imide film.[34] More complete investigations of this process are proceeding.

Acknowledgment. I thank Kevin S. Peters of University of Colorado at Boulder for the use of the picosecond flash photolysis apparatus. Many useful discussions were held with R. K. Waring, S. Mazur, and S. Maerov. Sam Tonik and Gloria Worrell were extremely helpful with laboratory assistance.

Registry No. 1·DMA, 107576-77-2; (PMDA-ODA)(SRU)·DMA, 107558-03-2; (PMDA-ODA)(copolymer)·DMA, 107558-07-6; (PMDA-ODA)(SRU)·TTF, 107558-04-3; (PMDA-ODA)(copolymer)·TTF, 107558-08-7; (PMDA-ODA)(SRU)·DMI, 107558-05-4; (PMDA-ODA)(copolymer)·DMI, 107558-10-1; (PMDA-ODA)(SRU)·4-$(CH_3)_2NC_6H_4N(CH_3)_2$, 107558-06-5; (PMDA-ODA)(copolymer)·4-$(CH_3)_2NC_6H_4N(CH_3)_2$, 107558-09-8.

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Electron Transport in Poly(3-vinyl-10-methylphenothiazine) Films

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ABSTRACT: Electrochemical properties of poly(3-vinyl-10-methylphenothiazine) (polyMPT) films spin coated on a Pt electrode were investigated by cyclic voltammetry and chronocoulometry. The polyMPT films showed electrochromism, and the oxidized films remained reddish purple in ambient air under open-circuit conditions for many months. Within the surface coverage range of $\sim 0.6\ \mu mol/cm^2$, over 90% of all the 10-methylphenothiazine (MPT) residues in the polyMPT films could readily be oxidized by electrolysis, presumably because of efficient self-exchanges of electrons. The apparent diffusion coefficient (D_{ap}) for electron transport through the film was determined by chronocoulometry to be 1.6×10^{-9} and $2.6 \times 10^{-9}\ cm^2/s$ for an anodic and a cathodic step, respectively. Copolymers of 3-vinyl-10-methylphenothiazine and methyl methacrylate with various mole fractions of the MPT units (f_{MPT}) were employed to study the dependence of D_{ap} on the concentration of the MPT units in the film, from which electron self-exchange rate constants (k_{ex}) were roughly estimated to be 4.0×10^5 and $5.9 \times 10^5\ M^{-1}\ s^{-1}$ for the anodic and cathodic processes, respectively. Absorption spectra of the oxidized polymer films showed a band due to dimer dications of the oxidized MPT units ($(MPT_2)^{2+}$). The intensity of this dimer band decreased with decreasing f_{MPT}. These facts are indicative of a pairwise orientation of the MPT moieties in the oxidized film, which may explain the larger D_{ap} and k_{ex} values for the cathodic process.

Introduction

Recently, an increasing interest has been drawn to redox polymers as a promising electroactive material. A variety of macromolecules with redox functionality has so far been synthesized, and some of them have proven their usefulness for electrode modifications.[1,2] Unlike chemical derivatization of electrode surfaces with low molecular weight functional groups, layers of polymer-modified electrodes can consist of some thousands of monolayers equivalent. In such polymer layers a large number of remote electroactive sites that have virtually no chance to contact the underlying electrode surface can undergo oxidation and reduction by self-exchanges of electrons between neighboring redox sites. The electron-hopping mechanism for this process originally proposed by Kaufman et al.[3,4] is now accepted.

It has been suggested by Murray and co-workers that electron-donating and -accepting redox sites in polymer

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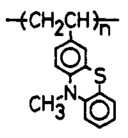
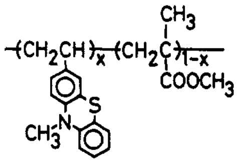
films have to come into a juxtaposition for an effective electron self-exchange to occur.[5] In fact, in the case that a polymer film is swollen with solvents to some extent, as is most of the cases of such electrochemical systems, the polymer would undergo segmental motions that in turn facilitate the redox sites to move into the right position for electron transfer. This process would involve a considerable entropy loss due to an ordering deformation of polymer chains.[5] Therefore, it is reasonable to assume that any exothermic electronic interaction between the redox centers in polymer films may strongly favor electron self-exchange processes by compensating the negative entropy. The rate-controlling factor for the electron flow, however, can be the barrier for either the self-exchange of electrons or the compensating counterion motion.[3,4]

