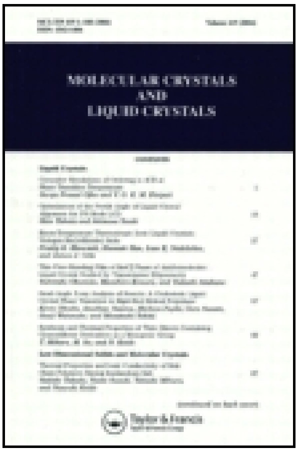

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Yeong-Soon Gal [a] , Sung-Ho Jin [b] , Jong-Wook Park [c] & Kwon Taek Lim [d]

[a] Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Gyeongsan, 712-701, Gyeongsangbuk-do, Korea

[b] Department of Chemistry Education, Pusan National University, Busan, 609-735, Korea

[c] Department of Chemistry, Center for Display Research, The Catholic University of Korea, Bucheon, 420-743, Korea

[d] Division of Image and Information Engineering, Pukyong National University, Busan, 608-739, Korea

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Synthesis and Properties of Poly(4-vinylpyridine-co-styrene) with Sulfobetaine Moieties

YEONG-SOON GAL,[1,*] SUNG-HO JIN,[2] JONG-WOOK PARK,[3] AND KWON TAEK LIM[4]

[1]Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Gyeongsan 712-701, Gyeongsangbuk-do, Korea
[2]Department of Chemistry Education, Pusan National University, Busan 609-735, Korea
[3]Department of Chemistry, Center for Display Research, The Catholic University of Korea, Bucheon 420-743, Korea
[4]Division of Image and Information Engineering, Pukyong National University, Busan 608-739, Korea

A new ionic polymer, poly(4-vinylpyridine-co-styrene) [PVPS] with pendant sulfobetaine moieties was prepared by the polymeric reaction of PVPS and 1,4-butanaesultone. The polymer structure was characterized by various instrumental methods to have PVPS backbone system with the designed sulfobetaine moieties. The cyclovoltammograms of this ionic polymer showed irreversible oxidation and reversible reduction response properties in a polymer unit. The plot of the oxidation current density of polymer versus the scan rate showed approximately a linear relationship in the range of 30 mV/sec ∼150 mV/sec. The exponent of scan rate, when we apply power law to our data, was found to be 0.53.

Keywords Ionic polymer; poly(4-vinylpyridine-co-styrene); 1,4-butanesultone, polymer reaction; cyclovoltamogram

Introduction

Polyelectrolytes are charged macromolecules containing a large number of ionizable or ionic groups. The natural polyelectrolytes have been used in water-cleaning processes for centuries. The very building blocks of life, the nucleic acids and proteins, are polyelectrolytes. Synthetic polyelectrolytes have been utilized in many applications including enhanced oil recovery (EOR), drag reduction, water-purification, papermaking, mining, and formulation of personal care items and controlled drug delivery [1–3]. The first cyclopolymer, poly(diallyldimethylammonium chloride), now manufactured by a number of suppliers, has been shown to possess optimum functional properties to be applied for electrographic paper reproduction processes [4, 5].

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[*] Corresponding author. E-mail: ysgal@kiu.ac.kr

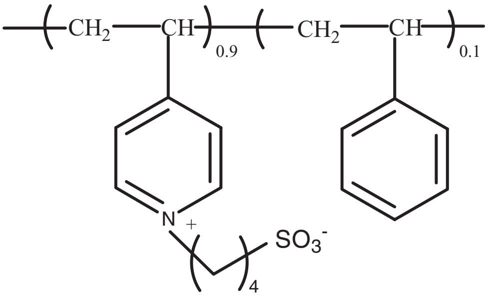


Figure 1. Chemical structure of PVPS with sulfobetaine moieties.

Various ionic co- and terpolymers of the industrially important monomer acrylamide have been prepared utilizing anionic, cationic, or zwitterionic comonomers. Block copolymer polyelectrolytes and polybetaines have been prepared by conventional free radical copolymerization in aqueous media, heterogeneous micellar inverse emulsion, inverse microemulsion techniques, and atom transfer radical polymerization (ATRP) [1, 6–8]. The ionic polymers with conjugated backbone system have been also prepared by the addition polymerization of ionized acetylenic monomers, and the polymeric reaction of precursor polymers, and the activated polymerization of ethynylpyridines utilizing functional alkyl halides [9, 10]. Due to their extensive conjugation and peculiar nature, conjugated organic materials have potentials as materials for light-emitting diodes and photovoltaic cells [11–16]. We have also reported the preparation of various ionic conjugated polymers having different functionalities [17–22].

