

Synthesis and properties of poly(dipropargyl-16-crown-5)

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Received: 12 December 1995/Revised version: 8 January 1996/Accepted: 10 January 1996

Summary

We have synthesized a polyacetylene derivative, poly(dipropargyl-16-crown-5), through the cyclopolymerization of the corresponding monomer by metathesis catalysts. The polymer containing crown-ether units was characterized by spectroscopic and thermal techniques. The polymer structure is believed to be a cyclized form with both five- and six-membered rings. The polymer exhibits high cation-binding properties and ionochromic effects. The order of the selectivity of alkali-metal cations for both the monomer and the polymer was found to be $\text{Na}^+ > \text{K}^+ > \text{Li}^+$ and the polymer shows the largest red shift by approximately 40 nm in λ_{max} for Na^+ .

Introduction

Various classes of crown ethers attached to backbones of polymers have been of special interest due to their selective ionic binding on complexes with metal cations. Most of the studies have been limited to the flexible vinyl polymers having crown-ether groups on their side chains, such as polystyrenes (1-2), polyacrylates (3-4), and polyethers (5) with potential applications as ion-selective materials of chromatography and phase-transfer catalysis.

In recent years, some attention has been focused on the study of molecular recognition of metal ions (6) and macromolecules (7) by crown ethers and cyclodextrins, respectively. In particular, π -conjugated polymers such as polypyrroles (8-9) and polythiophenes (10-11) functionalized with crown-ether were extensively investigated to explore the ion-selective electrodes and sensory materials. It is very interesting that these conducting polymers showed ion complexation as well as a real-time chemoresistive response on the electrochemistry (6). The selective binding of the polymers with cations in the different conductive states would allow the modulation or switching of the ion-transport behavior of the conjugated materials. Additionally, Swager et al. reported the syntheses and characteristics of various polythiophenes containing crown-ether moieties

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which exhibit an ionochromic activity (12). To our knowledge, however, there is only one report in the literature concerning polyacetylene containing the crown ether as a conducting polymer to study characteristics of the ion binding and molecular recognition (13).

In this paper, we describe the results on the preparation and properties of a novel class of a polyacetylene derivative containing crown-ether moiety, poly(dipropargyl-16-crown-5), which is obtained from cyclopolymerization of the corresponding monomer with metathesis catalysts.

Experimental

Materials

Propargyl bromide (Aldrich Chemical Co., 80 wt.% solution in toluene) was dried over calcium hydride and fractionally distilled before use. Tungsten (VI) and molybdenum (V) chlorides (Aldrich Chemical Co., resublimed, 99.9 %) were used without further purification. Ethylaluminum dichloride (Aldrich Chemical Co.) was used as received, and tetrabutyltin was distilled under reduced pressure. All solvents and other chemicals used were a reagent grade and purified by ordinary methods (14). Diethyl dipropargylmalonate was prepared by the reaction of diethyl malonate with propargyl bromide as described in the literature (15).

Preparation of 4,4-Bis(hydroxymethyl)-1,6-heptadiyne (I)

To a suspension of lithium aluminum hydride (8.83 g, 0.22 mol) in 300 ml of diethyl ether cooled in an ice-water bath was added dropwise a solution of diethyl dipropargylmalonate (33.0g, 0.14 mol) in 80 ml of diethyl ether over a period of 1h. After the addition, the cooling bath was removed and the reaction mixture was stirred for additional 24h at room temperature. The reaction mixture was then cooled in an ice-water bath and excess of lithium aluminum hydride was destroyed by a slow addition of water until it turned into a white granular solid. The reaction mixture was filtered and dried over anhydrous magnesium sulfate. The ether was removed in vacuo to give white cakes that were purified by recrystallization from ether (18.3g, 0.12mol, 86%), mp 80~81°C: ^1H NMR δ 3.69 (s, 4H, OCH_2), 2.55 (s, 2H, OH), 2.34 (d, 4H, CH_2), 2.01 (t, 2H, $\equiv\text{CH}$); ^{13}C NMR δ 80.1 ($-\text{C}\equiv$), 71.0 ($\equiv\text{CH}$), 66.3 (OCH_2), 42.0 (C_{quat}), 21.6 ($\text{CH}_2\text{C}\equiv$). Anal. Calcd for $\text{C}_9\text{H}_{12}\text{O}_2$: C, 71.03; H, 7.95. Found: C, 71.01; H, 7.99.