10-Methylphenothiazine (MPT) undergoes reversible one-electron oxidation, leading to the formation of a very stable radical cation.[6] A previous article was concerned with the electrochemical behavior of solutions of poly(3-vinyl-10-methylphenothiazine) (polyMPT) and the copolymers of 3-vinyl-10-methylphenothiazine (VMPT) with methyl methacrylate (MMA) (copolyMPT).[7] We have demonstrated that polyMPT undergoes exhaustive oxidation in voltammetric processes, whereas in copolyMPT a significant number of the redox centers remained unoxidized.[7] This is an implication that an exhaustive oxidation of a redox polymer is largely assisted by the interaction between neighboring redox centers.

In the present study we deal with the electrochemistry of the polyMPT and copolyMPT films attached to a Pt electrode. Electrochemical oxidation and reduction would cause structural changes of a redox polymer film deposited on an electrode as a result of a massive charge acquirement and loss that occurs within the film. In addition, a flux of solutions and charge-compensating counterions flow through the film during the electrochemical process. Therefore, films must have durability and adhesiveness, properties that strongly depend on the molecular weight of the polymers. We have succeeded in obtaining high molecular weight polyMPT by free radical polymerization of highly pure VMPT, which offers sufficiently tough and adhesive coatings on electrodes.



PolyMPT



CopolyMPT

Experimental Section

Materials. Poly(3-vinyl-10-methylphenothiazine) (polyMPT) was prepared by the free radical polymerization of 3-vinyl-10-methylphenothiazine (VMPT)[7] as follows: An ampule containing 2.39 g (10 mmol) of VMPT, 1.64 mg (0.001 mmol) of 2,2′-azobis(2-methylpropionitrile) (AIBN), and 10 mL of tetrahydrofuran (THF) was outgassed by three freeze–pump–thaw cycles and sealed under vacuum. The polymerization was carried out at 60 °C for 45 h. The resulting polymer was purified by reprecipitating 3 times from a THF solution into an excess of acetone: yield, 0.79 g (33% conversion); number-average molecular weight, $M_n = 1.3 \times 10^5$ (GPC).

Poly(3-vinyl-10-methylphenothiazine-*co*-methyl methacrylate) (copolyMPT) was prepared as reported previously.[7] The mole fractions of the VMPT units in the copolymer were determined by the C/N ratios.

Procedures and Measurements. A 9 mm × 15 mm Pt plate electrode was used for cyclic voltammetry. A Pt disk electrode with a 0.283-cm^2 area tightly mounted in a Teflon rod was used for chronocoulometry. A drop of a solution of a known concentration of polyMPT or copolyMPT in ethylene dichloride was placed on an electrode, which was then spun at a rate of about 1000 rpm for about a minute. The resulting film was allowed to air dry. In the case of the Pt plate electrode a portion of the film was removed by wiping to secure the electrical contact with a lead wire. The amount of surface coverage was varied from 0.01 to 0.6 μmol/cm^2 by varying the concentration of the polymer solution (0.2–10 wt %). The surface coverage of the polymers was determined by UV absorption spectra of an *N,N*-dimethylformamide (DMF) solution of the film dissolved in a known volume of the solvent with the aid of sonication.

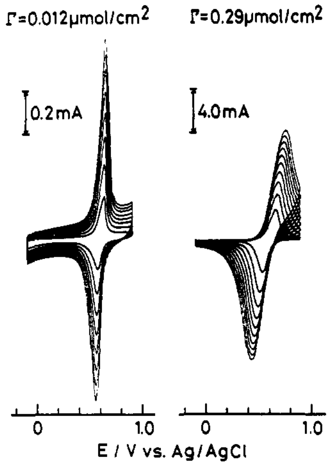


Figure 1. Cyclic voltammograms for polyMPT films on a Pt plate electrode in 0.4 M LiClO$_4$/ACN at various scan rates: 20–140 and 20–200 mV/s for the films with 0.012 and 0.29 μmol/cm^2, respectively.

