Studies of Arenediazonium Salts as a New Class of Electropolymerization Initiator

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ABSTRACT: Electropolymerization holds great potential as a novel process for applying surface coatings onto a variety of substrates. Cathodic electropolymerization has been conducted successfully on metal substrates using initiation systems, such as sulfuric acid and potassium persulfate. However, each of these initiation systems has its own deficiency. This provided the motivation for investigating arenediazonium salts as a new class of cathodic electropolymerization initiators. Our studies found that arenediazonium salts can be easily reduced at reduction potentials lower than that of water to generate initiating free radicals. The reduction efficiency is very high. A copolymer of methyl acrylate and acrylonitrile has been polymerized onto steel surfaces using one of these salts, 4-methyl benzenediazonium tetrafluoroborate, as initiator. Cyclic voltammetry and reflection absorption infrared spectroscopy (RAIRS) studies suggest a strong interaction exists between the initiator and the substrate, which can potentially enhance coating adhesion. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2265–2272, 1999

Key words: electropolymerization; conformal coating; initiator; arenediazonium salts

INTRODUCTION

Electropolymerization is a process in which polymerization is achieved simply by applying an electrical current through a solution of the monomer, solvent, electrolyte, and initiator, if necessary. The reaction mechanism can be free radical, anionic, cationic, or a combination of these. The initiation of polymerization may be direct, through oxidation or reduction of the monomer; or indirect, through the formation of an active intermediate from one of the other components in the solution. The polymer formed will either precipitate onto the electrode surface if it is insoluble in the solution, or dissolve if soluble.

Electropolymerization has been used as a means of providing coatings on substrate surfaces. One significant effort uses this technique to apply a layer of coating onto a graphite fiber surface to absorb impact energy, relieve stress concentration around the fibers, and heal fiber surface flaws. Subramanian et al.[1,2] and Bell et al.[3–5] studied the cathodic electropolymerization of a variety of monomers onto graphite fiber surfaces. By this method, the impact strength of the fabricated graphite fiber composites was improved without lowering the interlaminar shear strength.

Another important area for electropolymerization process is to provide metals with protective coatings. Many vinyl monomers have been polymerized onto metallic cathodes.[3,4,6–11] Bezugli and coworkers[11] obtained adhering poly(methyl methacrylate) (PMMA) and polystyrene films on

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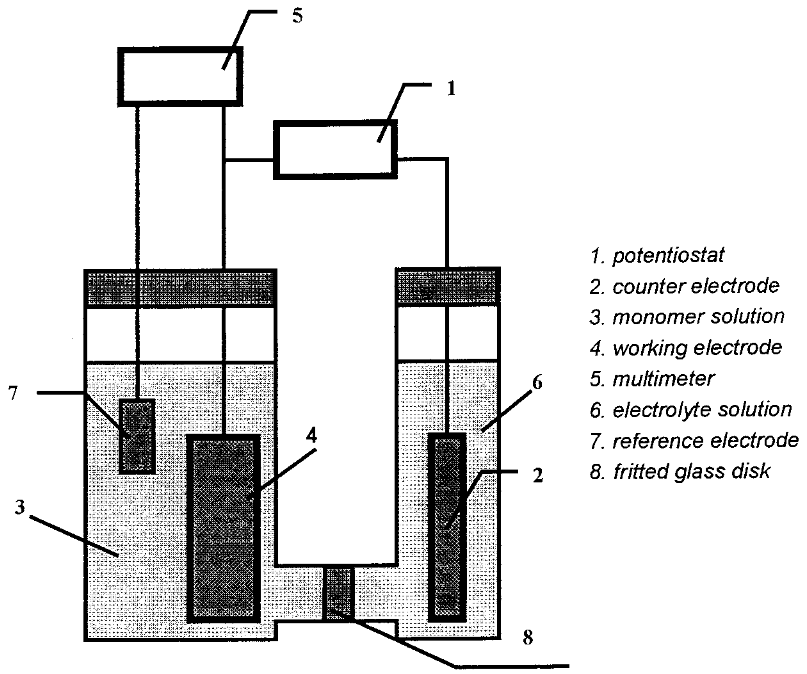

Figure 1 Schematic diagram of a two-chamber electrochemical cell.

