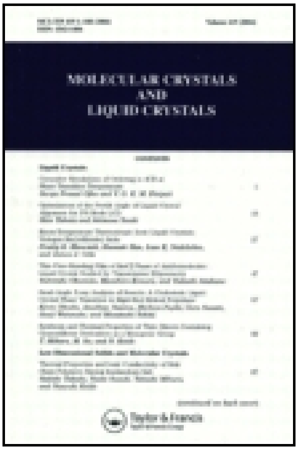

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Synthesis and Electro-Optical Properties of Poly(4-ethynylaniline)

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A new conjugated polymer with amine groups was synthesized in high yields by the polymerization of 4-ethynylaniline with various transition metal catalysts. The polymer structure was identified by various instrumental methods to have a conjugated polymer backbone system with p-aminophenyl substituents. The

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photoluminescence peak of poly(4-ethynylaniline) is located at 478 nm corresponding to the photon energy of 2.60 eV. From the CV measurements, the HOMO energy level of the polymer was calculated to be 5.03 eV.

Keywords: 4-ethynylaniline; conjugated polymer; HOMO; photoluminescence; polyacetylene

INTRODUCTION

Over the last three decades, conjugated polymers have been of great research interest for an important class of electroactive and photoactive materials [1–5]. Promising materials for electronic devices and molecular electronics can be obtained by introducing of π-conjugated systems. Acetylenic triple bonds can be a good candidate to introduce pi-conjugated systems due to rich pi-electrons and yield the linear conjugate polymer systems [6–11].

Conjugated polymeric materials from acetylene derivatives have been studied as organic semiconductors [12], as membranes for gas separation and for liquid-mixture separation [13], as materials for chiroptical switching [14,15], as a side-chain liquid crystal [16,17], and as materials for nonlinear optical property and for photoluminescence and electroluminescence properties [18–22].

The acetylene monomers having various functional groups such as hydroxy, carboxylic acid, sulfide, amine, and esters, were prepared and polymerized by various catalyst systems [23]. To our knowledge, there has been no report on the polymerization of ethynylanilines. The surface behavior and polymerization kinetics of 2- and 3-(1-octadecynyl)aniline at the air-aqueous interface were studied for well-defined Langmuir film [24]. In our previous paper, we reported the synthesis and properties of some aliphatic amines such as propargylamine [25], 1,1-diethylpropargylamine [25], dipropargylamine [26], and tripropargylamine [27].

This article describes the synthesis of a new polyacetylene with aniline functionalities and the electro-optical properties of the resulting conjugated polymer.

EXPERIMENTAL

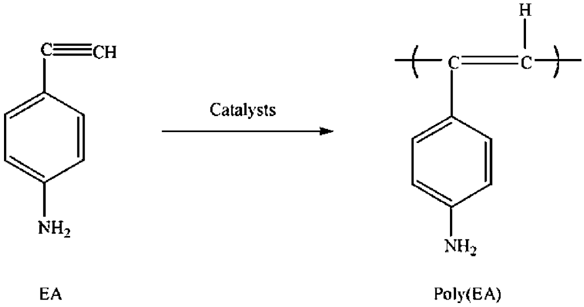
4-Ethynylaniline (4-EA, Aldrich Chemicals., 97%) was used after drying at vacuum oven at 40°C for 24 hrs. $PdCl_2$ (Aldrich Chemicals, 99.9 + %), $PtCl_2$ (Strem), and $RuCl_3$ (Aldrich Chemicals), (NBD)$PdCl_2$

(Aldrich Chemicals), $[Rh(NBD)Cl]_2$ (Aldrich Chemicals) were used as received. $MoCl_4$ (Aldrich Chemicals), $MoCl_5$ (Aldrich Chemicals, 99.9+%), WCl_6 (Aldrich Chemicals., 99.9+%), and $EtAlCl_2$ (Aldrich Chemicals.) were also used without further purification. Ph_4Sn (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

A typical synthetic procedure of 4-EA is as follows: In a 20 mL reactor equipped with rubber septum, 1.0 g (8.54 mmol) of 4-EA, 50.4 mg (0.0285 mmol, M/C = 30) of $PdCl_2$, and 10 mL of DMF ($[M]_0 = 0.78$ M) were added in that order given. Then the polymerization was carried out at 90°C for 24 hrs under nitrogen atmosphere. The polymerization mostly proceeded in homogeneous manner. After the polymerization time, the polymer solution diluted with 10 mL DMF was precipitated into a large excess of ethyl ether. The precipitated polymer was filtered and dried in vacuum oven at 40°C for 24 hrs. The black powder was obtained in 85% yield. The polymerization of 4-EA by W- and Mo-based transition metal catalysts was performed as described earlyer [28]. 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. X-ray diffractograms were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD). The optical absorption spectra were measured by a Shimadzu UV-3100 UV-VIS-NIR spectrometer. The inherent viscosities of polymers were determined at a concentration of 0.5g/dL in DMF at 30°C. 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 750 M), and a photomultiplier (Hamamatsu R943–02). Electrochemical measurements were carried out with a KOSENTECH (KST-P1) instrument (Pt disk electrode, CH_3CN, $(TBA)PF_6$, 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

The polymerization of 4-EA, a phenylacetylene with amine functionality, was attempted with various transition metal catalysts (Scheme 1). Table 1 shows the results for the polymerization of 4-EA by transition metal catalysts.



