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Notes

Synthesis of Poly(1,6-heptadiyne) Derivatives Containing Bulky Substitutents by Metathesis Polymerization

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Abstract: Poly(1,6-heptadiyne) derivatives with phenoxy and 3,7-dimethyloctyloxyphenoxy substituents were synthesized using metathesis polymerization. Polymerizations using $MoCl_5$ as the sole catalyst gave high yields and the resulting polymers were completely soluble in organic solvents. The polymers' structures and thermal properties were characterized using NMR and UV-Vis spectroscopy, as well as with TGA and DSC thermograms. From the analysis of the high-resolution ^{13}C-NMR spectra, we was found that these polymers contain six-membered rings. The number-average molecular weights and polydispersities of the polymers were ca. 7.0~20 $\times 10^3$ and 3.1~5.8, respectively. The glass transition temperatures of the polymers were found to be in the range 91~159 °C.

Keywords: polyacetylene, poly(1,6-heptadiyne), metathesis polymerization, six-membered ring, conductivity.

Introduction

Since the discovery of soluble polyacetylene derivatives,[1-3] there has been a lot of interest in the synthesis and applications of poly(1,6-heptadiyne) derivatives owing to their electrical conductivity,[4] nonlinear optical properties,[5] potential use as electroluminescence emitting materials,[6] as well as in other electronic applications. Among the π-conjugated polymers, polyacetylene is structurally one of the simplest π-conjugated polymers. However, polyacetylene and its derivatives have several drawbacks in that they are typically insoluble and not fusible, and exhibit undesirable mechanical properties such as oxidation in air and poor thermal stability.[7] Among the various acetylenic monomers, 1,6-heptadiyne and its homologs are known to produce π-conjugated polymers that promise to solve these problems, because of the facile introduction of various substituents at the 4-position of 1,6-heptadiyne.[8-10]

In this article, we report the synthesis, cyclopolymerization, and characterization of a novel class of π-conjugated polymers with a 1,6-heptadiyne backbone and bulky pendant group substituents. The presence of alkyloxyphenoxy substituents on the 1,6-heptadiyne polymer backbone induces unique properties, which include good flexibility, solubility, and facile control of optical properties. The characterization and physical properties of the resulting polymers are also discussed.

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Experimental

Synthesis of 3-(3,7-Dimethyloctyloxy)phenol. In a 250 mL three-neck flask, resorcinol (8.80 g, 80 mmol), KOH (1.32 g, 20 mmol), 1-bromo-3,7-dimethyloctane (3.53 g, 16 mmol), and a catalytic amount of KI were dissolved in 150 mL of methanol and heated to reflux for 24 hr with stirring. After confirmation of the appearance of a new peak on a TLC plate, the reaction mixture was cooled to room temperature, poured into an excess of water, then extracted with ether. The combined organic layers were washed several times with water, dried over anhydrous $MgSO_4$, and then filtered. The crude product was purified by column chromatography on silica gel using a hexane and ethylacetate (10 : 1) mixture as an eluent to give 3-(3,7-dimethyloctyloxy)phenol (2.80 g, 70%). ^1H-NMR ($CDCl_3$): δ (ppm) 0.9-1.8 (m, 19H, $-CH_3$ and CH_2-), 3.9 (t, 2H, $-OCH_2$-), 6.4-6.5, and

7.05-7.15 (m, 4H, aromatic protons).

Synthesis of 1-[3-(3,7-Dimethyloctyl)oxy]phenyldipropargyl Acetate (DMOPhDPA). Dipropargyl acetyl chloride was prepared as described in the literature.[11] Under a nitrogen atmosphere, a flask was charged with a THF solution (30 mL) of 4-(3,7-dimethyloctyloxy)phenol (2.83 g, 11.3 mmol), and triethylamine (1.52 g, 15.0 mmol) was added to the reaction solution at room temperature. After completion of the addition, a mixture of dipropargyl acetyl chloride (1.55 g, 10.0 mmol) and THF (30 mL) was slowly added dropwise at 0 °C for 30 min. The reaction mixture was then stirred at room temperature for 24 hr. Water was added and the reaction mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and then the residual solvent was removed by evaporation. The crude product was recrystallized with methanol to give DMOPhDPA (2.9 g, 80%). ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.9-1.75 (m, 19H, -CH_3 and -CH_2- at alkyl chain), 2.1 (t, 2H, ≡ CH), 2.75 (m, 4H, -CH_2-), 3.0 (m, 1H, -CH), 3.95 (t, 2H, -OCH_2-), 6.7, 6.8, and 7.3 (m, 4H, aromatic protons).

