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12. The ¹H NMR spectra of other Cbz-protected intermediates exhibited broad peaks due to the hindered nitrogen inversion.

The Preparation of Poly(*N*-methylpyrrole) Bilayers with Entrapped Anthraquinone-2-sulfonate

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Anthraquinone-2-sulfonate (AQS) release from poly(*N*-methylpyrrole anthraquinone-2-sulfonate) (PNMP-AQS) was investigated at open circuit and compared with electrochemically stimulated release during potential cycling. It was found that the fast AQS release from PNMP-AQS single layers is substantially retarded and the amounts of spontaneously and electrochemically releasable AQS can be reduced by constructing bilayers, consisting of PNMP-AQS inner layers and PNMP outer layers. PNMP-Cl outer layers exhibited higher effectiveness for entrapping AQS within inner layers than PNMP/poly(styrene sulfonate). The effects of outer layer thicknesses on AQS release were also examined with PNMP-AQS:PMP-Cl. The electroactivity enhancement of PNMP-AQS:PNMP-Cl bilayers due to entrapped AQS was confirmed by chronocoulometry.

Introduction

Various interesting properties[1] of conducting polymers have been extensively studied since it was reported by Chiang et al.[2] that polyacetylene could obtain a 12 order of magnitude increase of conductivity upon oxidative doping. Most of them come from reversible switches of conducting polymers between insulating and conducting states within a certain potential range. During redox switches in electrolyte solutions, conducting polymers incorporate or release ionic species to maintain charge neutrality in a polymer matrix.[3] It is well known that conducting polymer films containing small dopant anions such as poly(pyrrole chloride) balance the charge through anion movements, while cations are mainly involved in ion transport mechanism for ones containing immobile dopant anions such as polypyrrole/poly (styrene sulfonate) (PP/PSS).[4]

These ion transport behaviors can be controlled by con-

structing bilayers where two electroactive polymer films are physically segregated and no electrical contact exists between the electrode and the outer layer. For example, Reynolds et al.[5] addressed that anion dominant transport behaviors of polypyrrole/poly(styrene sulfonate) at higher potential regions can be alleviated through construction of polypyrrole/poly(styrene sulfonate):poly(vinyl ferrocene) bilayers, in which an individual layer sustain its typical ion transport mechanism during redox switching. They also reported that the presence of the outer layer retards the diffusion rate of ionic species, responsible for the inner layer doping-dedoping process.

In this paper, we describe electrochemical behaviors of poly(*N*-methylpyrrole anthraquinone-2-sulfonate) (PNMP-AQS) single layers and bilayers consisting of PNMP-AQS as inner layers and PNMP with various dopant anions as outer layers, in which entrapped AQS can play a role of charging capacity increase of the film as well as a dopant,

1196   *Bull. Korean Chem. Soc.* **1997**, Vol. 18, No. 11

Myoungho Pyo and Hyunsook Kim

since AQS itself is electroactive. Spontaneously and electrochemically stimulated release of AQS from PNMP-AQS single layers was spectroscopically examined and compared with those of bilayers. In a bilayer configuration, it was concluded that the outer layers, electrochemically polymerized on top of the PNMP-AQS films, could block or alleviate the AQS release. These results were further investigated by electrochemical methods.

Experimental

Pyrrole and *N*-methylpyrrole were passed over aluminum oxide until colorless before use. Tetraethylammonium chloride (TEACl), anthraquinone-2-sulfonate sodium salt (NaAQS), anthraquinone-2,6-disulfonate disodium salt (NaAQDS), and poly(styrene sulfonate) sodium salt (NaPSS) were purchased from Aldrich and used without further purification. Acetonitrile (ACN) was distilled over P_2O_5 prior to use and water was double distilled, having a resistance of *ca.* 10^6 Ωcm. Electrolyte solutions were purged with Ar and separated from the air by an Ar blanket throughout the experiments.