SCHEME 1 Polymerization of 4-ethynylaniline.

$PdCl_2$ is found to be very effective for the present polymerization. The polymerization of 4-EA by $PdCl_2$ occured well in homogeneous manner to give a high yield of polymer (85%). Other similar catalysts such as $PtCl_2$ and $RuCl_3$ showed similar catalytic activities to give 82% and 87%, respectively. (NBD)$PdCl_2$, which showed good solubility in the polymerization solvent, was found to be very effective to give a quantitative yield of polymer. Rhodium dimer catalyst, $[Rh(NBD)Cl]_2$, also polymerizes 4-EA to give the corresponding polymer in 75% yield. Mo- and W-based catalysts were also used for the polymerization of 4-EA. Mo-based catalysts including $MoCl_5$, $MoCl_5$-$EtAlCl_2$, $MoCl_5$-Ph_4Sn were effective for the polymerization (polymer yield: 52%, 67%, and 60%, respectively). On the other hand, we failed to observe the polymerization of present monomer with WCl_6 itself to give only a trace amount of oligomeric product. However, WCl_6-$EtAlCl_2$ polymerize 4-EA to give the poly(4-EA) in 70% yield.

We characterized the chemical structure of poly(4-EA) by various instrumental methods such as IR, NMR, UV-visible spectroscopies.

TABLE 1 Polymerization of 4-Ethynylaniline by Transition Metal Catalysts[a]

No	Catalyst	Polymer yield (%)[b]	η inh (dL/g)[c]
1	$PdCl_2$	85	0.11
2	$PtCl_2$	82	0.09
3	$RuCl_3$	87	0.16
4	(NBD)$PdCl_2$	100	0.15

[a] Polymerization was carried out at 90°C for 24 hrs in DMF. Monomer to catalysts mole ratio (M/C) and initial monomer concentration ($[M]_0$) were 30 and 0.78 M, respectively.

[b] Ethyl ether-insoluble polymer.

[c] Inherent viscosities were determined at a concentration of 0.5 g/dL in DMF at 30°C.

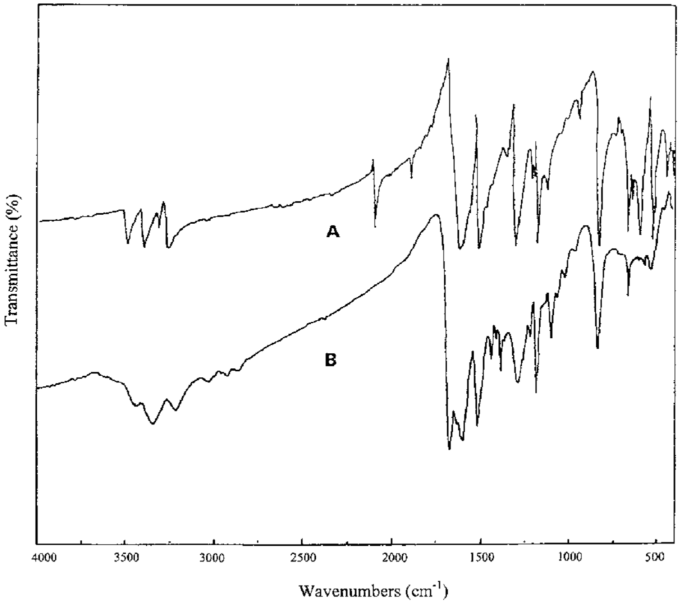


FIGURE 1 FT-IR spectra of 4-ethynylaniline (A) and poly(4-ethynylaniline) (B) in KBr pellet.

Figure 1 shows the FT-IR spectra of 4-EA and poly(4-EA) in KBr pellet. The FT-IR spectrum of the polymer did not show the acetylenic C≡C bond stretching (2097 cm^{-1}) and acetylenic ≡C−H bond stretching (3256 cm^{-1}) frequencies of the monomer. Instead, the C=C stretching frequency peak of conjugated polymer backbone around 1665 cm^{-1} became more intense than that of the monomer. The characteristic broad peaks of primary amine in polymer were observed at 3338 and 3430 cm^{-1}. The peak at 1095 cm^{-1} is due to the C−N stretching frequency. The ^{1}H-NMR spectrum of poly(4-EA) showed the aromatic protons broadly in the range of 5.6–7.5 ppm and also showed the amine protons broadly around 5.0 ppm. The ^{13}C-NMR spectrum of poly(4-EA) showed the vinyl carbons of conjugated backbone and phenyl carbons at 111–152 ppm.