steel by electrolysis of the corresponding monomers using dimethylformamide (DMF) as a solvent. Through the use of free radical and anionic inhibitors, the reaction mechanism was established to be anionic. Collins[12] coated steel electrodes with polyacrylamide crosslinked by bisacrylamide in an aqueous solution. The anodic polymerization of phenol and its derivatives on metals has also been extensively investigated.[13]

The investigation of several anodic electropolymerization initiators which included nitrate ion, perchlorate ion, sulfate ion, and alkyoxide, has been reported in the literature.[14–22] Free radicals were generated through the oxidation of these initiators at the anode in an aprotic medium. However, when Lee and Bell[23,24] studied these initiators in an aqueous environment, no polymer could be obtained on an aluminum surface. This phenomenon was attributed to the oxidation of water at the anode under the experimental conditions. The generated oxygen inhibited free radical polymerization and could disrupt coating formation. Serious oxidation of the aluminum substrate was observed. The oxidation was aggravated by the acidification of the anolyte during the reaction.

On the other hand, the cathodic electropolymerization in aqueous medium has been conducted successfully on metals and on graphite fibers.[3–5,8,24–26] Sulfuric acid has been used by several research groups to conduct electropolymerization on graphite fibers.[2,3,8,27] The true initiation species is the hydrogen radical in this case.[28] Potassium persulfate has been used to generate sulfate radicals on the aluminum surface.[23,24]

The sulfuric acid system tends to have low initiation efficiency because of recombination of radicals to give hydrogen gas, which disrupts the coating as it is formed on the surface. The acidic environment may also cause corrosion of the metal substrate during the process. The persulfate ion has a relatively high reduction potential and is not very thermally stable. Its decomposition can cause polymerization in the solution. A new initiation system is thus highly desired. In this article, we report the development of a new cathodic electropolymerization initiator.

EXPERIMENTAL

All chemicals were obtained from Aldrich Chemical Company, Inc., and were used as received, except for the monomers, which were purified by passing dropwise through a DHR-4 inhibitor removal column from Scientific Polymer Products, Inc. SAE 1010 steel coupons from the Q-Panel

Company (Cleveland, OH) were used as the substrate for the study.

A H-shaped, two-compartment glass cell was used in the study. A schematic diagram of the cell is shown in Figure 1. The larger compartment was capped with a rubber stopper, which helped to position the steel electrode, reference electrode, and nitrogen inlet and outlet. A stainless steel plate was placed in the smaller compartment and was used as a counter electrode. The two compartments were separated by a sintered glass disk. A Princeton Applied Research potentiostat Model 363 was used to supply constant potential or current to the cell. A saturated calomel electrode (SCE) was used as the reference electrode and was placed near the steel electrode during polymerization.

The substrate was thoroughly cleaned using an ammonia-based, Micro® laboratory detergent and then etched in a 3 wt % citric acid solution for 5 min. The etching solution temperature was maintained at 70°C, and the pH was adjusted to 4.0 using ammonium hydroxide. The substrate was then washed with an ample amount of distilled water and dried in an oven at 90°C prior immediate use. Previous studies[29] have shown that citric acid forms a water-soluble complex with iron cations and can effectively dissolve the oxide on surface. A monomer solution was prepared by dissolving an appropriate amount of monomer in a 0.025*M* aqueous $NaNO_3$ electrolyte solution. The monomer solution was poured into the working compartment while the counter compartment was filled with the electrolyte solution.

A BAS-100 electrochemical analyzer from Bioanalytical Systems, Inc., was used to study the electroactivity of the new initiators. A glassy carbon electrode, a saturated Calomel electrode (SCE), and a platinum electrode were used as the working, reference, and counter electrode, respectively. A Mattson Polaris Fourier transform infrared (FTIR) spectrometer equipped with a variable-angle reflection absorption infrared spectroscopy (RAIRS) accessory from Spectratech, Inc., was used for IR analysis. The incident angle used for RAIRS was 82°. At least 256 scans were collected for each spectrum. Ultraviolet (UV) spectra from 250 to 900 nm were collected on a Lambda Array 3840 UV–visible (UV–vis) spectrophotometer from Perkin–Elmer. The morphology of the substrate and the electropolymerized coating was examined using an Olympus optical microscope in the reflection mode.