All the electrochemical experiments described in this study were performed at room temperature using the BAS CV-50W with a conventional three electrode configuration. A glassy carbon (GC) button (electrochemical area=0.064 cm^2) and Pt plate (geometrical area=2.0 cm^2) were used as working electrodes for electrochemical and spectroscopic measurements, respectively. The area of a GC electrode was determined by chronocoulometry. The potential was stepped from +0.40 to +0.10 V *vs.* Ag/AgCl in an 1 mM $K_3Fe(CN)_6$ aqueous solution (1 M KCl, Dox=7.63×10⁻⁶ cm^2/sec) with a pulse width of 500 msec.⁶ The counter electrode was a Pt plate with a Ag/AgCl reference electrode. Spectroscopic measurements for AQS release studies from PNMP-AQS films were carried out with a UV-Vis spectrophotometer (HITACHI U-3210). After continuous potential cycling in a 10 mL aq. solution of 0.1 M TEACl, a portion of electrolyte solutions was taken in a quartz cuvett for spectroscopic measurements and, when necessary, was put back into an electrochemical cell to maintain the volume of the medium to be 10 mL throughout the measurement.

PNMP-AQS films were prepared potentiostatically at +0.9 V. After thorough washing with copious amounts of distilled water, outer films were made on top of PNMP-AQS in a same manner by stepping the potential to +0.9 V. The polarization was applied immediately after PNMP-AQS films were immersed in the polymerization media to prevent the diffusion of NMP into the inner film domain, which results in erroneous film thickness calculation and inefficient blocking of AQS release. Each film thickness was calculated from the charge passed during film preparation, using a conversion factor of 2.5 $\mu mC^{-1}cm^2$. Krishna *et al.*⁷ showed that the thickness of sulfonate-doped polypyrrole films was linearly related to the polymerization charge with a factor of 2.5 $\mu mC^{-1}cm^2$ on the average.

Results and Discussion

A PNMP-AQDS single layer (240 nm) was redox switched in a 0.1 M TEACl/aq. solution between −0.9 and +0.4
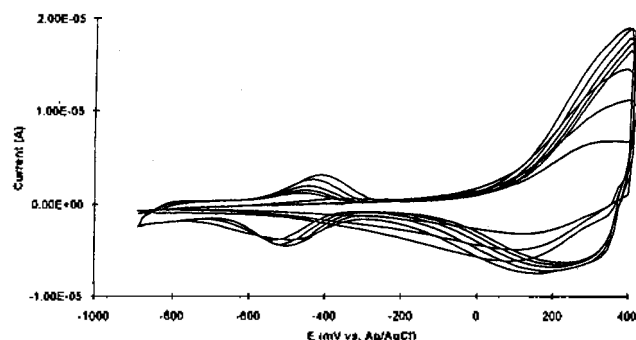

Figure 1. Cyclic voltammograms of PNMP-AQS (120 nm) in TEACl/aq. at 50 mV/s. The top CV was obtained after 30 cycles and successively after 50, 60, 70, 80, 120, 140, 150 cycles.

V to examine whether AQDS $\rightleftarrows$ AQDS⁻ redox process is stable within the reduced PNMP matrix during continuous potential cycling, as shown in Figure 1. The redox peaks at the low potential region ($E_{1/2}$=−0.46 V) due to AQDS $\rightleftarrows$ AQDS⁻ attain the maximum electroactivity after 40 potential cycles and begin to decrease to the complete loss of electroactivity at *ca.* 100 potential cycles, indicating that AQDS is not permanently incorporated in the PNMP matrix. This result, however, does not necessarily imply the fact that AQDS is immobile during initial 30 potential cycles. Comparing the maximal oxidation peak areas of AQDS- and PNMP (top CV of Figure 1), AQDS appears to be released without an induction period as the area under the PNMP oxidation is *ca.* 8 times larger than that under the AQDS oxidation.

When dopant anions are changed to AQS, a cyclic voltammogram of PNMP-AQS in a same medium exhibits that dopant anions are released much faster than the case of PNMP-AQDS (not shown). This is quite likely since, in general, multi-valent ions are more mobile than monovalent ions. For example, Reynolds *et al.*⁸ claimed that, when PP is redox-switched in phosphate buffer solutions of various pH's, anion dominant ion transport behavior of PP in acidic media changes to cation dominant in basic media. It should be noted that PP-AQS and PP-AQDS films also undergo the same trend, but slightly faster release than PNMP systems. While AQS from PP-AQS films seems to be released completely within 5 potential cycles, AQDS remains in the PP matrix until 40 potential cycles.