Preparation of Dipropargyl-16-crown-5 (II)

A mixture of 4,4-bis(hydroxymethyl)-1,6-heptadiyne (7.6g, 50 mmol) and 1,2-bis(2-bromoethoxy)ethane (16g, 50 mmol) dissolved in 15ml of tetrahydrofuran(THF) was added dropwise to a mixture of 250ml of hexane and 50wt% of aqueous sodium hydroxide (16g, 0.4mol) containing 0.2g of tetrabutylammonium hydrogen sulfate(TBAH) at room temperature over a period of 3h. The reaction mixture was stirred for 12h and then refluxed

for 1h. The organic layer was isolated and dried over anhydrous magnesium sulfate. The volatile components were removed in vacuo to afford viscous oil, which was crystallized from cold hexane to yield a white solid (3.8g, 12 mmol, 24%), mp 58–59°C: ^1H NMR δ 3.60 (m, 16H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.49 (s, 4H, OCH_2), 2.34 (d, 4H, CH_2), 1.94 (t, 2H, $\equiv\text{CH}$); ^{13}C NMR δ 80.8 ($-\text{C}\equiv$), 71.8 ($\equiv\text{CH}$), 70.3–70.7 (OCH_2), 41.7 (C_{quat}), 21.5 ($\text{CH}_2\text{C}\equiv$). Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_5$: C, 65.81; H, 8.39. Found: C, 65.70; H, 8.42.

Instruments and Measurement

^1H - and ^{13}C -NMR spectra were recorded with the use of a Bruker AM-300 spectrophotometer and chemical shifts were reported in a ppm unit with tetramethylsilane as the internal standard. The spectra were obtained in CDCl_3 at 25°C unless otherwise noted. Infrared spectra were measured as KBr pellets on a Bomem MB-100 spectrometer, and frequencies were given in reciprocal centimeter. A Hewlett Packard HP 8452A diode array spectrophotometer was used for UV-VIS spectral data. The number average molecular weight (\overline{M}_n) and polydispersity were determined using THF as an eluent by a Waters GPC-150C calibrated with polystyrene standards. Elemental analysis was performed with a Carlo Erba EA 1108 Elemental Analyser. Thermal analysis was carried out on a Dupont TGA 9900 thermogravimetric analyzer in nitrogen atmosphere at the heating rate of 10°C/min. Electrical conductivity was measured with an Ando AG-4303 LCR meter by the four-point probe method.

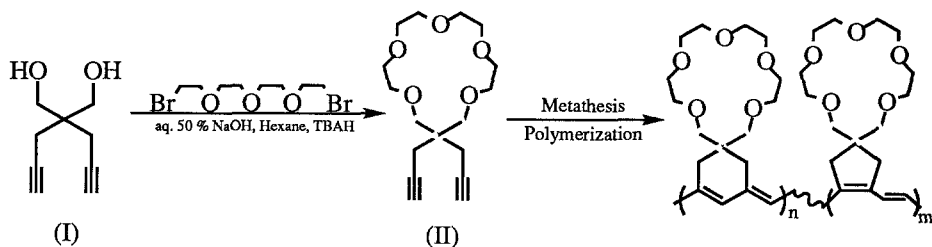
Polymerization

All procedures for the preparation of the catalyst system and polymerization were carried out under dry nitrogen atmosphere. Transition metal halides and organometallic compounds were dissolved in appropriate solvents to make 0.1M solutions before use. A typical polymerization procedure was as follow: solvent, catalyst solution, and when needed, cocatalyst solution were injected in the order given into a 20-ml ampule equipped with a rubber septum. When the cocatalyst was used, the catalyst system was aged at 30°C for 15 min prior to the use. Finally, the monomer dissolved in the same solvent was injected into the polymerization ampule. After the reaction mixture was allowed to react at 60°C for 24h, the polymerization was terminated by adding a small amount of methanol. The resulting mixture was dissolved in chloroform and precipitated in a large excess of hexane. The precipitated polymer was filtered from the solution and then dried under vacuum at 40°C for 24 h. The polymer yield was determined by gravimetry.

Results and Discussion

The crown ether monomer, dipropargyl-16-crown-5 (II), was synthesized by the reaction of 4,4-bis(hydroxymethyl)-1,6-heptadiyne (I) and 1,2-bis(2-bromoethoxy)ethane in the presence of the phase-transfer catalyst (TBAH). Scheme 1 outlines the synthesis

Scheme 1



route of the monomer and the cyclopolymerization of the monomer in the transition metal catalyst system.

