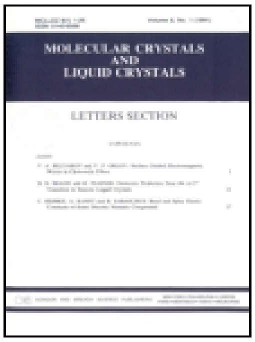

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A Polyacetylene via the Cyclopolymerization of 4,10-Bis(diethylmalonate)-1,6,11-dodecatriyne: Synthesis and Characterization

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A new class of polyacetylene was synthesized via the cyclopolymerization of 4,10-bis(diethyl malonate)-1,6,11-dodecatriyne by using $MoCl_5$-$EtAlCl_2$ catalyst system. The polymerization proceeded in mild homogeneous manner to give 32% yield of polymer. The chemical structure of resulting polymer was characterized by NMR (^1H-, ^{13}C-), IR, and UV-visible spectroscopies to have a conjugated backbone system. The polymer showed characteristic wide UV-visible absorption band and PL maximum peak at 530 nm corresponding to the photon energy of 2.34 eV. The cyclic voltammogram of polymer showed the stable electrochemical window in the range of of $-1.50V$ to $+1.50V$. From the CV measurements, the HOMO energy level of the polymer was calculated to be 5.55 eV.

Keywords polyacetylene; cyclopolymerization; non-conjugated triyne; photoluminescence; cyclic voltammetry

Introduction

The conjugated polymers with rich π–electrons have stimulated key notice owing to the fundamental advantages over the saturated polymers. These polymers have such unique properties as electrical conductivity, photoconductivity, low-energy optical transitions, high electron affinity, chemical reactivity and complex formation ability, high gas permeability, and high nonlinear optical susceptibility [1–10].

The incorporation of various substituents to acetylene and their subsequent polymerization by using effective polymerization methods yielded the corresponding conjugated organic materials with the designed peculiar properties [1,11–13]. Among the various conjugated polymers obtained from acetylenic monomers, poly(1,6-heptadiyne) and its homologues are the powerful candidate of π-conjugated backbone material because these

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polymers can improve the solubility and oxidative stability of acetylenic polymers by the introduction of functional substitutents at 4-position of 1,6-heptadiyne [2,3,14–22].

In this article, we report the synthesis of a novel class of polyacetylene with two cyclic recurring unit by the double ring-forming cyclopolymerization of a triyne monomer, 4,10-bis(diethyl malonate)-1,6,11-dodecatriyne, and the characterization of polymer properties.

Experimental

Materials

Diethyl malonate (Aldrich Chemicals., 99%) and 1,4-dichloro-2-butyne (Aldrich Chemicals., 99%) were used as received. Propargyl bromide (Aldrich Chemicals., 80 wt% solution of toluene) was dried with CaH_2 and distilled under reduced pressure. $MoCl_5$ (Aldrich Chemicals, 99.9+%) and $EtAlCl_2$ [Aldrich Chemicals, 25 wt.% (1.8 M) solution in toluene] were used without further purification. The catalyst solutions of $MoCl_5$ and $EtAlCl_2$ were prepared in 0.1 M and 0.2 M chlorobenzene solutions, respectively.

1,4-Bis(diethyl malonate)-2-butyne

Diethyl malonate (38.64 g, 0.242 mol) was added to the absolute ethanol (200 mL) containing sodium ethoxide (from sodium metal, 5.55 g, 0.242 mol). After 10 min, 1,4-dichloro-2-butyne (12.87 g, 0.11 mol) was slowly added to this solution to keep the reaction temperature below the 60°C. The reaction mixture was stirred in this temperature for overnight. After cooled down to room temperature, the acidic water was added to the reaction mixture, and organic layer was extracted three times with ethyl acetate. The solution was concentrated by evaporating the solvent after drying the solution with an anhydrous $MgSO_4$. The crude product was purified by a vacuum distillation. Yield = 47%; bp = 163°C/0.1 mmHg.

1,4-Bis(diethyl malonate)-1,6,11-dodecatriyne (BDMDT)

1,4-Bis(diethyl malonate)-2-butyne (7.0 g, 18.9 mmol) diluted in 150 mL THF was slowly dropwise to the dispersed NaH (6.75 g, 0.169 mol) in 300 mL THF solution. Propargyl bromide (4.76 g, 40.01 mmol) was slowly added to this reaction mixture. The reaction mixture was stirred at room temperature for 24 h, and then poured into a large excess of water. Organic layer was extracted three times with ethylacetate. The solution was concentrated by evaporating the solvent after drying the solution with an anhydrous $MgSO_4$. The crude product was recrystallized with hexane. Yield = 26%; mp = 44°C. ^{1}H-NMR (δ, ppm, $CDCl_3$): 1.21 (t, 12H), 1.97 (t, 2H), 2.91 (d, 8H), 4.21 (q, 8H). ^{13}C-NMR (δ, ppm, $CDCl_3$): 13.9 ($-CH_3$), 22.3, 22.7 ($-CH_2-$), 56.3 (-C-), 61.9 ($-OCH_2-$), 71.4 (terminal acetylene, $\equiv$CH), 77.6 (terminal acetylene, $\equiv$C-), 78.6 (internal acetylene, -C$\equiv$).