Electrochemical measurements were performed in acetonitrile (ACN) solutions containing 0.4 M LiClO$_4$, in which polyMPT and copolyMPT films were insoluble both before and after oxidation. Cyclic voltammograms were obtained with a Hokuto potentiostat HA-301 driven by an NF function generator FG-121B. Chronocoulometric experiments were performed with a Hokuto digital Coulomb meter HF-202D combined with the above potentiostat. Charge–time data were acquired on an Iwatsu transient memory D901 (8 bit, 4096 word). To minimize uncompensated resistance due to polymer coatings, positive feedback techniques[8] were employed.

For spectroelectrochemical measurements a 10 mm × 10 mm × 50 mm quartz cell was employed, which was equipped with a Luggin capillary for a reference Ag/AgCl electrode and an optically transparent In$_2$O$_3$/SnO$_2$ electrode (OTE) coated with a polyMPT or copolyMPT film. The absorption spectra of the films were recorded at constant potentials on a Hitachi 124 spectrophotometer.

Results

Figure 1 shows cyclic voltammograms for a Pt electrode covered with poly(3-vinyl-10-methylphenothiazine) (polyMPT) films with different surface coverages. Acetonitrile (ACN) was chosen for a solvent because polyMPT was not soluble but only slightly swollen in both neutral and oxidized forms. An electrode coated with a low surface concentration of polyMPT ($\Gamma = 0.012$ μmol/cm^2) exhibited a wave shape typical of a surface confined species, i.e., narrow, symmetrical peaks with a very small peak-to-peak separation. On the other hand, an electrode with a high coverage ($\Gamma = 0.29$ μmol/cm^2) showed a wave with a diffusion nature, i.e., rather broad peaks with nonzero peak-to-peak separations and diffusional tails. These electrode coatings are so stable in both neutral and oxidized forms that there was neither a sign of degradation nor a loss of surface adhesion after hundreds of cyclic scans of the electrode potential between −0.1 and +0.9 V vs. a Ag/AgCl reference electrode.

Anodic peak currents (i_p) were plotted against the scan rate (v) and also against the square root of the scan rate

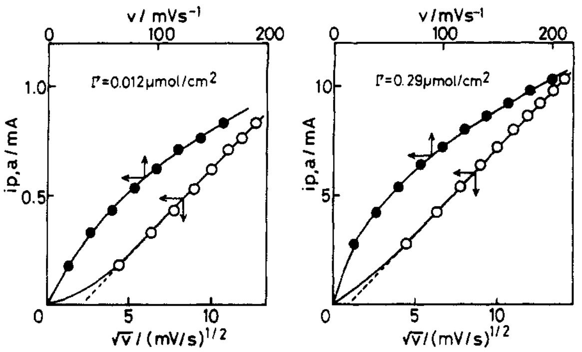


Figure 2. Anodic peak currents plotted as a function of the scan rate (v) and the square root of the scan rate ($v^{1/2}$) for polyMPT films.

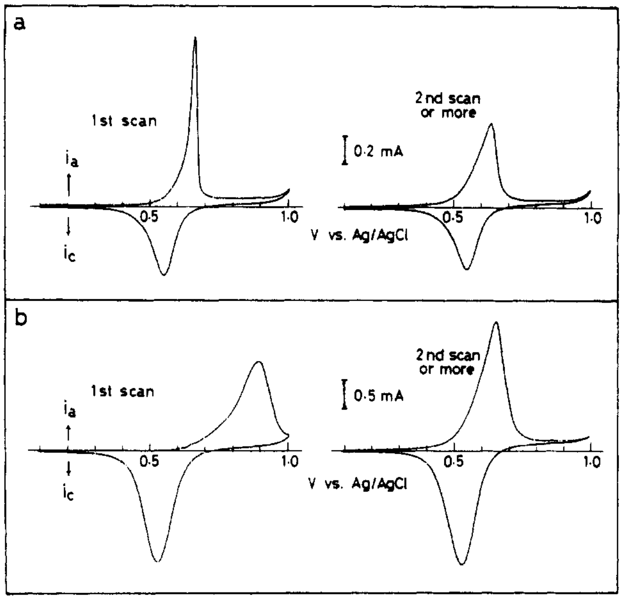


Figure 3. Cyclic voltammograms of polyMPT films on a Pt electrode obtained at a scan rate of 36 mV/s in 0.4 M $LiClO_4$/ACN. Film thickness: (a) $\Gamma = 0.062$ μmol/cm^2; (b) $\Gamma = 0.228$ μmol/cm^2.