In general, it has been known that the classical metathesis catalyst systems such as WCl_6 - and MoCl_5 -based catalysts would not tolerate functionalities of monomers, which resulted mostly in low molecular weight or insoluble polymers (16). However, the polymerization of the present monomer with a high concentration of oxygen proceeded well to give high molecular weight and soluble polymers. MoCl_5 -based catalysts were used because their catalytic activities were known to be greater than those of WCl_6 -based catalysts for the polymerization of highly functionalized dipropargyl monomers (17). The polymerization results are summarized in Table 1. High polymer yields with number

Table 1. Polymerization of Dipropargyl-16-crown-5 with Various Transition Metal Catalysts^a

Expt. No.	Catalyst System (mole ratio)	Solvent	Polym. Yield ^b (%)	\bar{M}_n ($\times 10^{-3}$) ^c	\bar{M}_w / \bar{M}_n
1	MoCl_5	Chlorobenzene	94	22.2	3.6
2	MoCl_5	Dioxane	87	16.5	3.1
3	$\text{MoCl}_5/\text{EtAlCl}_2$ (1:4)	Chlorobenzene	93	21.6	3.3
4	$\text{MoCl}_5/\text{EtAlCl}_2$ (1:4)	Dioxane	85	18.4	2.7
5	$\text{MoCl}_5/(\text{n-Bu})_4\text{Sn}$ (1:4)	Chlorobenzene	91	19.1	3.6
6	$\text{MoCl}_5/(\text{n-Bu})_4\text{Sn}$ (1:4)	Dioxane	87	13.4	3.2

a : Polymerization was carried out at 60°C for 24h. Initial monomer concentration and monomer to catalyst mole ratio were 0.25M and 50, respectively. b : Hexane-insoluble polymer. c : Values were obtained by GPC analysis with polystyrene standards calibration.

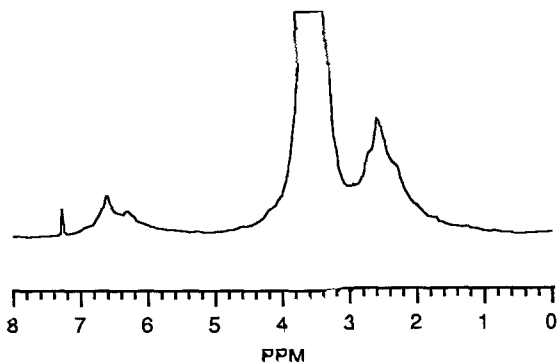


Figure 1. $^1\text{H-NMR}$ Spectrum of the Polymer in CDCl_3

average molecular weight (\overline{M}_n) of a range of $1.3\text{--}2.2 \times 10^4$ with a calibration of polystyrene standards were obtained. The resulting polymers were highly soluble in various organic solvents such as chloroform, THF, and dioxane to be cast on glass plates to give reddish thin films.

It was observed that the IR spectrum of the polymer showed absorption neither at 3261 nor at 2112 cm^{-1} which were expected to be present for the stretching vibration bands of acetylenic carbon-hydrogen and carbon-carbon triple bonds of the monomer, respectively. The development of the characteristic stretching vibration band of a conjugated double bond was clearly identified at 1634 cm^{-1} . The $^1\text{H-NMR}$ spectrum of the polymer (expt. No. 1 sample) is shown in Figure 1. As the polymerization proceeded, the sharp acetylenic proton peak of the monomer at 1.94 ppm disappeared and new multiple-vinyllic proton peaks appeared in the range of $6.0\text{--}7.0\text{ ppm}$. Also, in the $^{13}\text{C-NMR}$ spectrum (Figure 2),