Yoneyama *et al.*⁹ performed electrochemical and spectroelectrochemical studies of poly(pyrrole anthraquinone-1-sulfonate) films in 0.1 M tetraethyl ammonium perchlorate/ACN solutions and addressed that anthraquinone-1-sulfonate was immobile, exhibiting two electron redox processes, and poly(pyrrole anthraquinone-1-sulfonate) films could be utilized as the high energy density materials for rechargeable batteries. These differences from our results do not appear due to solvent effects since PNMP-AQS and PP-AQS show even faster AQS release behaviors in TEACl/ACN than in TEACl/aq. solutions. The reason is not clear, but their results might be obtained from the initial potential cycles.

AQS release from PNMP-AQS films was further investigated spectroscopically. We focused on this system since the amount of dopant anions is halved in PNMP-
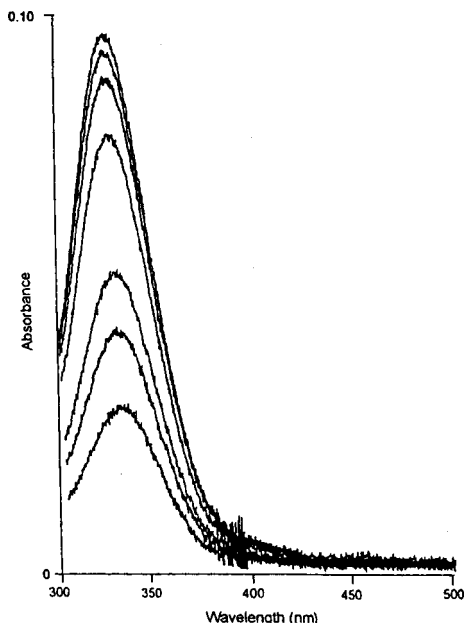
The Preparation of Poly(N-methylpyrrole) Bilayers

Bull. Korean Chem. Soc. **1997**, Vol. 18, No. 11   1197

Figure 2. UV-Vis spectra of a 3 mL TEACl/aq. at open circuit. A PNMP-AQS film was immersed in an electrolyte solution and measurements were made after 17, 28, 80, 115, 316, 800, 1346 min.

AQDS, although PNMP-AQDS films can entrap dopant anions slightly longer than PNMP-AQS films. Figure 2 shows UV-Vis spectra of 3 mL TEACl/aq. in which a PNMP-AQS film (120 nm) was immersed at open circuit. The increase of UV absorption peak intensities at 330 nm results from spontaneous release of AQS. This was further investigated during a longer period of time, by monitoring the UV absorbance *vs.* time at the wavelength of maximum absorption, as shown in Figure 3A. The fast initial AQS release is followed by relatively slow intensity increases and finally reaches a certain steady state value.

In order to determine the fraction of the amount of AQS incorporated during electropolymerization, doping level of the PNMP-AQS was calculated from S/N atomic ratio, obtained by elemental analysis. The result indicates that 1 mole of PNMP repeat units is counter-balanced by 0.24 mole of AQS. Since the PNMP-AQS film (93.8 mC), elec-
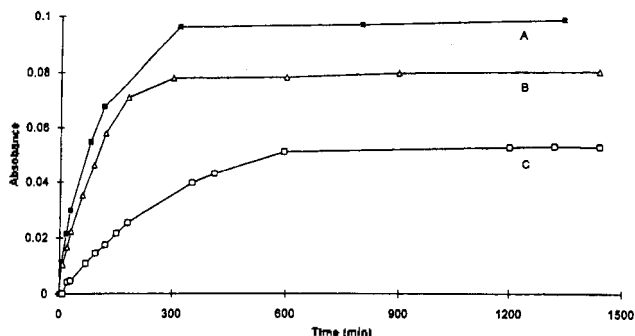