The reactivity of nitrogen lone pair electrons in pyridine-containg polymers have been used for the conversion of uncharged functional groups to charged groups. Self-doped polyaniline was synthesized by using the reaction of the emeraldine base with propanesultone as well as butanesultone [23]. The proposed mechanism involves nucleophilic attack by the nitrogen lone pair of electrons on the C-O bonding carbon of the sultone. Chen et al. prepared a self-doped polyaniline derivative, poly(aniline-co-sulfobenzoic anhydride) by the direct reaction of polyaniline with o-sulfobenzoic anhydride [24]. The highly conductive and thermally stable self-doped mercaptopropanesulfonic acid-substituted polyanilines were prepared by the concurrent reduction and substitution reaction between polyaniline and a nucleophile [25, 26].

Here, we report on the synthesis of a new ionic polymer with sulfobetaine moieties (Figure 1) by the polymer reaction of PVPS with 1,4-butanesultone, including characterization for the polymer structure and the electrochemical properties of the resulting ionic polymer.

Experimental

PVPS (powder, styrene content: 10%, Mn: 130,000, DPI: 1.69) and 1,4-butanesultone were purchased from Aldrich Chemicals and used as received. The analytical grade solvents were dried with appropriate drying agents and distilled.

PVPS with pendant sulfobetaine moieties was prepared by the polymer reaction of PVPS and 1,4-butanesultone as follows. In a stirred 50 mL reactor, PVPS (1.0g, 9.52 mmol for PVPS, 8.57 mmol for 4-vinylpyridine moieties), 1,4-butanesultone (1.20 g, 8.81 mmol) and DMF (20 mL) were added in that given order and sealed by a rubber septum after flushing with purified nitrogen gas. The reaction was carried out at 80°C for 12 hrs. The reaction solution became more viscous. After a given time of polymerization, the reaction solution was diluted with additional DMF (10 mL), was precipitated into a large excess amount of ether. The precipitated polymer was filtered and dried under vacuum oven at 40°C for 24 hrs. The final product was obtained in white fibrous form (1.90 g).

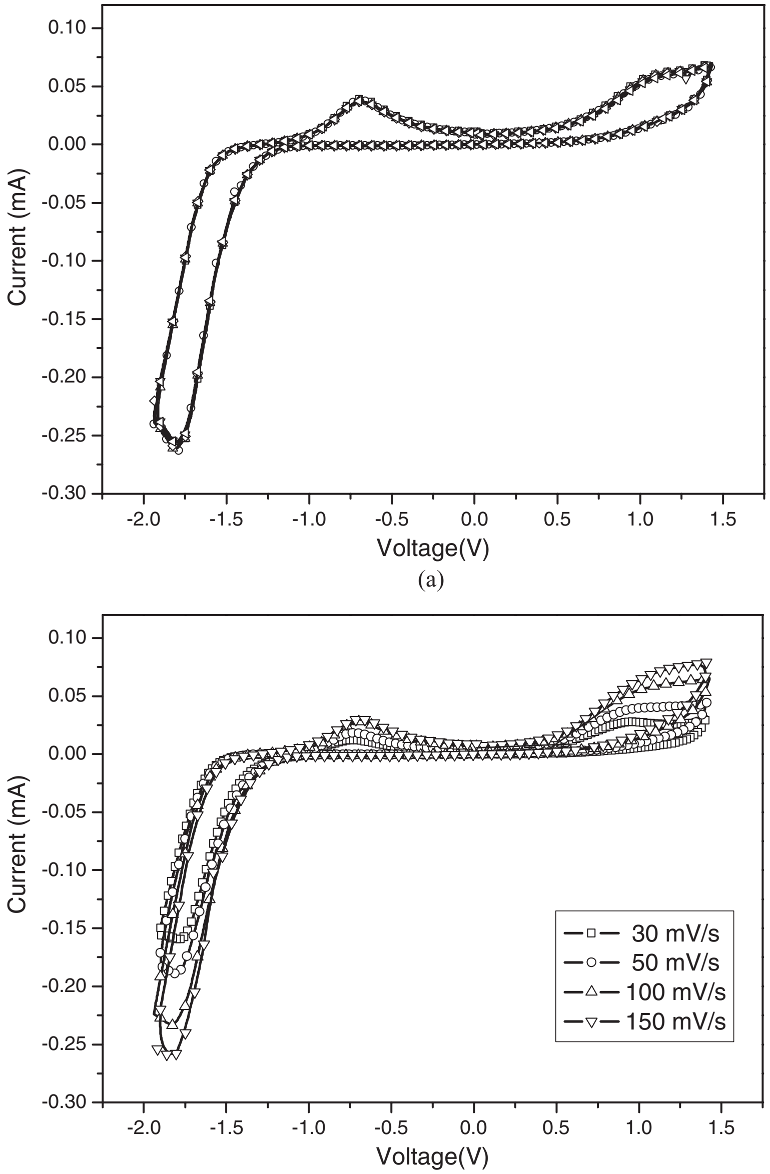
NMR (^{1}H- and ^{13}C-) spectra of polymer were recorded on a Varian 500MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d_6. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10°C/min with a DuPont 2200 Thermogrvimetric Analyzer. DSC thermograms were taken on a DuPont 910 Differential Scanning Calorimeter under nitrogen atmosphere at a heating rate of 10°C/min. Electrochemical measurements were carried out through utilizing a Potentionstat/Galvanostat Model 273A(Princeton Applied Research). To examine the property of electrochemical, a polymer solution was prepared and the electrochemical measurements were performed under a 0.1M tetrabutylammonium perchlorate solution containing DMF. ITO, Ag/$AgNO_3$ and platinum wires were used as an operating, reference and counter electrode, respectively.