($v^{1/2}$) for comparison in Figure 2. There is a linear relationship between i_p and $v^{1/2}$ when $v > 20$ mV/s, suggesting a diffusion-limiting voltammetric process. However, the extrapolation of the linear plot yielded a nonzero intercept, implying that some kind of nonideality is involved.

Cyclic voltammograms show that the polyMPT films undergo a single oxidation to give oxidized films which then undergo a single re-reduction to give neutral films. It is noted, however, that the anodic peak at the first scan for a freshly coated film showed an anomalous wave with a significant overpotential, as exhibited in Figure 3. This wave distortion was observed only at the first anodic scan, and the cathodic scan that immediately followed yielded a normal wave that reproduced at the subsequent scans. This anomaly at the first anodic process was also observed in potential-step experiments. The first oxidation process for as-coated films was considerably slow, which was followed by reproducible time response curves at the subsequent steps. This apparently peculiar behavior that is obviously resulting from the overpotential involved in the first anodic process may be explained in terms of the electrical conductivity of the polyMPT film. The as-coated polyMPT films are virtually insulator ($\sigma < 10^{-11}$ S/cm). However, upon partial oxidation of 3–4 mol % of the MPT moieties in the film, the electrical conductivity is increased to the order of 10^{-5} S/cm as reported previously.[9] This conductivity was retained after the films were reduced.

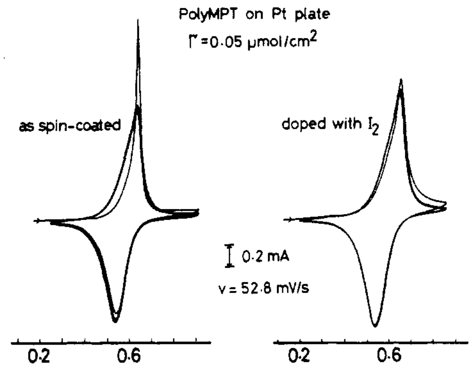


Figure 4. Comparison of the cyclic voltammograms for a polyMPT film on a Pt electrode before and after an iodine dope. The doping was performed by placing the polyMPT film in a flask containing a small amount of I_2 for 3 min at ordinary pressure.

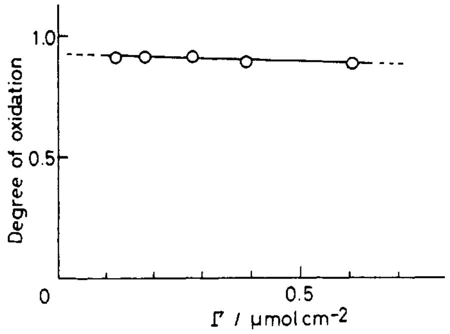


Figure 5. Dependence of the degree of oxidation of the polyMPT film on the surface concentration after electrolysis at +0.75 V vs. Ag/AgCl for 60 s in 0.4 M $LiClO_4$/ACN.

This explanation is supported by the fact that an as-coated polyMPT film treated with iodine vapor for a few minutes showed considerably reduced overpotential at the first anodic scan in the cyclic voltammogram as illustrated in Figure 4. This is due to an increase in the electrical conductivity of the polyMPT film to the order of 10^{-5} S/cm as a result of an iodine dope.

Upon oxidation, the polyMPT films undergo a color change from colorless to reddish purple. The color change was reversible between the oxidized and re-reduced forms over a number of cycles. The oxidized reddish purple films were extremely stable to ambient air and moisture for many months after they were disconnected in the oxidized form, washed with ACN, and dried. Thus, the polyMPT film retained an open-circuit color memory, with the depth of the color reflecting the degree of oxidation.

