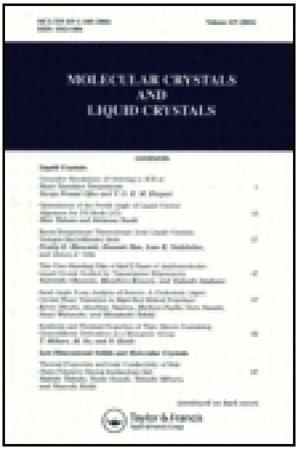

Molecular Crystals and Liquid Crystals

Synthesis and chiro-optical properties of polyacetylene derivative with optically active moieties

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SYNTHESIS AND CHIRO-OPTICAL PROPERTIES OF POLYACETYLENE DERIVATIVE WITH OPTICALLY ACTIVE MOIETIES

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The polymerization of 17α-ethynyltestosterone, an optically active compound, was carried out by such transition metal catalysts as [Rh(nbd)Cl]$_2$, PdCl$_2$, and PtCl$_2$. The polymerization proceeded well to give a high yield of polymer, regardless of the bulky substituents. The polymer structure was identified by various instrumental methods to have a conjugated ionic polymer bearing the corresponding chiral substituents. The magnitude of CD for the polymers was dependent on the catalyst and polymerisation condition used. The Rh-based polymer showed more intense CD signal than those of Pd- and Pt-based polymers

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INTRODUCTION

The conjugated polymer systems are expected to show unique properties such as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [1–3]. Because of these properties, polyacetylene and its homologues have been promising as organic semiconductors [4–8], as membranes for gas separation and for liquid-mixture separation [9], as side-chain liquid crystals [10–13], as materials for chemical sensors [14], and as materials for nonlinear optical property [15–18] and for photoluminescence and electroluminescence properties [19–23]. A number of mono- and di- substituted polyacetylenes has been prepared by the simple linear polymerization of the corresponding acetylene monomers by various catalyst systems [2,3,9,12].

The high functionalities of naturally occurring macromolecules such as proteins and genes arise from their precisely ordered stereostructures. In such systems, the helix is often found among the most fundamental structures of the polymer chain and plays important roles in realizing biological activities [24,25]. The elaboration of synthetic and analytical methods for the preparation and structural analysis of the *cis- and trans*-streoisomers for polyphenylacetylene and other poly(arylacetylene)s enabled the discovery of novel functions and properties that are not exhibited by the same streoisomers of polyacetylene itself [26–28]. Polyacetylenes can exhist in four different conformations: the *cis-cisoid, cis-transiod, trans-cisoid*, and *trans-transoid* conformations. With the aim of preparing membranes for optical resolution, various acetylenic polymers were synthesized for which, on the basis of the high optical activity, a helical conformation was proposed [29].

Now we report on the synthesis of a polyacetylene derivative carrying the bulky optically active moieties and its chiro-optical properties.

EXPERIMENTAL

17α-ethynyltestosterone (ETT, Aldrich Chemicals) was used as received. $[Rh(nbd)Cl]_2$, $PdCl_2$, and $PtCl_2$ was used as received. All procedures for the polymerization of ETT were carried out under nitrogen atmosphere. The polymerization by $PdCl_2$ was carried out at 90°C in DMF for 24 hrs (the monomer to catalyst mole ratio $= 30$, $[M]_0 = 0.25\,M$). After the polymerization time, the polymerization was terminated by adding a small amount of methanol. Then 10 mL of DMF/ethanol (3:1 volume ratio) was added and the resulting polymer solution was precipitated into a large excess of distilled water. The polymer was filtered from the solution and dried under vacuum at 40°C for 24 hrs.

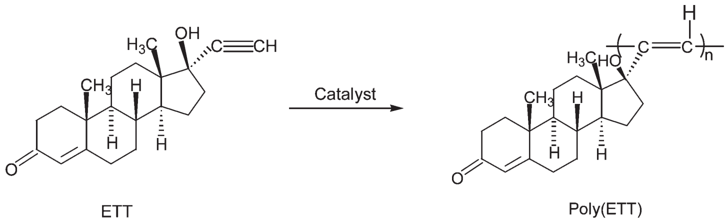
FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet, and frequencies are given in reciprocal centimeters. NMR spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA). UV-visible spectra of polymer solution were taken on a Shimadzu UV-3100S spectrophotometer. The photoluminescence spectra were obtained by a 488 nm Ar laser as an excitation or Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube). Circular dichroism (CD) spectra were recorded on a Jasco J-810 spectropolarimeter. The molecular weight was determined in THF solvent by a Waters GPC-150C calibrated with polystyrene standards. X-ray diffractograms were measured with a PHILIPS X-ray diffractometer (Model: X'Pert-APD).