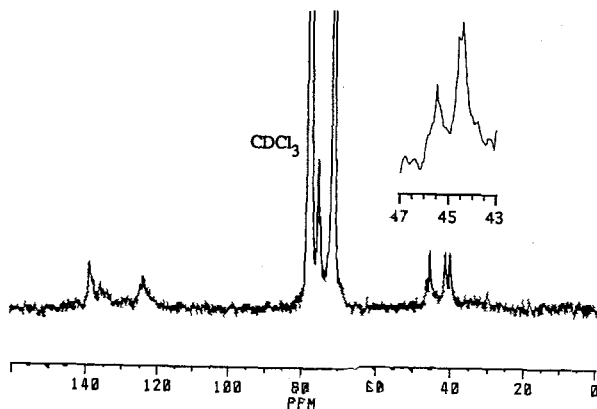


Figure 2. $^{13}\text{C-NMR}$ Spectrum of the Polymer in CDCl_3

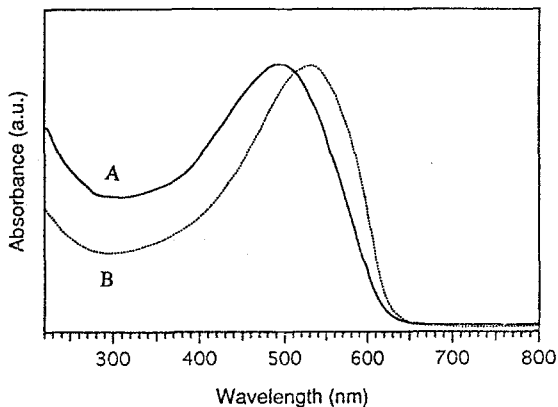


Figure 3. UV-Visible Spectra of the Polymer (A) and the Polymer / 0.1M NaClO₄ (B) in Acetonitrile.

the polymer shows no acetylenic carbon peaks at 71.8 and 80.8 ppm while the monomer gave these peaks. The peaks around 70.5 ppm are assigned to carbons from the ethylene oxide unit. Instead, there are several olefinic carbon peaks in the range of 120~140 ppm, which proves the presence of the conjugated polyene. The major peaks at 44.5 and 45.5 ppm can be assigned to quaternary carbons of five- and six-membered rings, respectively. By determination of the ratio based on the literature (18), the amount of the five-membered ring is about 65% and the major resonance was found at approximately 44.5 ppm. It was observed that UV-VIS spectrum (Figure 3) of the polymer in acetonitrile exhibits the characteristic broad absorption peak at 350~640 nm ($\lambda_{\text{max}} = \text{ca.} 494 \text{ nm}$), which should be due to the $\pi\text{-}\pi^*$ transition of the conjugated polyene.

Since it has been known that crown ether possesses the selective cation binding property, extraction of an alkali-metal ion such as Li⁺, Na⁺, or K⁺ was carried out by the similar method described in the literature (19). The extraction results by both the monomer and the corresponding polymer are shown in Table 2. It is interesting to note that the enhanced extraction is to occur considerably for Na⁺. The order of the selectivity of alkali-metal cations for both the monomer and the polymer was found to be Na⁺ > K⁺ > Li⁺. It has been also known that ionochromic effect was observed in crown-ether containing conjugated polymers such as polythiophenes, which showed large shifts in λ_{max} with the appropriate metal ions and so dramatic a color change (12). In our system, the polyacetylene derivative with the crown-ether moiety also displayed the ionochromic effect as shown in Table 3.

As expected from the binding preferences of its crown-ether analogue, the polymer shows the largest red shift in the absorption for Na⁺ with the largest change of approximately 40 nm (Figure 3) and significant shifts also for K⁺ and Li⁺, which may

Table 2. Extraction of the alkali metals by monomer and polymer (%)^a

Sample	Li ⁺	Na ⁺	K ⁺
Monomer	4.9	19.9	14.8
Polymer ^b	6.1	21.0	17.5

a : % extraction = $(1 - C / C_0) \times 100$ normalized to 100mg of the samples, where C and C₀ are concentrations of ions in solution after and before extraction, respectively. b: expt. No.1 sample.

be attributed to a change in the conformation of the conjugated polymer backbone because of complexation of the crown-ether units with the ions (20). It was found that the solubility of the polymer in acetonitrile was enhanced by an addition of a metal salt such as LiClO₄, NaClO₄ or KSCN, which should be a similar behavior to the polythiophene analogue (21). On the other hand, the TGA thermogram under a nitrogen atmosphere showed that the polymer was stable up to 210°C and the electrical conductivity when doped with I₂ at room temperature was found to be 10⁻³S/cm. Further investigations of this polymer and its homologues will be done to explore electrochemical behavior as well as ion binding properties.

Table 3. Ionochromic Response of Polymer as Red Shift^a

Sample	λ_{\max} (nm)	$\Delta \lambda_{\max}$ (nm)		
		Li ⁺	Na ⁺	K ⁺
Polymer ^b	494	28	40	32

a: Ionochromic effects were measured in 0.1M metal-salt solutions in acetonitrile by UV-Visible spectroscopy. b: expt. No.1 sample.

Acknowledgments We gratefully acknowledge the support of this work by KIST with Grant 2N13662 and 2N1231C.

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