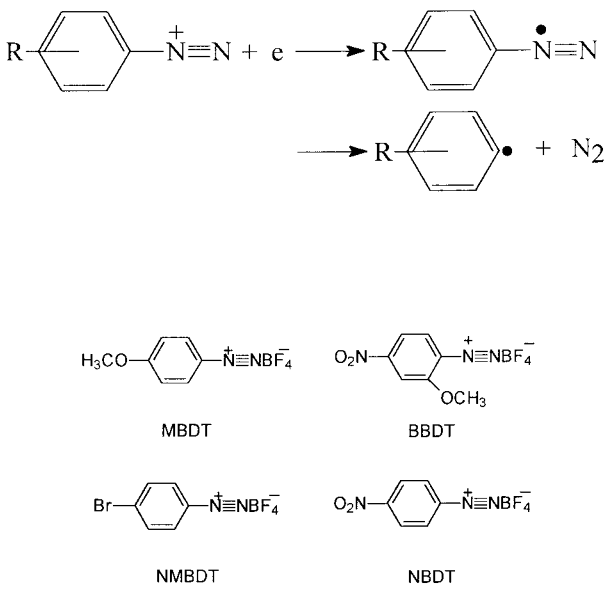
MBDT
BBDT
NMBDT
NBDT

Figure 2 Electrochemical reduction mechanism of aromatic diazonium salts.

RESULTS AND DISCUSSION

There have been several studies in the literature on the direct electrochemical reduction of arenediazonium compounds, using polarographic techniques.[30–38] The general consensus from these studies is that the reaction occurs through a two-step process, as shown in Figure 2. In the first step, the diazonium cation obtains one electron from the electrode at a fairly low reduction potential to generate a radical. This step is pH-independent, as no hydrogen ion is involved. In the second step, the radical decomposes to give an aryl radical and nitrogen. The aryl radical is very reactive and can potentially react with olefins to initiate polymerization. The low reduction potential of diazonium salts minimizes the decomposition of water in the electropolymerization process. This avoids a large amount of hydrogen gas being generated at the cathode surface, disrupting the coating formation or introducing defects into the coating. Also, neutral conditions can be used, which reduce the corrosion of the metal substrate in the monomer solution. These advantages of the arenediazonium salts provided the motivation for their investigation as an cathodic electropolymerization initiator.

In this study, the electrochemical activity of four arenediazonium salts was studied in acetonitrile. These salts have different substitution groups on the phenyl ring, as shown in Figure 2.

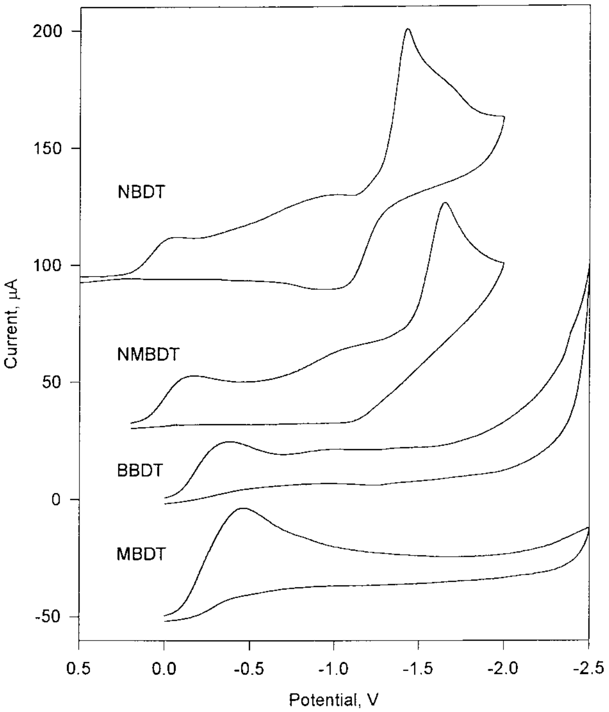

Figure 3 Cyclic voltammogram of arenediazonium salts (scan rate, 200 mV/s).