RESULTS AND DISCUSSION

The polymerization of ETT was performed by such transition metal catalysts as $PdCl_2$, $PtCl_2$, (bicyclo[2.2.1]hepta-2,5-diene)chlororhodium(I) dimer {$[Rh(nbd)Cl]_2$} catalysts (Scheme 1).

Table I shows the typical results for the polymerisation ETT by transition metal catalysts. In general, the polymerisation of ETT by $PdCl_2$ and $PtCl_2$ proceeded well in DMF solvent at 90°C, regardless of the bulkiness of the substituent. However, the molecular weights of the resulting polymers were relatively low. The polymerisation of ETT by $[Rh(nbd)Cl]_2$ proceeded at more mild reaction conditions (at 50°C). The polymer yield and molecular weight (Mn) were 47% and 5610, respectively. The poly (ETT) obtained by rhodium-catalyst was generally yellow, whereas the polymers by $PdCl_2$ and $PtCl_2$ were generally brown.

The resulting polymer was completely soluble in aromatic and halogenated hydrocarbon solvents such as benzene, chlorobenzene, chloroform, and 1,1,1-trichloroethane, but insoluble in methanol and n-hexane.



SCHEME 1 Polymerization of ETT.

TABLE I Polymerization of 17α-ethynyltestosterone by Transition Metal Catalysts[a]

Catalyst	Temperature (°C)	Polymer yield (%)	Mn[b]	$[\alpha]_D$[c] (deg)
$PdCl_2$	90	83	3680	−32
$PtCl_2$	90	61	2070	−26
$[Rh(nbd)Cl]_2$	50	47	5610	−98

[a] Polymerization was carried out for 24 hrs.
[b] Determined with GPC by using polystyrene standards.
[c] The concentration was 0.15 g/dL in chloroform.

The polymer structure of poly(ETT) was characterized by various instrumental methods such as NMR, IR, and UV-visible spectroscopies. The IR spectrum of poly(ETT) showed neither the acetylenic ≡C−H stretching band nor the acetylenic C≡C stretching band, which were presented at the IR spectrum of monomer.

The ^{1}H-NMR spectrum of poly(ETT) showed the vinyl protons in the polymer backbone and the α, β-unsatureted ketone of the substituent around 5.8 ppm, and the hydroxy protons at about 2.9 ppm. The UV-visible spectrum of poly(ETT) showed the characteristic broad absorption peak at the visible region, which are originated from the $\pi \rightarrow \pi$ conjugation band transition of the polyene main chain.

It was known that the rhodium-catalyzed polymerisation of some acetylene derivatives affords essentially perfect stereoregular (*cis-transoidal* structure) polymers, which leads to the induction of one-handed screw sense conformation in the presence of chiral substituents [30]. The Rh-based poly(ETT) showed a very large optical rotation ($[\alpha]_D = -98°$, c = 0.15 g/dL in chloroform), whereas Pd- and Pt-based poly(ETT)s were much smaller (−32° and −26°, respectively). Even though the monomer (ETT) contains a chiral center, it did not show any CD signal. This means that the stereocenter does not affect the conformation of the bulky substituents, which have large transition moments. However, the Rh-based poly (ETT) showed an intense CD signal at around 320 nm. This CD signal indicates that the chiral conformation of the monomeric repeat units along the polymer chain was formed and/or the exciton coupling between vicinal monomeric units were presented.

The photoluminescence (PL) spectrum of poly(ETT) was measured in DMF solution. The photoluminescence peak is located at 487 nm corresponding to the photon energy of 2.55 eV. Because the peaks in the X-ray diffraction pattern were broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta / 2\theta$) is greater than 0.35 [2], the present polymers were mostly amorphous.

CONCLUSIONS

Soluble conjugated polyacetylene [poly(ETT)] bearing chiral moieties were synthesized and characterized. In general, the polymerisation proceeded well to give a high yield of polymer. The photoluminescence peak is located at 487 nm corresponding to the photon energy of 2.55 eV. The magnitude of the CD for the polymers was dependent on the catalyst and polymerisation condition used. The Rh-based poly(ETT) showed more intense CD signal than those of Pd- and Pt-based poly(ETT)s.

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