For an estimate of the relative number of electrochemically active MPT units that actually can undergo electrochemical redox reactions, the charges that passed through the electrode during electrolysis were compared with the total numbers of the MPT units in the film determined by spectroscopy. Figure 5 shows that about 90% of all the MPT units in the film can be oxidized even for thicker films corresponding to thousands of monolayers; e.g., a film with $\Gamma = 0.6$ μmol/cm^2 has a thickness of about 1.4 μm, which corresponds to approximately 2000 monolayers. This means that a large number of the remote MPT moieties that have no access to the electrode surface can actually participate in the electrochemical reaction. This is only possible by self-exchanges of electrons between neighboring electroactive sites,[3-5] i.e., in the anodic process localized oxidation states can migrate through the film away from the electrode surface via the electron-exchange reaction with adjacent reduction states which in turn migrate toward the electrode surface. It is well established

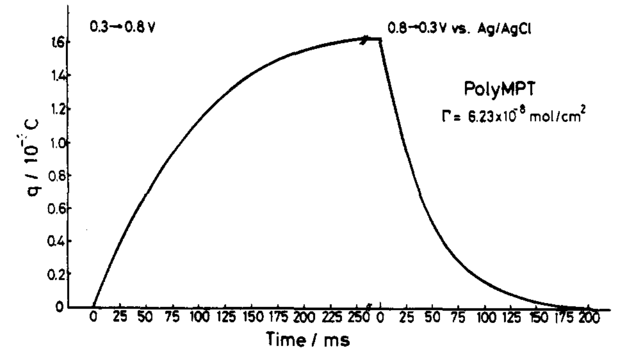


Figure 6. Chronometric charges vs. time: polyMPT film (Γ = 0.062 μmol/cm^2) on a Pt disk electrode. Potential step, from +0.3 to +0.8 V vs. Ag/AgCl and back again.

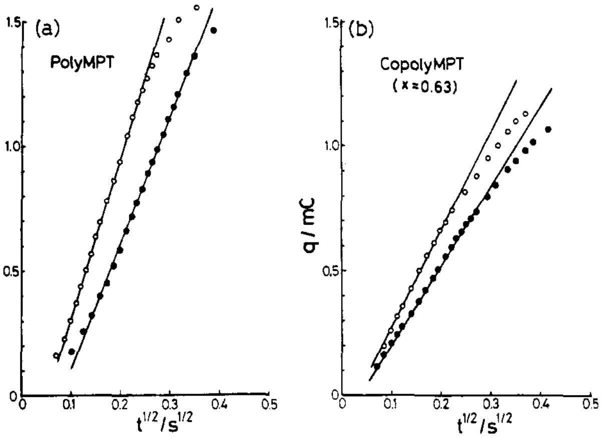


Figure 7. Chronocoulometric charges vs. square root of time: (a) polyMPT film (Γ = 0.062 μmol/cm^2), (b) copolyMPT ($f_{\rm MPT}$ = 0.63) film (Γ = 0.055 μmol/cm^2). Potential step: (●) from +0.3 to +0.8 V; (○) from +0.8 to +0.3 V vs. Ag/AgCl in 0.4 M LiClO$_4$/ACN.

that this migration process can be treated mathematically as a diffusion process.[10,11]