The cyclic voltammograms (CV) of these salts are shown in Figure 3. There is a small irreversible reduction peak appearing at a fairly low potential in each voltammogram. This peak corresponds to the first step in the previously discussed reduction mechanism. Depending upon the substitution group on the phenyl ring, this peak shifts accordingly. The potential is lowest for *p*-nitrobenzenediazonium tetrafluoroborate (NBDT), which has a strong electron-withdrawing nitro group on the phenyl ring. The potential is highest for *p*-methoxy substituted (MBDT), which has a electron-donating methoxy group on the phenyl ring. Therefore, electron-withdrawing substituents increase the ease of reduction of the salt, while electron-donating substituents stabilize the starting diazonium salt, decreasing its tendency to acquire an electron. Such a trend is in agreement with the results of polarographic studies[33] and is consistent with theoretical predictions.[39] All these values are lower than the reduction potential of other initiation systems, such as sulfuric acid and potassium persulfate, as well as the reduction potential of water.[23,24] The reduction peak appearing at much more negative potentials in two voltammograms is due to the formation of hydrazine as shown below and is not relevant in this study.

$$\mathrm{ArN_2^+} + 4e + 3\mathrm{H^+} \rightarrow \mathrm{ArNHNH_2}$$

All the arenediazonium salts studied can be reduced at a fairly low reduction potential and are therefore potentially capable of initiating electropolymerization. MBDT was selected for further study since it has the highest reduction potential among the four and is therefore most stable towards undesirable reductions. Its electrochemical reduction was monitored using UV–vis spectroscopy. In an acetonitrile medium, MBDT shows three absorption peaks in the UV region, as shown in Figure 4. The peaks at 194 and 230 nm are assigned to the benzene ring, while that at 312 nm is attributed to the diazonium functional group. An electrolysis experi-

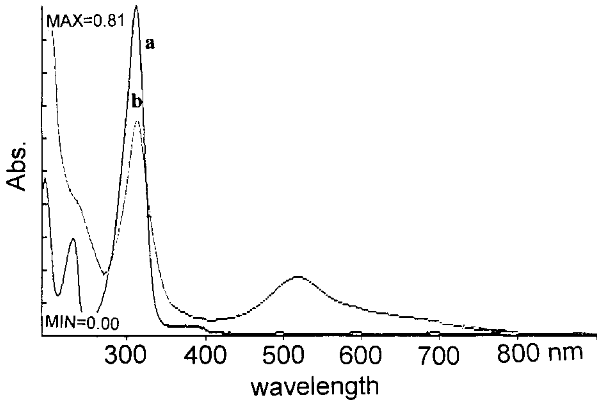

Figure 4 UV–vis spectra of (a) MBDT and (b) DPPH in acetonitrile.

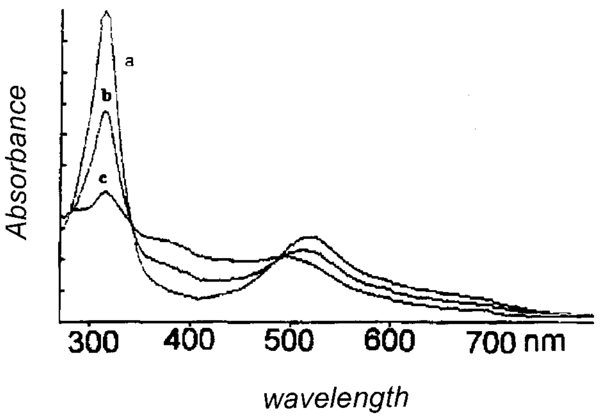

Figure 5 UV spectra of a mixture of MBDT and DPPH, electrolyzed in acetonitrile for (a) 0, (b) 30, and (c) 60 min.

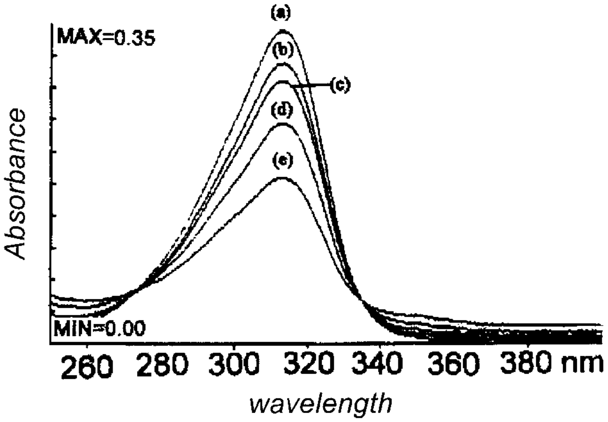

Figure 6 UV–vis spectra of MBDT electrolyzed in water for (a) 0, (b) 30, (c) 60, (d) 90, and (e) 120 min. Sodium nitrate was used as an electrolyte.