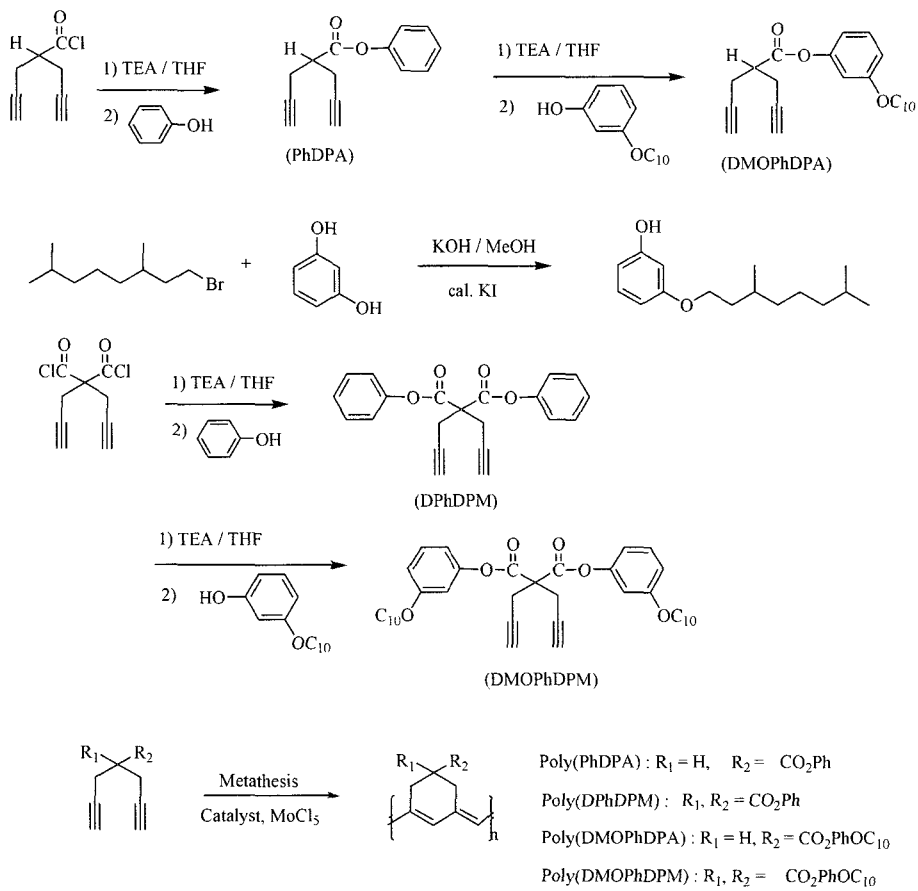
Other dipropargyl monomers such as phenyldipropargyl acetate **(PhDPA)**, diphenyldipropargyl malonate **(DPhDPM)**, and bis[(3-(3,7-dimethyloctyl)oxy)phenyl]dipropargyl malonate **(DMOPhDPM)** were prepared using the same procedure as described for the preparation of DMOPhDPA.

Results and Discussion

To investigate these polymerizations, and to improve the physical properties of the 1,6-heptadiyne derivatives, we introduced both single and paired phenoxycarbonyl and 3,7-dimethyloctyloxyphenoxycarbonyl substituents at the 4-position of the 1,6-heptadiyne unit. Scheme I illustrates the synthesis of the monomers and the corresponding polymers.

Diethyldipropargyl malonate (DEDPM), dipropargyl malonyl dichloride, and dipropargyl acetyl chloride were synthesized as described in the literature.[1,8] The monomers were synthesized using the reactions of the corresponding acid chlorides of dipropargyl malonic acid and dipropargyl acetic acid with phenol or 3,7-dimethyloctyloxyphenol in the presence of triethylamine and THF as the solvent.

The polymerizations of these dipropargyl monomers were carried out using a molybdenum-based catalyst.[11,12] Polymerization results for these monomers are summarized in Table I. The use of $MoCl_5$ as the sole catalyst polymerized effectively the dipropargyl malonate and dipropargyl acetate



Scheme I. Synthetic routes for the monomers and polymers.

Table I. Polymerization of the Dipropargyl-Based Monomers by $MoCl_5$ Catalyst

Exp. No.	Monomers	$[M]_o$[a]	Solvent	Time (hr)	P.Y.[b] (%)	M_n ($\times 10^3$)	M_w/M_n	TGA[c] (°C)	DSC (°C)
1	PhDPA	0.25	THF	1	87	7.0	5.8	276	91
2	DPhDPM	0.25	THF	24	91	9.0	3.1	270	88
3	DMOPhDPA	0.125	1,4-Dioxane	10	85	20	4.0	235	122
4	DMOPhDPM	0.125	1,4-Dioxane	1	83	13	3.7	290	159

[a]Initial monomer concentration. [b]Polymer yield. [c]5 % Weight loss.

derivatives containing phenyl or 3,7-dimethyloctyloxyphenyl substituents and resulted in high polymer yields. We used THF or 1,4-dioxane as the polymerization solvent because they are known as effective solvents for the polymerization of dipropargyl monomers. The polymerization of PhDPA proceeded rapidly within 1 hr; further polymerization resulted in partially insoluble polymers. In contrast, as the polymerization time was relatively increased, the polymer yield of poly(PhDPA) was increased and poly(DPhDPM) has higher degree of polymerization than poly(PhDPM).

