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Electro-optical and Electrochemical Properties of a Disubstituted Polyacetylene: Poly(1-phenyl-2-trimethylsilylacetylene)

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The electro-optical and electrochemical properties of poly(1-phenyl-2-trimethyl silylacetylene), which is a disubstituted polyacetylene with bulky phenyl and trimethylsilyl groups as substituents, were studied. The photoluminescence (PL) spectra of polymer showed that the photoluminescence peaks are located at 484 and 532 nm, corresponding to a photon energy of 2.56 and 2.33 eV, respectively. The cyclic voltamograms of the polymer exhibited reversible electrochemical behaviors between the doped and undoped peaks. It was found that the kinetics of the redox process of polymer is controlled by the reactant diffusion process.

Keywords 1-phenyl-2-trimethylsilylacetylene; conjugated polymer; cyclovoltamogram; electro-optical; polyacetylene

Introduction

For the past four decades, considerable research efforts have been dedicated to various types of conjugated polymers because of their extraordinary electronic and optical properties [1–5]. Recently examined applications of conjugated organic materials include organic light-emitting diodes (OLEDs), chemical sensors, photovoltaic cells, field-effect transistors, and so on [6–12]. The acetylenic triple bonds have rich π-electrons, which can be polymerized to yield the linear conjugated polymer systems [13–16]. A number of

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substituted acetylenes has been polymerized using a wide range of catalysts and polymerization conditions [13–16]. Polymerization systems include homogeneous and heterogeneous Ziegler-Natta catalysts, transition metal complexes (W, Mo, Pd, Ni, Co), free radical initiators, cationic initiators, and anionic initiators [14,17]. Among the disubstituted polyacetylenes, poly(1-trimethylsilyl-1-propyne) exhibits the highest gas permeability among all the existing polymers [18,19]. Further, poly[1-(p-trimethylsilyl)phenyl-2-phenylacetylene], which is obtained by the polymerization with $TaCl_5$-n-Bu_4Sn, showed both very high gas permeability and thermal stability [20]. Such potential applications of poly[1-(p-trimethylsilyl)phenyl-2-phenylacetylene] as thermosensor, electrooptical optical nanofiber, highly polarized fluorescent film, and fluorescence image patterning have been reported [21–26].

In our previous works, we synthesized a number of disubstituted polyacetylene, poly(1-aryl-2-trimethylsilylacetylene)s (aryl: phenyl, 2-thienyl, 2-furyl, 2-pyridyl) by the polymerization of the corresponding disubstituted monomers with various transition metal catalysts [27–29].

In this article, we present the research results on the electro-optical and electrochemical properties of poly(1-phenyl-2-trimethylsilylacetylene) [(poly(PTSA)] prepared by W-based transition metal catalyst.

2. Experimental

Phenylacetylene (Aldrich Chemicals, 98%) was dried over CaH_2 and fractionally distilled at reduced pressure. PTSA was prepared according to the literature procedure [27,30]. WCl_6 (Aldrich Chemicals., 99.9+%) and Me_4Sn (Aldrich Chemicals.) were also used without further purification. The polymerization solvent, chlorobenzene, was dried with calcium hydride and distilled. Poly(PTSA) was obtained in 33% yield from the polymerization of PTSA by using the WCl_6-Me_4Sn catalyst system [27].

NMR spectra of polymers were recorded on a Varian 500MHz 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. The optical absorption spectra were measured by a HP 8453 UV-visible Spectrophotometer. Electrochemical measurements were carried out with a Potentionstat/Galvanostat Model 273A(Princeton Applied Research). To examine electrochemical properties, polymer solution was prepared and the electrochemical measurements were performed under 0.1M tetrabutylammonium tetrafluoroborate solution containing DMF. ITO, $Ag/AgNO_3$ and platinum wire were used as a working, reference and counter electrode, respectively. The photoluminescence spectra were obtained by Perkin Elmer luminescence spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz.

3. Results and Discussion

A disubstituted polyacetylene, poly(PTSA), was prepared by the polymerization of PTSA by WCl_6-Me_4Sn (1:1) catalyst system. The orange polymer powder was obtained in 33% yield. And the number-average molecular weight (Mn) was 27,100. This polymer was completely soluble in organic solvents such as chloroform, THF, benzene, chlorobenzene, and toluene. The FT-IR spectrum of poly(PTSA) did not show the acetylenic C≡C bond stretching frequency of PTSA. Instead, the C = C stretching frequency peak of conjugated polymer backbone at 1530–1620 cm^{-1} became more intense than that of the monomer.