ment was conducted in acetonitrile with both MBDT and a free radical inhibitor, diphenylpicryl hydrazyl hydrate (DPPH), present. DPPH has been widely used in the literature to study mechanisms of polymerization. It shows two absorption peaks at 328 and 521 nm, respectively, as shown in Figure 4. UV spectra recorded at different electrolysis times are shown in Figure 5. The top curve is the spectrum of the solution before the electrolysis. The absorption of DPPH at 328 nm overlaps with that of MBDT at 312 nm to form a single peak at 317 nm. The absorption of DPPH at 521 nm is, however, far away from the absorption region of MBDT. The middle and bottom spectra are those of the solution at electrolysis time of 30 and 60 min, respectively. It is clear from the absorbance change of the 512 nm peak that the concentration of DPPH decreases with time. The same trend is also observed for the peak at 317 nm. Although this peak has contributions from both MBDT and DPPH, it is apparent from the magnitude of the absorbance change that the concentration of both components decreases with time. This is consistent with the cyclic voltammetry results in that free radicals are generated during electrolysis. These radicals react readily with DPPH to decrease its concentration.

In a separate experiment, the efficiency of the diazonium reduction reaction was estimated. Electrolysis was carried out in an aqueous solution of MBDT. The reaction was monitored by following the 312 nm peak. As shown by the spectra in Figure 6, the absorbance decreases with increasing reaction time. Using a calibration plot, the rate of MBDT disappearance can be determined from the change of absorbance with time. Since the experiment was conducted in a constant current mode, the rate of Coulombic input into the solution is known exactly. From these, the efficiency of MBDT reduction is estimated to be 20.7%, which suggests that the reduction process is very efficient.

Electropolymerization was conducted using $0.01M$ MBDT as initiator in an aqueous solution. The first monomer studied was acrylamide. Upon the application of a constant potential of -0.8 V versus SCE, no coating formation was observed. However, the viscosity of the solution increased dramatically during the experiment. This suggests that the polymer formed dissolved back into the solution, as polyacrylamide has very high solubility in water.

The copolymerization of methyl acrylate (MA) and acrylonitrile (AN) was also studied using a feed composition of $0.24M$ AN, $0.36M$ MA, and $0.005M$ MBDT in water. The reaction was conducted at a constant potential of -1.0 V versus SCE. During the reaction, a white layer of coating formed on the electrode surface. In the meantime, there was a dramatic drop of the current through

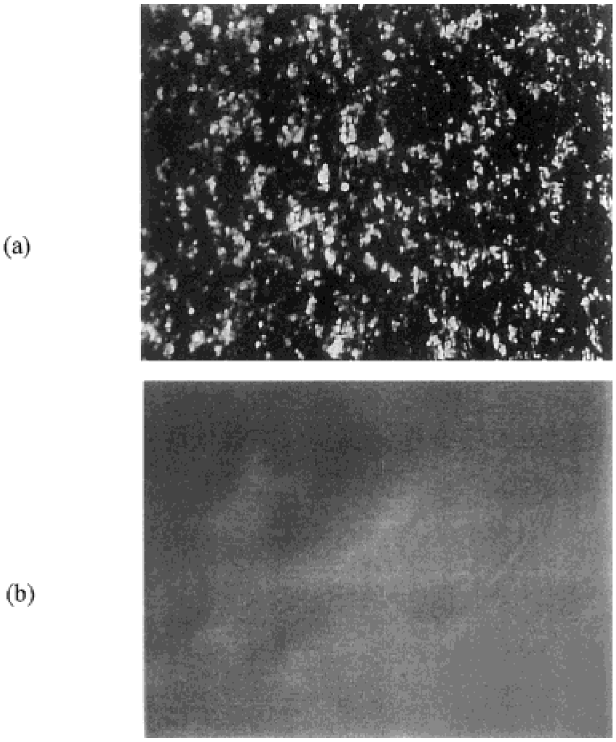

Figure 7 Micrograph of (a) citric acid etched steel surface and (b) steel surface coated with methyl acrylate–acrylonitrile copolymer (magnification, 250×).