Results and Discussion

An ionic polymer with sulfobetaine moieties was prepared by the polymeric reaction of PVPS by using 1,4-butanesultone. The polymer reaction of PVPS proceeded well in a homogeneous manner. The final PVPS with pendant sulfobetaine moieties was white fibrous form. The modified PVPS showed about 5% weight loss in the range of 80–150°C, whereas the original PVPS polymer was found to be stable up to 390°C. The modified PVPS showed an abrupt weight loss after 300°C. This polymer retained 2.5% of its original weight at 100°C, 5.0% at 150, 5.1% at 250°C, 71.2% at 350°C, 13.5% at 400°C, and 3.2% at 700°C. In the DSC thermogram, it was found that a broad exothermic reaction was observed in the range of 233–303°C.

The ^{1}H- and ^{13}C-NMR spectra of PVPS with pendant sulfobetaine moieties were measured in DMSO-d_6. In ^{1}H-NMR spectrum, the characteristic peaks of aromatic protons of original PVPS polymer were observed at 6.3-8.5 ppm. The internal aliphatic methylene proton peaks were observed at 1.0-2.2 ppm. The ^{13}C-NMR spectrum of PVPS with pendant sulfobetaine moieties shows the aromatic (phenyl and pyridyl) carbon peaks in the range of 120–154 ppm (122.8, 126.2, 127.2, 128.2, 143.9, 149.4, 152.5, 153.1 ppm). The aliphatic carbon peaks were observed in the range of 30.7-44.7 ppm. The IR spectrum of PVPS with pendant sulfobetaine moieties indicated that the aliphatical and aromatic C-H stretching frequencies were observed at 2925 and 3023 cm^{-1}, respectively. The C=C stretching frequency of aromatic rings was also observed in the range of 1597 cm^{-1}.

We studied the electrochemical kinetic behaviors by measuring the cyclic voltammograms of PVPS with pendant sulfobetaine moieties with the various scan rates (30 mV/s ~ 150 mV/s) as well as consecutive scans. Figure 2 (a) shows the cyclic voltammograms of PVPS with pendant sulfobetaine moieties. It shows very stable cyclic voltammograms behavior from the consecutive scans (up to 30 cycles). This result suggests that the electrochemical process of PVPS with pendant sulfobetaine moieties is reproducible in the potential range of $-1.93 \sim 1.43$ V vs Ag/$AgNO_3$. Additionally, the oxidation of PVPS



(a)

(b)

Figure 2. Cyclic voltammograms of PVPS with sulfobetaine moieites in 0.1 M TBAP/acetonitrile solution: (a) 30 consecutive scans under 100 mV/sec, (b) various scan rates of 30 mV/sec ∼150 mV/sec.

with pendant sulfobetaine moieties began to activate slightly at 0.49 V, where the pendant sulfobetaine and pyridinium moieties could be oxidized in the scan and showed irreversible oxidation in positive potential region. However, in the negative potential region, PVPS with pendant sulfobetaine moieties showed reversible reduction and oxidation potentials. And the potential peaks of reduction and oxidation slightly increased as the scan rate of CV increased (see Figure 2 (b)).

