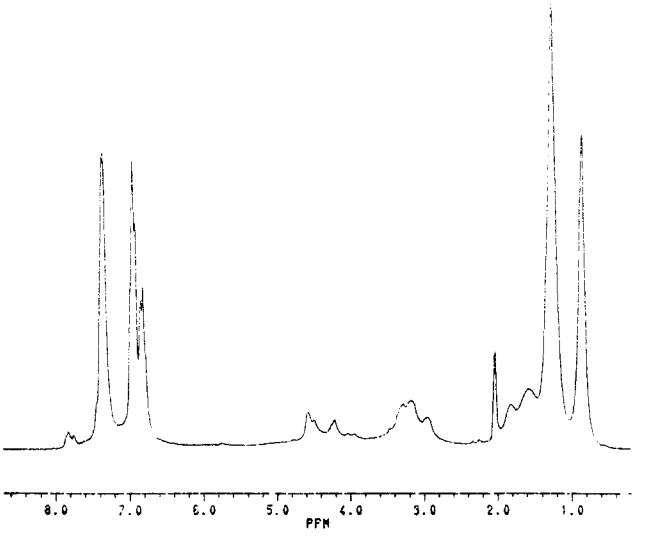


Figure 1. ^1H NMR spectrum of poly(DHDPATB) in acetone-d_6.

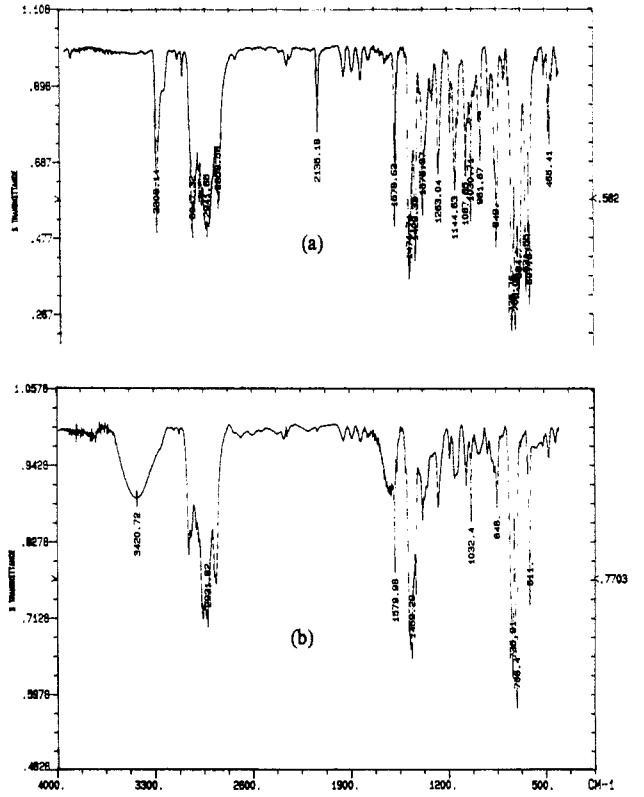


Figure 2. FT-IR spectra of the monomer (a) and the polymer (b) in a KBr pellet.

stretching bands at 3308 and 2135 cm^{-1}, respectively, present in the monomer are absent. The UV–visible spectra of the polymeric products provide additional evidence for the extended conjugation when compared with that of the monomer. The UV–visible spectra (Figure 3) of poly(DHDPATB) obtained in THF exhibit characteristically broad absorption bands at 400–600 nm which are due to the $\pi \rightarrow \pi^*$ transition of conjugated polyene. Extensive conjugation shifts its electronic spectrum to a longer wavelength.

The absolute values of molecular weights and polydispersity were difficult to determine for this system because of its polyelectrolyte nature and the intense color of its solution. Therefore, relative values were estimated by inherent viscosity and UV–visible spectra data and are given in Table 1.