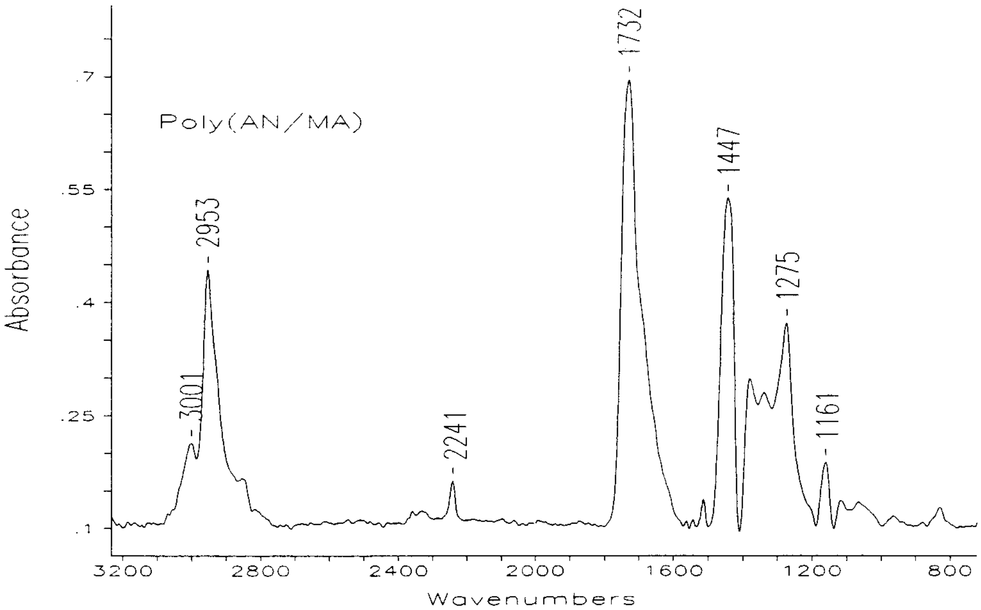

Figure 8 IR spectrum of an acrylonitrile–methyl acrylate copolymer coating on steel obtained using MBDT as an electrochemical initiator.

the cell, suggesting that a very compact layer was formed on the surface. This is because the copolymer of AN and MA is completely insoluble in water. The penetration by monomers and ions through this layer of coating is very difficult. This results in the increased total resistance of the electrochemical cell and also limits the attainable coating thickness. For a reaction time of 30 min, a coating about 1 μm thick was obtained on a steel substrate. Before the experiment, the surface was fairly rough, as shown in Figure 7. After electropolymerization, a layer of smooth and uniform coating was formed on the surface. The IR spectrum of the copolymer is shown in Figure 8. The characteristic nitrile peak from AN functionality at 2241 cm^{-1} and the ester carbonyl absorption from MA at 1732 cm^{-1} are present in the spectrum, confirming the formation of a MA–AN copolymer on the substrate surface.

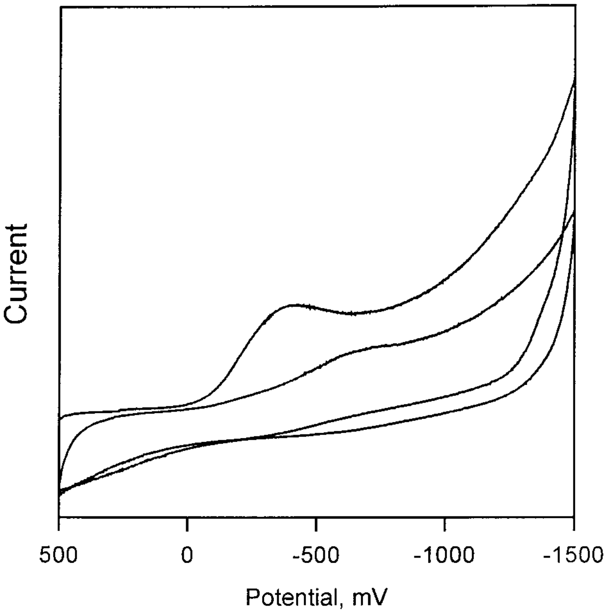

Figure 9 Cyclic voltammogram of MBDT in water: (a) first scan; (b) second scan (scan rate, 200 mV/s).