The polymerizations of DMOPhDPA and DMOPhDPM were carried out in 1,4-dioxane, which is widely used instead of THF in metathesis polymerizations. It is thought that the high catalytic activity of $MoCl_5$ in the cyclopolymerizations of these dipropargyl monomers implies that the $MoCl_5$ catalyst is activated by the oxygen atoms of the monomers. It has been known that acetylenic protons and oxygen atoms activate $MoCl_5$ in the polymerization of acetylenic monomers.[13-15] The polymer yields and the number average molecular weights of the resulting polymers were in the ranges 83~91% and 7.0~20 $\times$ 10^3 respectively.

The polymers arising from the dipropargyl malonate derivatives with 3,7-dimethyloctyloxyphenyl substituents exhibited better solubility in various organic solvents than those arising from dipropargyl acetate with phenyl substituents. The presence of the dimethyloctyloxy group on the phenyl ring of the repeating unit enhances the solubility and processability of the polymer due to its plasticizing effect on the interaction between the polymer main chains. Poly(DPhDPM) and poly(DMOPhDPM) were easily spun cast onto glass substrates to give dark violet and shiny thin films. The molecular structures of the monomers and the corresponding polymers were obtained with ^{1}H-, ^{13}C-NMR, and UV-Vis spectroscopies. In the ^{1}H-NMR spectra of DMOPhDPM, the acetylenic proton peaks at 2.1 ppm disappeared and new vinylic proton peaks of poly(DMOPhDPM) appeared in the region of aromatic proton peaks. The broad peaks at 2.9~3.9 ppm were assigned to the methylene protons of the π-conjugated cyclic polymers. The polymer microstructure can be determined by examining the resonances of the carbonyl carbon atoms.[16,17] It has been reported that the two clusters of resonances for the carbonyl carbon atoms in poly(DEDPM) can be assigned to carbonyl carbons in five-membered rings (172.0 ppm) and six-membered rings (170.8 ppm) respectively. As shown in Figure 1 (^{13}C-NMR, $CDCl_3$, 500 MHz), there are no peaks at 172.0

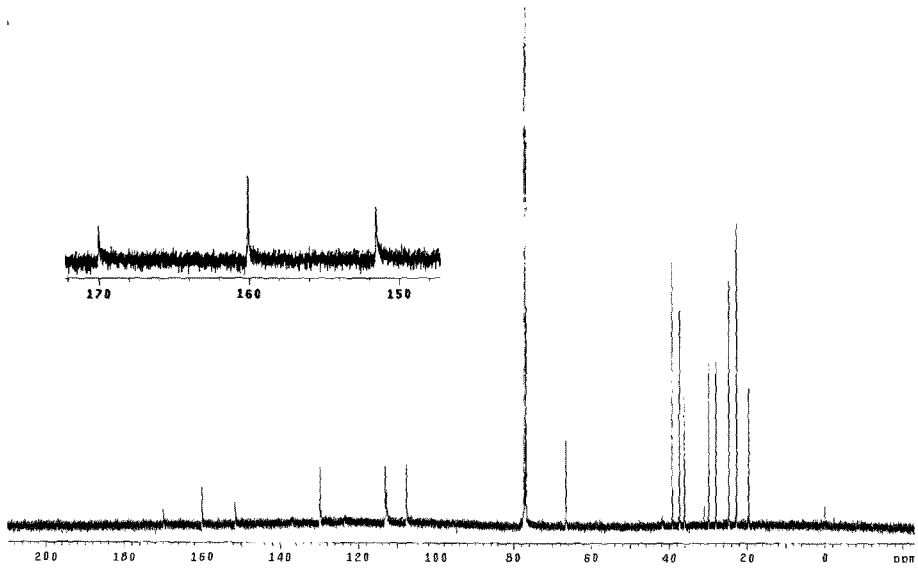


Figure 1. ^{13}C-NMR spectrum of the poly(DMOPhDPM) in $CDCl_3$.