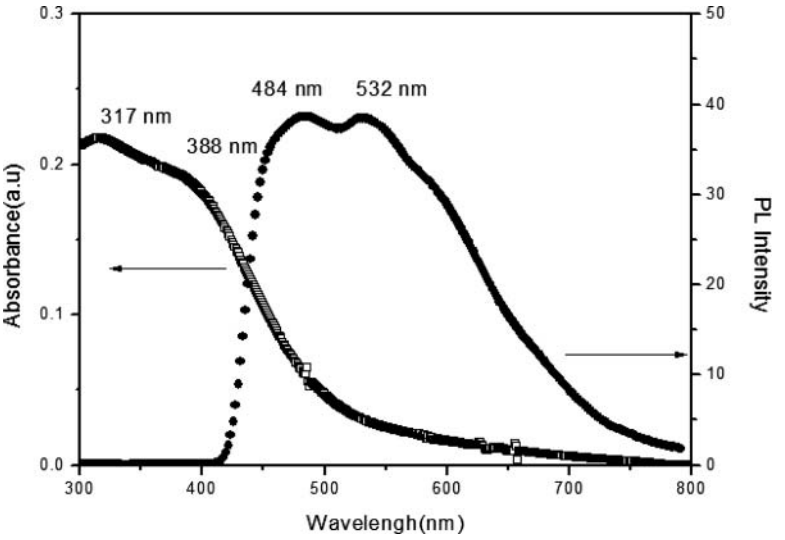

Figure 1. Optical absorption and photoluminescence spectra of poly(PTSA) solution.

From the ^{1}H-NMR spectrum of poly(PTSA), we found that the present polymer has partially desilylated molecular structure although the reason of spontaneous desilylation is not clear. The extent of desilylation of the present poly(PTSA) prepared by WCl_6-Me_4Sn (1:1) catalyst system was calculated as 39% from the ^{1}H-NMR peak integration [27].

The absorption and photoluminescence spectra of poly(PTSA) were measured and discussed. Figure 1 shows the UV-visible and photoluminescence (PL) spectra of poly(PTSA) solution (0.1 wt.%, DMF). Poly(PTSA) exhibits characteristic UV-visible absorption band, which starts from 600 nm and has maximum value of 388 nm. It is also found that this polymer has two photoluminescence maximum peaks of 484 and 532 nm, corresponding to the photon energy of 2.56 and 2.33 eV, respectively.

We studied the electrochemical kinetic behavior of poly(PTSA) by using the cyclic voltametry. The measured cyclic voltammograms of poly(PTSA) with the various scan rates (30 mV/s $\sim$ 150 mV/s) are shown in Fig. 2(a). The peak potentials are constant as the scan rate is increased. Also we have observed very stable cyclic voltammograms of poly(PTSA) from the consecutive scan (up to 30 cycles) in Fig. 2(b), which means that this material has relatively stable redox process. In Fig. 2, the oxidation of poly(PTSA) was occurred at 0.35 V (vs $Ag/AgNO_3$) and it also showed the irreversible reduction peak at -1.42 V. The oxidation current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of poly(PTSA) is reproducible in the potential range of –1.50 $\sim$+1.35 V vs $Ag/AgNO_3$.

It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [31,32].

$$i_{p,a} = k\nu^x \tag{1}$$

$$\mathrm{Log}i_{p,a} = \log k + x \log \nu \tag{2}$$

where $i_{p,a}$ = oxidation peak current density, ν = scan rate, k = proportional constant, and x = exponent of scan rate. Fig. 3