Figure 3. UV absorbance at 330 nm *vs.* time. PNMP-AQS (120 nm) single layer (A), PNMP-AQS : PNMP/PSS (120 nm : 120 nm) (B), and PNMP-AQS : PNMP-Cl (120 nm : 120 nm) (C) bilayers were immersed in 3 mL TEACl aq. solutions at open circuit.
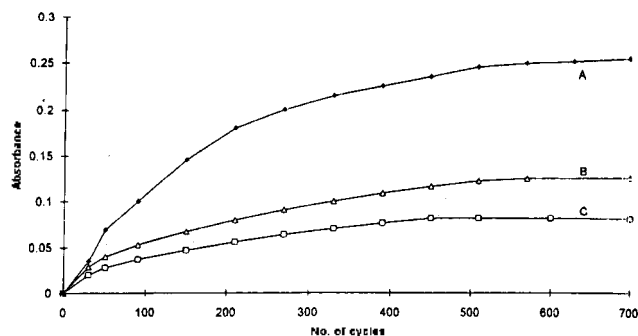

Figure 4. UV absorbance at 330 nm *vs.* time. PNMP-AQS (120 nm) single layer (A), PNMP-AQS : PNMP/PSS (120 nm : 120 nm) (B), and PNMP-AQS : PNMP-Cl (120 nm : 120 nm) (C) bilayers were cycled in 10 mL of 0.1 M TEACl aq. solutions between − 0.7 and +0.4 V at 100 mV/s. Absorbance values were multiplied by a factor of 3.33 to directly compare with Figure 3.

tropolymerized on a Pt plate (2.0 cm^2), are composed of 4. 3×10^{-7} mole of NMP units and 1.0×10^{-7} mole of AQS, when AQS is completely released in the electrolyte medium of 3 mL, the UV absorbance should be 0.24. (ε=7.1×10^3 M^{-1} cm^{-1}) Therefore, we believe that *ca.* 41% of dopant anions are released without electrochemical stimuli, based on the steady state value of 0.099 in Figure 1A.

To reduce the amount of spontaneous AQS release, PNMP-Cl (120 nm) and PNMP/PSS (120 nm) overlayer were electrochemically prepared on top of the PNMP-AQS (120 nm) and UV absorbances were examined in the same manner as above. Figure 3 B and C indicate that the presence of the overlayer retards the rates of AQS release as well as reduces the absolute amount of spontaneously releasable AQS. While PNMP-PSS outer layer slightly alleviates spontaneous AQS release, only 22% of the total AQS is mobile in the PNMP-AQS : PNMP-Cl bilayer. Higher blocking efficiency of PNMP-Cl than PNMP/PSS outer layer towards AQS entrapment is likely due to the smaller ionic conductivity of reduced PNMP-Cl outer layers. It is well known that polyanion dopants implanted in the polymer matrix increase the rate of ion transport.[10]

Since the bilayer configuration does not necessarily imply the fact that electrochemically stimulated AQS release will be also decreased, AQS release from the PNMP-AQS films (PNMP-AQS, PNMP-AQS : PNMP/PSS, PNMP-AQS : PNMP-Cl, each layer thickness=120 nm) were studied under electrochemical stimulation. The films were placed in 10 mL TEACl/aq. solutions and the potential was continuously cycled between − 0.7 and +0.4 V at 100 mV/s. Figure 4 A shows that the potential switches accelerate the rate of AQS release and, finally, alter PNMP-AQS to anion dominant PNMP films. The maximum absorbance (0.25), which is approximately 2.5 times higher than the case at open circuit, corresponds to the calculated value within an experimental error. It should be noted that the absorbance values in Figure 4 were adjusted to the 3 mL TEACl electrolyte solution base, to directly compare with Figure 3. Figure 4B and C clearly demonstrate that the outer layers suppress the AQS release behavior from the inner layers under redox switches as well as at open circuit. PNMP-AQS : PNMP/PSS and PNMP-AQS : PNMP-Cl bilayers release 50 and 32% of the
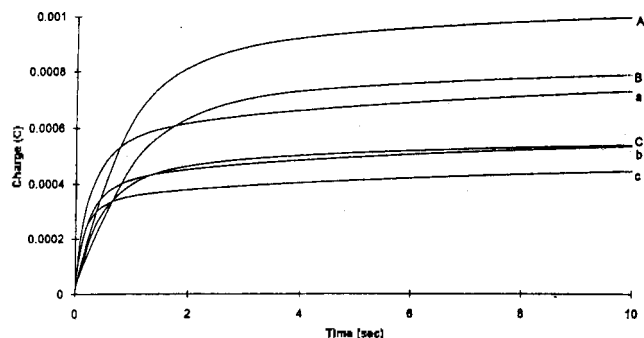
Figure 5. Chronocoulometry during potential steps from -0.7 to +0.4 V in 0.1 M TEACl aq. solutions after potential cycling until no releasable AQS remains in the films. The bilayers were PNMP-AQS:PNMP-Cl with 120 nm:240 nm (A), 120 nm:120 nm (B), and 120 nm:60 nm (C) thicknesses. PNMP-Cl single layers with 360 nm (a), 240 nm (b), and 180 nm (c) thicknesses were also studied for comparison.