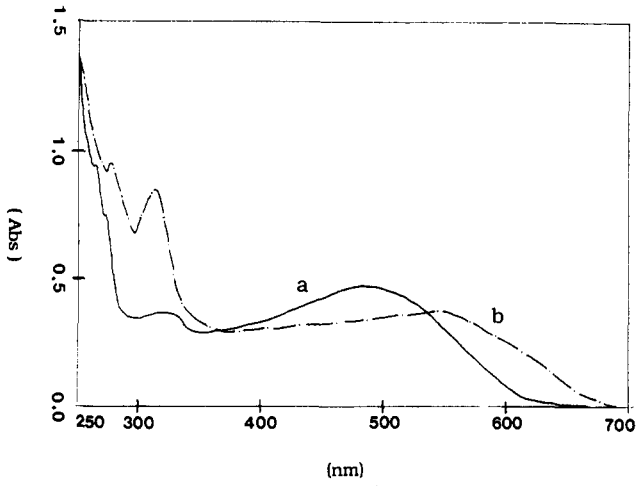


Figure 3. UV-visible spectra of poly(DHDPATB) in THF solution: (a) $MoCl_5$ (exp no. 3); (b) WCl_6–$EtAlCl_2$ (exp no. 9).

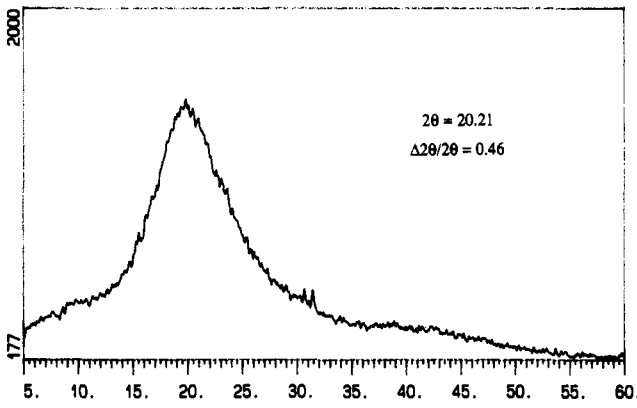


Figure 4. X-ray diffractogram of poly(DHDPATB) [sample: exp no. 3 in Table 1; scanning rate = 4°/min].

In spite of its ionic nature, the present polymer is insoluble in highly polar solvents such as methanol and ethanol, a behavior of which is in contrast to those of poly(DHDPAB) and poly(DHDPAT), but soluble in moderately polar organic solvents such as chloroform, THF, methylene chloride, acetone, DMF, etc. The present ionic polymer is found to be less hygroscopic than those containing bromide and tosylate counterions.

Similar to those of poly(DHDPAB) and poly(DHDPAT), the X-ray diffractogram (Figure 4) indicates that the present ionic polymer is amorphous and the DSC thermogram confirms the absence of crystallinity.

The poly(DHDPATB) is environmentally stable: there is no observable change in IR, NMR and UV-visible spectra upon exposure to air for 3 weeks. This stability, reluctance for the backbone toward air oxidation, is thought to be due to the positive charge in the neighborhood of the conjugated backbone.

Since the polymer film cast from THF solution is brittle and could not be used to measure electrical conductivity, we prepared a tough, free-standing film by blending the polymer with poly(vinyl chloride) (PVC) in acetone and THF cosolvent.[17] The blended polymer films exhibited poor electrical conductivity in their undoped state ($<10^{-10}$ S/cm). We measured the conductivity after the samples were pumped under a high vacuum over a long period of time (12 h), and, therefore, the contribution of polyiodide anions to the conductivity of the iodine-doped polymers should be negligible. When we studied the effects of dilution in blend conductivity to estimate the intrinsic conductivity of poly(DHDPATB), we observed a leveling off of the conductivity (0.5×10^{-3} S/cm) at over 40% for poly(DHDPATB) in blends with PVC, in which the extent of doping determined by the weight uptake method was about 0.32 in a mole ratio of I_2 to the repeating unit of poly(DHDPATB).

The presently described metathesis polymerization provides a relatively simple route for the synthesis of a new class of conjugated ionic polyacetylenes highly soluble in common organic solvents. Work is continuing on the design and synthesis of a new type of antipolyelectrolyte, poly(sulfobetaines) with the present conjugated backbone. Due to their π-electron conjugation, these materials could be of considerable interest especially in their possible third-order nonlinear optical susceptibilities (χ^3).

References and Notes

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