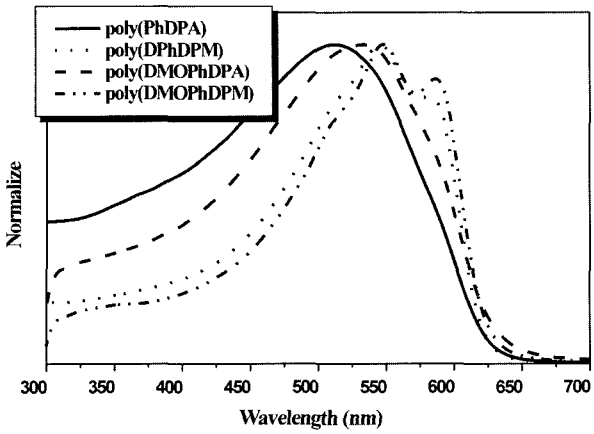


Figure 2. UV-Visible spectra of the polymers in chloroform solution.

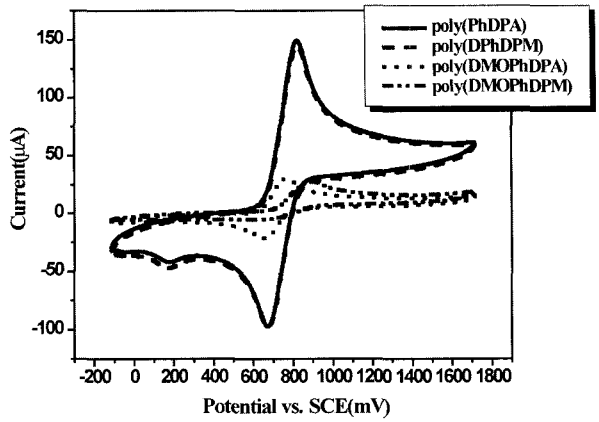


Figure 3. Cyclic voltamograms of the polymer thin films on the glassy carbon disk electode (measured in DMF solution of Et4NBF4 (0.1 M) at a scan rate of 100 mV/s, referenced vs. Ag/AgCl).

ppm that could correspond to the carbonyl carbon atoms of five-membered ring moieties. However, there is one peak at 170 ppm corresponding to carbonyl carbon peaks. From these results, we conclude that poly(DMOPhDPM) predominantly consists of six-membered ring moieties, because of less steric hindered α-addition pathway.[16]

Figure 2 shows the UV-Visible absorption spectra of the polymers in chloroform solution. Poly(dipropargyl acetate) which has phenyl and dimethyloctyloxyphenyloxy substituents exhibited characteristic absorption peaks at 512 and 534 nm. However, poly(dipropargyl malonate)-based polymers exhibited a maximum absorption peak at a longer wavelength, 547 nm with a shoulder at 583 nm. The band gaps (taken from the onset of the absorption spectrum) of the polymers were found to be in the range 1.95~1.99 eV. The band gaps of poly(dipropargyl malonate) derivatives are larger than those of the poly(dipropargyl acetate)s. The introduction of two substituents at the 4-position of the polymer backbone shortens the effective conjugation length of the doubly substituted polymers with respect to that of the singly substituted polymer, because in these polymers there is more steric hindrance between the polymer backbones.

The thermal stabilities and glass transition temperatures of the polymers were investigated using TGA and DSC thermograms, and the results are summarized in Table I. The onset temperature of 5% weight loss of poly(DMOPhDPM), which has bulkier substituents, was found to be about 290 °C under a nitrogen atmosphere. The thermal stabilities of the poly(dipropargyl malonate) derivatives are higher than those of the poly(dipropargyl acetate) derivatives, and this is probably due to the rigidity and symmetry of the former polymers structures.

Figure 3 shows the cyclic voltammograms of the polymers. Thin films of the polymers were prepared by solution casting onto glassy carbon electrodes. The resulting thin films exhibited reversible electrochemical behavior between the doping and undoping peaks. The current of the phenoxy substituent are higher than those of 3,7-dimethyloctyloxyphenoxy substituent into the poly(dipropargyl acetate) and poly(dipropargyl malonate) derivatives. From these results, we postulate that the electrical conductivities of the poly(1,6-heptadiyne) derivatives with phenoxy substituents are higher than those of the poly(1,6-heptadiyne) derivatives with 3,7-dimethyloctyloxyphenoxy substituents. The highly ordered polymer backbones with phenoxy substitutents is attributed to the higher electrical conductivity compared to sterically hindered 3,7-dimethyloctyloxy phenoxy substitutents as a pendant group.

In summary, we have investigated the polymerizations of 1,6-heptadiyne homologues with a transition metal catalyst. The use of $MoCl_5$ as sole catalyst easily polymerized these 1,6-heptadiyne derivatives with substituents of different sizes to give the corresponding π-conjugated cyclopolymers in high yields. The resulting polymers were completely soluble in common organic solvents and easily cast as shiny metallic thin films. The resulting polymers showed reversible doping and undoping behavior.

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