electrochemically releasable AQS, respectively. This is interesting since it is known that adenosine 5'-triphosphate (ATP), which is high molecular weight and multivalent anion, is completely released through PNMP outer layers during reduction of poly(pyrrole ATP) inner layers, although ATP is immobile at open circuit.[11]

The effect of outer layer thicknesses on the electrochemically stimulated AQS release was also investigated. As expected, the ratio of released AQS was reduced as the increase of outer film thicknesses, but was not linearly (not shown). While the bilayer, consisting of 60 nm thick PNMP-Cl, releases 80%, PNMP-AQS:PNMP-Cl with 120 nm or thicker outer films release less than 32% of the electrochemically releasable AQS. Although it can be anticipated from this result that larger amount of AQS (quite likely no AQS) will be entrapped with the increase of outer film thicknesses, the preparation of abnormally thick outer films is unfavorable since the relative contribution of the presence of AQS to the overall charging capacity of bilayers is also lowered as the increase of bilayer thicknesses (see below).

Figure 5 shows the increase of electroactivity through PNMP-AQS:PNMP-Cl bilayers, of which the inner layer thicknesses are fixed as 120 nm and the outer layer thicknesses varies (240, 120, 60 nm). The bilayers were cycled in 0.1 M TEACl between -0.7 and +0.4 V at 100 mV/s, until the AQS concentration of the electrolyte medium is invariant, and the potential was stepped from -0.7 to +0.4 V. Figure 5A, indicating the electroactivity of the 120 nm:240 nm thick bilayer, shows that the entrapped AQS in the inner layer contribute to the increase of the electroactivity of the bilayer by 37% relative to the same thickness of PNMP-Cl (Figure 5a). It should be noted that the decrease of the outer film thickness could enhance the effectiveness of the electroactivity increase, although the amount of AQS remaining in the inner film becomes smaller. This is the case in the 120 nm:120 nm thick bilayer since the bilayer shows 46% electroactivity increase which is higher than in the 120 nm:240 nm thick bilayer (Figure 5B and b). The 120 nm:60 nm thick bilayer, however, exhibits relatively low effectiveness (20% electroactivity increase) due to insufficient AQS entrapping capability of the

outer film. This fact coincides with the spectroscopic results, indicative of non-linearity between the outer film thickness and the amount of entrapped AQS.

Conclusion

The stability to spontaneous exchange processes and electrochemically stimulated release of AQS has been investigated for PNMP-AQS and PNMP bilayers. While spontaneous AQS release levels off after 10 hours in all cases, the absolute amount of released AQS shows the dependence on outer layer materials. PNMP-AQS:PNMP-Cl (120 nm:120 nm) bilayers, which is a more efficient configuration than PNMP-AQS:PNMP/PSS in terms of AQS entrapment, spontaneously release about 54% of the spontaneously releasable AQS and 21% of the electrochemically releasable AQS.

Meanwhile, electrochemical potential switches of PNMP-AQS single layers stimulate the rates of AQS release and result in the complete release of AQS, incorporated during electropolymerization. The bilayer construction reduces the amount of released AQS as well as the AQS releasing rate, depending on the outer film thickness. The amount of electrochemically released AQS does not appear to be linearly decreased with the outer film thickness. PNMP-AQS:PNMP-Cl (120 nm:120 nm) bilayers electrochemically release *ca.* 32% of the electrochemically releasable AQS and possess about 46% higher electroactivity than the same thickness of PNMP-Cl, indicating that the bilayer concept can be utilized to prepare conducting polymer modified electrodes of high charging-discharging capacity.