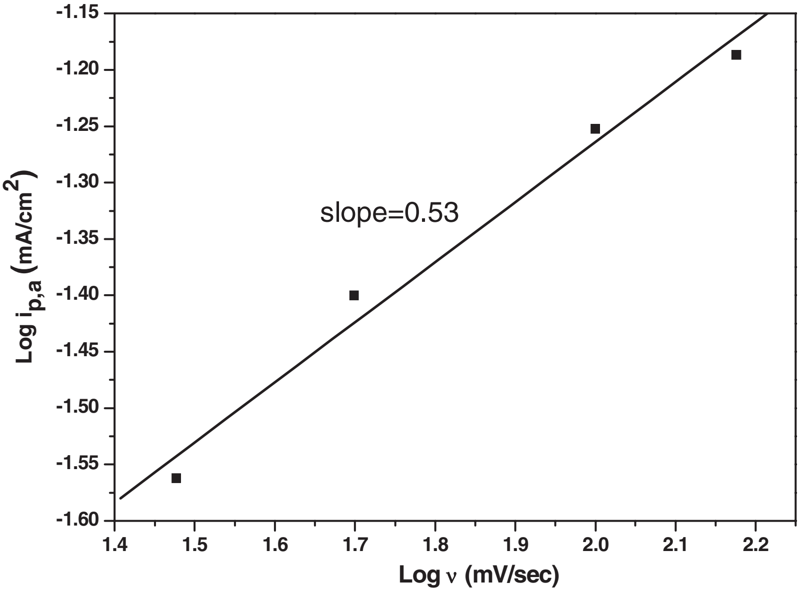


Figure 3. Plot of log $i_{\mathrm{p,a}}$ *vs* log v for PVPS with sulfobetaine moieites.

It has been known that the relationship between the scan rate and the redox peak current is expressed as follows [27–29].

$$i_{\mathrm{p,a}} = kv^{x} \tag{1}$$

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

where $i_{\mathrm{p,a}}$ = oxidation peak current density, v = scan rate, k = proportional constant, and x = exponent of scan rate.

Regarding that electrode kinetics satisfy Eq (1), the electrochemical redox reaction is controlled by either the electron transfer process, where x = 1, or the reactant diffusion process, where x = 0.5. The plot of the oxidation current density (log $i_{\mathrm{p,a}}$) as a function of the scan rate (log v) is shown in Figure 3. The oxidation current of PVPS with sulfobetaine moieties versus the scan rate is approximately linear relationship in the range of 30 mV/sec ∼ 150 mV/sec and the exponent of scan rate, x value is found to be 0.53. It means that the kinetics of the redox process in this case is controlled by the diffusion process. As the pendant chemical structure is notified in experimental section, styrene moiety of pendant group is 10% and 90% of pendant group is mostly pyridinium moiety with sulfobetaine functional group. In our previous paper [30], we reported that the pendant group with azobenzene liquid crystal (LC) moiety instead of sulfobetaine moiety made polymer x value 0.35. It was attributed to the side group effect of long size to polymer orientation and molecular weight as well as the electrochemical property itself. It was not clearly explained, but one thing is clear that butyl sulfonate side group relatively increased the electrochemical activity from 0.35 to 0.53 compared to azobenzene side group.

Conclusions

In this article, we presented the research results on the synthesis and properties of a new ionic polymer with pendant sulfobetaine moieties via the polymer reaction of PVPS with 1,4-butanesultone. The cyclovoltammograms of PVPS with pendant sulfobetaine moieties exhibited irreversible oxidation and reversible reduction response properties. It was found that the kinetics of the redox process of PVPS with pendant sulfobetaine moieties could be controlled by the reactant diffusion process from the experiment of the current oxidation density of PVPS with pendant sulfobetaine moieties versus the scan rate.

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