It is worth mentioning that the characteristic reduction peak of arenediazonium salts observed in the first CV scan is absent in the subsequent scans, as shown for the case of MBDT in Figure 9. Even after vigorous agitation of the solution, the peak still cannot be recovered. Depletion of reactant at the electrode surface is therefore ruled out as a possible reason. It is likely that strong interaction exists between the initiator and the substrate. This prompted further studies using RAIRS.

Figure 10 shows the transmission IR spectrum of MBDT. The strong absorption at 2239 cm^{-1} is assigned to the diazonium group. The absorption at 2992 and 2841 cm^{-1} is from the C—H stretching of the methyl group, while those at 1583, 1003, and 839 cm^{-1} are from the phenyl ring. The symmetric and asymmetric bending of the C—O—C ether linkage appear at 1038 and 1290 cm^{-1}. RAIRS spectra were obtained using a clean steel coupon as background. Figure 11 shows a spectrum from a steel coupon reduced in a 0.005*M* MBDT water solution for 60 min and rinsed thoroughly with water. The absorption of the phenyl ring at 1583 cm^{-1} shifted to 1607 cm^{-1}, while the bending of the ether linkage now appeared at 1292 cm^{-1}. The absorption at 2239 cm^{-1} is absent, confirming the loss of the diazo group in the second step of reduction. Another spectrum was obtained on the same sample after 48 h of extraction in acetonitrile (Fig. 12). Although the signal intensity is lower, the same spectrum is still present. This supports the CV result in that there exists strong interaction between the diazonium initiators and the substrate, which can potentially impart good coating adhesion.

CONCLUSION

The electrochemical reduction of a series of arenediazonium salts was studied with the aim of developing a new initiator for cathodic electropolymerization on metals. All of them have a fairly low reduction potential. The reduction of MBDT was monitored using UV–vis spectroscopy, and the reaction efficiency was estimated to be 20.7%. A polymeric coating of poly(methyl acrylate-*co*-acrylonitrile) was obtained using MBDT as an electropolymerization initiator. The coating obtained was smooth and uniform. Both CV and RAIRS results suggest that there exists strong interaction between the substrate and the initiator, which could lead to better coating adhesion.

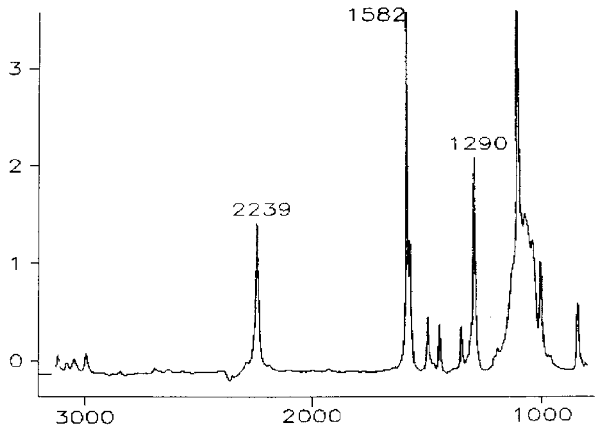

Figure 10 Transmission IR spectrum of MBDT (resolution, 4 cm^{-1}).

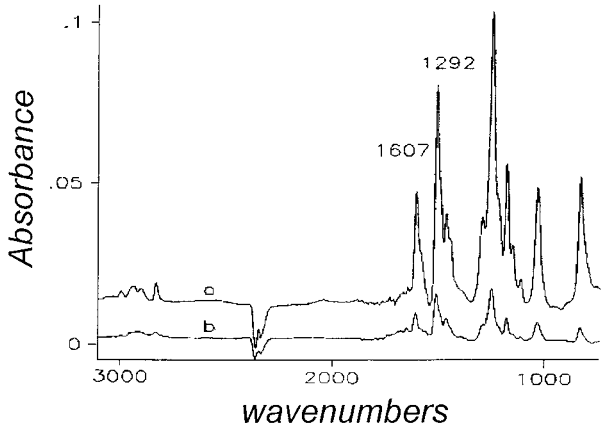

Figure 11 RAIRS spectra of (a) steel working electrode after 60 min electrolysis in MBDT water solution and (b) the same electrode after 48 h extraction in acetonitrile.

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