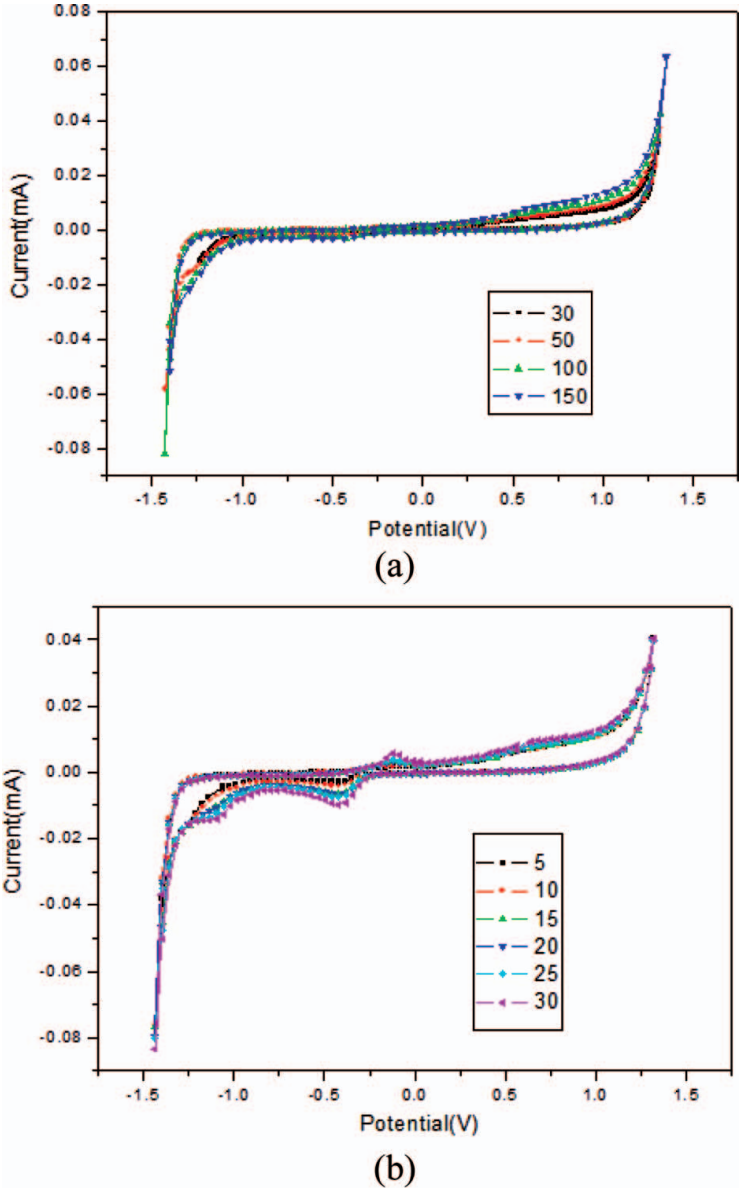

Figure 2. Cyclic voltammograms of poly(PTSA) [0.1M (n-Bu)$_4$NBF$_4$/DMF] (a) 30 mV/sec ~150 mV/sec with various scan rates and (b) consecutive 30 scans under 100 mV/s.

Assuming that electrode kinetics satisfies Eq. (1), the electrochemical redox reaction on the electrode is controlled by either the electron transfer process, where x = 1, or the reactant diffusion process, where x = 0.5 [31,33]. Relations satisfying Eq. (2) between the oxidation current density (log $i_{p,a}$) and the scan rate (log v) were obtained. The oxidation current density of poly(PTSA) versus the scan rate is approximately linear relationship in the range of 30 mV/sec ~ 150 mV/sec. The exponent of scan rate, x value of poly(PTSA),

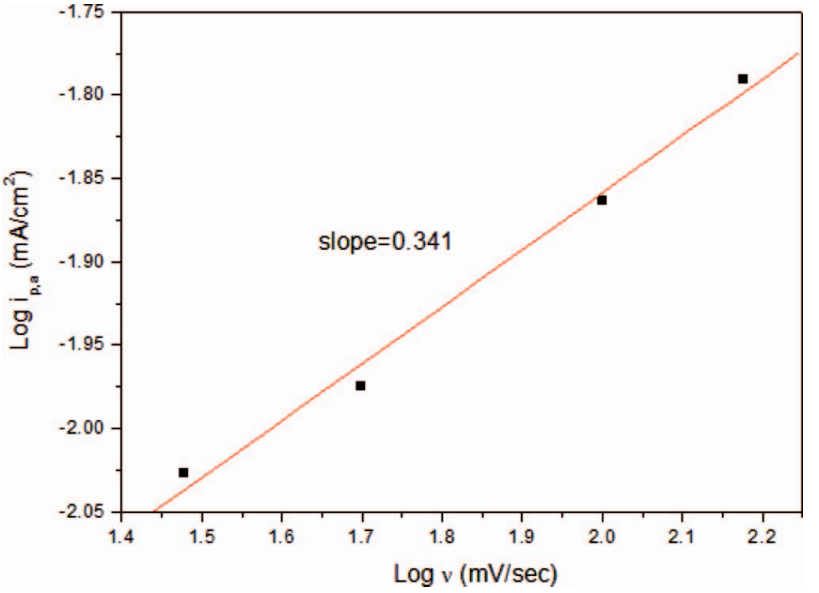

Figure 3. Plot of log $i_{p,a}$ *vs* log *v* for poly(PTSA) cyclic voltammograms.

is found to be 0.341 (Fig. 3). This value means that the kinetics of the redox process may be controlled by the reactant diffusion process [31–33].

4. Conclusions

In this article, we studied the electro-optical and electrochemical properties of poly(PTSA) prepared by WCl_6-Me_4Sn catalyst system. This polymer was completely soluble in organic solvents, thus well-processable. The photoluminescence (PL) spectra of poly(PTSA) indicated that the photoluminescence maximum peaks are located at 484 and 532 nm, which corresponded to the photon energy of 2.56 and 2.33 eV, respectively. The cyclovoltamograms of poly(PTSA) exhibited the reversible electrochemical behaviors between the doping and undoping peaks. It was found that the kinetics of the redox process of poly(PTSA) might be controlled by the reactant diffusion process from the experiment of the oxidation current density of poly(PTSA) versus the scan rate.

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