Cyclopolymerization of BDMDT

A mixture of $MoCl_5$ (1.12 mL of 0.1 M $MoCl_5$ solution, 0.112 mmol, M/C = 20) and $EtAlCl_2$ (1.12 mL of 0.2 M $EtAlCl_2$ solution, 0.224 mmol, $MoCl_5/EtAlCl_2$ mole ratio = 1/2) is aged at 30°C for 15 min. This catalyst mixture was injected into the monomer (BDMDT, 1.0 g, 2.24 mmol) solution in chlorobenzene (3.0 mL, $[M]_0 = 0.36$ M). The polymerization was carried out at 80°C. After a given time of polymerization, 10 mL of chloroform was added to the polymerization solution. The diluted polymer solution was precipitated into an excess of methanol, filtered from the solution, and then dried under vacuum at 40 °C for 12 hrs. Polymer yield = 32%. ^{1}H-NMR (δ, ppm, $CDCl_3$): 0.80-1.45 (12H, $-CH_3$), 2.22-3.68 (8H, $-CH_2-$), 3.80-4.40 (8H, $-OCH_2-$), 5.80–7.12 (2H, vinylic). ^{13}C-NMR (δ, ppm, $CDCl_3$): 16.1 ppm ($-CH_3$), 42.1 ppm ($-CH_2-$), 61.5 ppm ($-OCH_2-$), 120.2–143.2 (vinylic carbons), 173.1 (carbonyl carbon).

Characterization

NMR spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d_6. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. Vibration transition frequencies were reported in wavenumber (cm^{-1}). The optical absorption spectra were measured by a Shimadzu UV-3100 UV-VIS-NIR spectrometer. The molecular weight and polydispersity of polymers were determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Agilent 1100 series GPC, PL gel 5μm MIXED-C, refractive index detector) in THF solution. The photoluminescence spectra were obtained by a 488 nm Ar laser as an excitation or Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube). The emission signal was collected by using the conventional photoluminescence arrangement of a laser, samples, a cryostat (Air Products 1R02-A displex), a monochromator (Spex 750M), and a photomultiplier (Hamamatsu R943-02). Electrochemical measurements were carried out with a KOSENTECH (KST-P1) instrument (Pt disk electrode, CH_3CN, n-Bu_4NPF_6, sweep rate 20 mV/s). The HOMO energy level was calculated from electrochemical measurements, in particular by using CV with respect to a ferrocene standard.

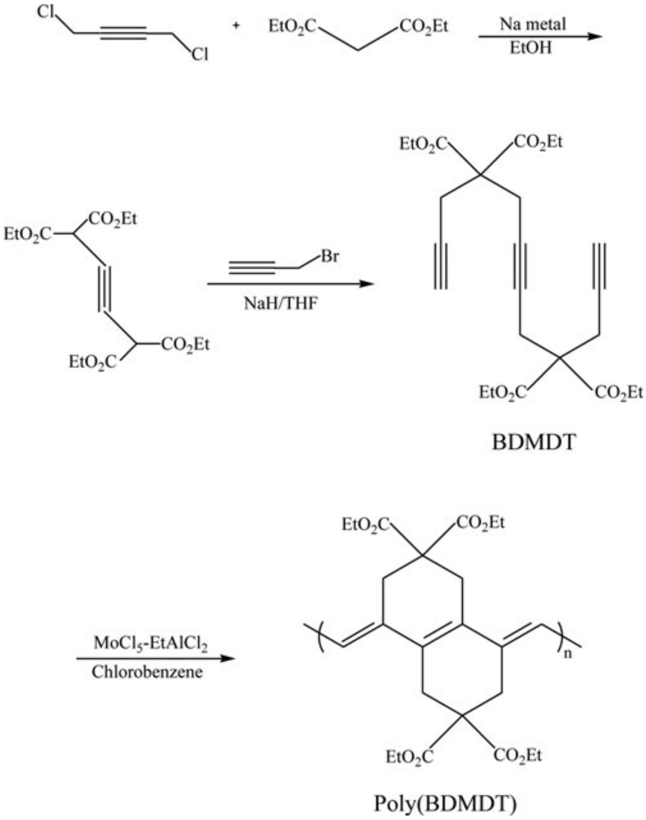
Results and Discussion

Synthetic procedures of BDMDT and poly(BDMDT) is depicted in Scheme 1. 1,4-Bis(diethyl malonate)-2-butyne was prepared by the reaction of diethyl malonate and 1,4-dichloro-2-butyne by using sodium ethoxide in absolute ethanol in 47% yield. The triyne monomer, BDMDT, was prepared by the reaction of 1,4-bis(diethyl malonate)-2-butyne and propargyl bromide by using sodium hydroxide in THF in 26% yield.