This polymer was soluble in such solvents as DMF, NMP, and DMSO. The inherent viscosities of the resulting polymers were in the range of 0.11–0.16 dL/g. The TGA thermogram of poly(4-EA) exhibited that the polymer is stable up to 350°C. The morphologies of poly(4-EA) were also investigated by X-ray diffraction analysis (Fig. 2). The peak in the diffraction pattern is broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than

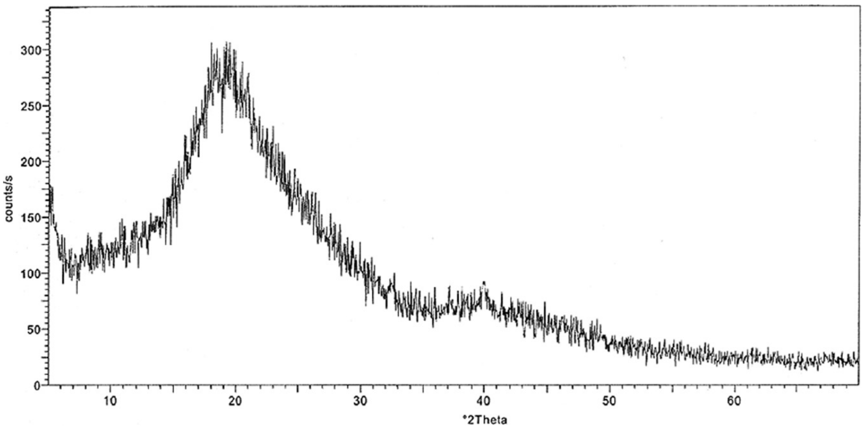


FIGURE 2 X-ray diffractogram of poly(4-ethynylaniline).

0.35 [29], indicating that the present polymers are amorphous. Figure 3 shows the UV-visible spectra and photoluminescence (PL) spectra of the resulting polymer. 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 this ionic conjugated polymer showed that the photoluminescence peak is located at 478 nm corresponding to the photon energy of 2.60 eV.

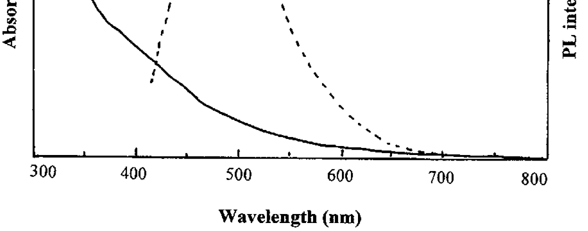


FIGURE 3 Optical absorption and photoluminescence spectra of poly(4-ethynylaniline).

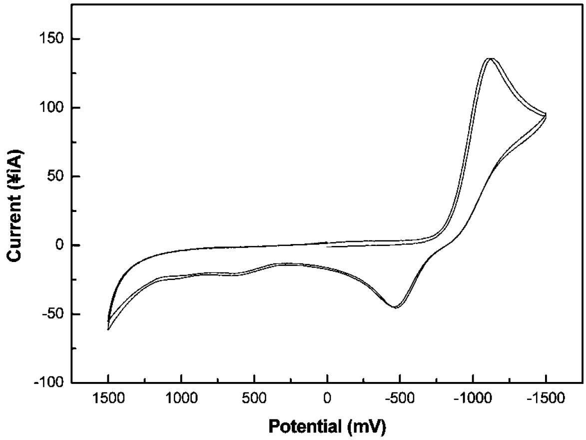


FIGURE 4 Cyclic voltamogram of poly(4-ethynylaniline) at 100 mV/s (0.1 M Et_4NBF_4/DMF).

In order to investigate the electrochemical properties of poly(4-EA), we performed the cyclic voltammetry (CV) experiment. The potentials were referenced to Ag/$AgNO_3$ and the reduction potential of ferrocene/ferrocenium (FOC) under 0.1 M $(t\text{-}Bu)_4NPF_6$/DMF solution. Figure 4 shows the typical CV of poly(4-EA). This exhibited the reversible 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 $= -(E^{ox} + 4.8\,\text{eV})$, where the SCE energy level of -4.8 eV below the vacuum level [30]. From the CV measurements, the HOMO energy levels of the present polymer, was calculated to be 5.03 eV.

CONCLUSIONS

The polymerization of 4-EA by various transition metal catalysts give the corresponding polyacetylene derivative in high yields. In general, Pd, Pt, Ru- and Mo-based catalysts were found to be effective. The structural characterization by various instrumental methods confirmed the resulting polymer to have the conjugated polymer backbone with aniline substituents. The X-ray diffraction data indicated that the present polymer is mostly amorphous. The photoluminescence spectra of the polymer showed that the photoluminescence peak is located at 478 nm corresponding to the photon energy of 2.60 eV.

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