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A Kinetic Study of Biphenyl Type Epoxy-Xylok Resin System with Different Kinds of Catalysts

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The investigation of cure kinetics of biphenyl epoxy (4,4-diglycidyloxy-3,3,5,5-tetramethyl biphenyl)-xylok resin system with four different catalysts was performed by differential scanning calorimeter using an isothermal approach. All kinetic parameters of the curing reaction including the reaction order, activation energy and rate constant were calculated and reported. The results indicate that the curing reaction of the formulations using triphenylphosphine (TPP) and 1-benzyl-2-methylimidazole (1B2MI) as a catalyst proceeds through a first order kinetic mechanism, whereas that of the formulations using diazabicycloundecene (DBU) and tetraphenyl phosphonium tetraphenyl borate (TPP-TPB) proceeds by an autocatalytic kinetic mechanism. To describe the cure reaction in the latter stage, we have used the semiempirical relationship proposed by Chern and Poehlein. By combining an nth order kinetic model or an autocatalytic model with a diffusion factor, it is possible to predict the cure kinetics of each catalytic system over the whole range of conversion.

Introduction

The biphenyl type epoxy resin is of great advantage to high reliable epoxy molding compound (EMC) for good adhesion, high toughness, and the feasibility of high filler loading. However, this resin system has very low reaction rate and it is difficult to control the curing reaction. Hence, EMC based on the biphenyl type epoxy could give rise to the molding problems. To obtain the optimum curing condition and good moldability of such EMC, the selection of the most adequate catalyst should be performed and it is very important to know the influence of the catalysts on the curing reaction of biphenyl epoxy resin compositions.

In the previous study,[1] we investigated the curing characteristics of the biphenyl type epoxy resin with different phenolic-functional hardeners using differential scanning calorimetric (DSC) technique and reported that the curing reaction of the formulation using phenol novolac with triphenylphosphine as a catalyst proceeds through an autocatalytic kinetic mechanism such as phenol novolac cured o-cresol novolac epoxy resin, and the curing reaction of formulations using xylok or dicyclopentadiene type phenol resin (DCPDP) under the same catalyst proceeds by a first order kinetic mechanism.

Although, recently, phenol novolac cured epoxy resin is most widely used for semiconductor encapsulation among the above epoxy-hardener systems,[2] it is expected that the formulation with xylok will be used for ultra large scale integrated circuit near future because of low moisture content, high heat resistance and good adhesion. However the investigations of catalyst effect on cure properties for this system have not been carried out. In this study, therefore, the effects of catalyst on the curing characteristics of the biphenyl type epoxy resin reacted with xylok curing agent were investigated using DSC technique. The curing mechanism of the formulations with different catalysts were interpreted by means of an nth order and an autocatalytic mechanism,[3-7] and the curing kinetics in the overall conversion region have been analyzed using the kinetic and diffusion model.

Experimental

Materials. Epoxy resin used in this study was commercially available biphenyl epoxy resin (YX-4000H) obtained from Yuka Shell Co. Hardener used was xylok obtained form Mitsui Tohatsu Chemical Co. Triphenylphosphine (TPP, Hokko Chemical Co.), 1-benzyl-2-methylimidazole (1B2MI, Nippon-Gosei Co.), diazabicycloundecene (DBU, SAN-APRO), and tetraphenyl phosphonium tetraphenyl borate (TPP-TPB, Hokko Chemical Co.) as a catalyst were used as received. Detailed descriptions of chemical structures are summarized in Table 1.

Sample Preparation. All epoxy resin compositions in this study contain the same equivalent weight ratio (1 : 1) of epoxy and phenolic group, and the content of each catalyst is fixed to 1.5 parts per hundred resin (phr) to epoxy resin. Epoxy resin and hardener were well mixed at 120 °C until a homogeneous solution was obtained. This mixture cooled down to 80 °C. The catalyst was added and fully