The double cyclopolymerization of BDMDT was carried out by using $MoCl_5$-based catalysts (Scheme 1), which had been known to be very effective for the cyclopolymerization of some substituted acetylenes [3, 4,23–25]. $MoCl_5$ alone yielded only low yield of oligomeric products. The $MoCl_5$-$EtAlCl_2$ catalyst system polymerized BDMDT to give the corresponding polymer in 32% yield. The resulting poly(BDMDT) was yellow-orange powder and completely soluble in such organic solvents as chloroform, chlorobenzene, DMF, etc. The number-average molecular weight and polydispersity was 13,200 and 4.5, respectively.

The polymer structure was characterized by NMR, infrared, and UV-visible spectroscopies. In the IR spectrum of poly(BDMDT), it did not show the acetylenic $C{\equiv}C$ bond stretching frequency (2110 cm^{-1}) and the terminal acetylenic $\equiv C-H$ stretching frequeny (3276 cm^{-1}). The strong carbonyl $C{=}O$ stretching frequency peak of polymer was observed at 1780 cm^{-1}. The multi peaks at 2850-2995 cm^{-1} is due to the aliphatic $C-H$ stretching frequencies of methylene and methyl substituents, whereas the strong peak at 1200 cm^{-1} is due to the antisymmetric $C-O-C$ stretching frequency of ester functional groups.

The ^{1}H-NMR spectrum of poly(BDMDT) did not show the acetylenic proton peaks of monomer at 1.97 ppm. Instead, a broad peak due to the vinyl protons of conjugated polymer



Scheme 1. Synthesis of BDMDT and poly(BDMDT).

backbone was newly observed in the range of 5.8–7.1 ppm. The ^{13}C-NMR spectrum of poly(BDMDT) did not show the acetylenic carbon peaks at 71.4, 77.6, and 78.6 ppm. Instead the carbon peaks of the conjugated polyene backbone were in the range of 120.2–143.2 ppm. The carbonyl carbon peak of ester functional groups was observed at 173.1 ppm. The UV-visible spectra and photoluminescence (PL) spectra of poly(BDMDT) were measured. The absorption spectrum starts around 700 nm, which is due to the $\pi \rightarrow \pi^*$ interband transition of these conjugated polymer system. The photoluminescence spectra of poly(BDMDT) showed that the photoluminescence peak is located at 530 nm corresponding to the photon energy of 2.34 eV.

In order to investigate the electrochemical properties of poly(BDMDT), we performed the cyclic voltammetry (CV) experiment. The potentials were referenced to Ag/AgNO$_3$ and the reduction potential of ferrocene/ferrocenium (FOC) under 0.1M n-Bu$_4$NPF$_6$/DMF solution. Typical cyclic voltammogram of poly(BDMDT) is depicted in Fig. 1. It exhibited the irreversible electrochemical behaviors between the doping and undoping peaks. The HOMO energy level was estimated from the onset oxidation data by means of empirical relationship by Leeuw et al. HOMO is equal to -($E^{ox} + 4.8$ eV), where the SCE energy level is -4.8 eV from the vacuum level [26]. From the CV measurements, the HOMO energy levels of the present polymer, was calculated to be 5.55 eV.

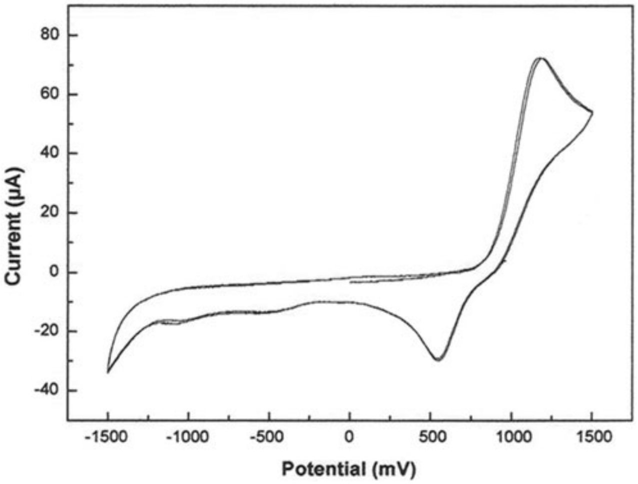


Figure 1. Cyclic voltammograms of poly(BDMDT) at 100 mV/s in 0.1M n-Bu_4NPF_6/DMF solution.

Conclusions

A new conjugated polymer with cyclic recurring unit was synthesized via the ring-forming cyclopolymerization of triyne monomer by transition metal catalyst. The polymerization proceeded in homogeneous manner to give the resulting polymer in 32% yield. Spectral analysis revealed that the poly(BDMDT) have a conjugated backbone system. The photoluminescence spectrum of polymer showed that the photoluminescence peak is located at 530 nm, corresponding to a photon energy of 2.34 eV. This polymer exhibited the irreversible electrochemical behaviors between the doping and undoping peaks.

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