In order to study electron migration through polymer films potential-step chronocoulometry[12] was performed for the random copolymers of VMPT with MMA (copolyMPT) with various MPT mole fractions ($f_{\rm MPT}$), wherein the MPT moieties are separated by the MMA spacing units. Figure 6 shows the chronometric charge response for a polyMPT film when the electrode potential was stepped from +0.3 to +0.8 V and was stepped back to +0.3 V. The charge response for the reduction process appears to be faster than that for the oxidation process. Figure 7 exhibits the plots according to the integrated Cottrell equation[12] for polyMPT and copolyMPT ($f_{\rm MPT}$ = 0.63) films. Straight lines were obtained for the plots of the chronometric charges against the square root of time. However, it should be noted that the straight lines yielded negative intercepts because of the presence of initial slower rise processes immediately after the step potential was applied. The resistance of the polymer film is apparently responsible for the initial slow rise. The problem of uncompensated resistance can be serious for coatings of polymers with a high density of redox species. Even though the film resistance per se may not be too high, the effect of the resistance is amplified because a high concentration of electroactive species at the electrode surface results in extremely large initial currents in response to a potential step. The positive feedback techniques[8] were very effective in minimizing the effect of the uncompensated resistance, but the initial rise could not be eliminated completely in the present case. There is a sign in Figure 7 that the effect of the film resistance is slightly less pronounced for copolyMPT ($f_{\rm MPT}$ = 0.63), presumably because the MPT concentration at the electrode surface (3.3 mmol/cm^3) is lower than that for the homopolymer (4.2 mmol/cm^3). From the slope of the linear portion of the q–$t^{1/2}$ plot were calculated apparent charge transport diffusion coefficients ($D_{\rm ap}$). Although the $D_{\rm ap}$ values thus estimated may have order-of-magnitude meaning because of the above problem, we consider that comparisons of these values for the various MPT polymers within the present experimental results are meaningful. The values of $D_{\rm ap}$ for the re-reduction step were slightly larger than those for the oxidation step for both polyMPT and copolyMPT films. In general, the rate-controlling step involved in charge migration processes may either be electron-hopping or a charge-compensating counterion motion.[4,5] For an effective electron self-exchange to occur in the film, the oxidized and neutral forms of the MPT units may align in the face-to-face orientation to some extent. Such a juxtaposition may either be preformed in the matrix of the film or occur as a result of segmental motions. Since the polyMPT film is slightly swollen with ACN, the MPT units in the film are free to move to some extent. In any event the proximity of the redox centers is considered to be of importance for an efficient charge migration. As expected the value of $D_{\rm ap}$ showed a sharp decrease with decreasing $f_{\rm MPT}$. Figure 8 displays the relationship between $D_{\rm ap}$ and the volume concentration of the MPT unit (C) in the film. The C values were calculated from the $f_{\rm MPT}$ values for dry films because the degree of swelling for the copolymer films with $f_{\rm MPT}$ higher than 0.51 was apparently low enough not to cause a significant error in the estimation of the C values. However, the swelling was noticeable for the films with $f_{\rm MPT}$ = 0.32. The copolymers with very low $f_{\rm MPT}$ were found to be soluble in ACN. Therefore, the data are limited in the high concentration region as displayed in Figure 8. Obviously, the concentration of the MPT unit in the film decreases as $f_{\rm MPT}$ decreases.

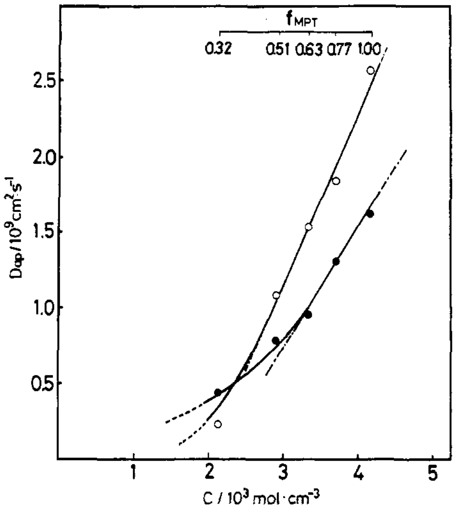


Figure 8. Dependence of the apparent diffusion coefficient ($D_{\rm ap}$) on the concentration of the MPT units (C) for the oxidative (●) and re-reductive (○) steps.

Discussion

Most of the electrochemical studies on redox polymer films reported so far have been concentrated on polyelectrolyte films with ionic redox species bound electrostatically,[1,2] where not only charge diffusion via the electron self-exchange but also actual physical diffusion of the redox species may be possible in swollen polyelectrolyte films. In this situation the apparent diffusion coefficient can be given by the combination of the each diffusion process[13-15]

$$D_{ap} = D_0 + (\pi/4)k_{ex}\delta^2 C \qquad (1)$$

where D_0 is the diffusion coefficient of actual physical diffusion, k_{ex} the second-order electron self-exchange rate constant for the redox couple, C the total concentration of the reduced and oxidized redox couples, and δ the center-to-center distance of the reactants when the electron transfer takes place. If redox centers are covalently linked to a polymer backbone, then the contribution from physical diffusion can be eliminated; thereby eq 1 predicts the linear relationship with the zero intercept in the D_{ap}–C plot, with the slope reflecting the k_{ex} value. However, this is not the case with the data presented in Figure 8; the plot can approximately be fitted to a linear line with a nonzero intercept. These facts may suggest that k_{ex} in the present study is dependent on C and is very small in the lower C region. This speculation may be rationalized by the following consideration. In the higher C region the possibility of a pairwise orientation of the MPT units can be high so that only small motion of the electron-donating and/or -accepting centers may be enough to achieve proper orientation for electron transfer. In the lower C region, on the other hand, a considerable degree of segmental motions may be required for the electron-exchanging redox centers to come into a juxtaposition, which would involve a higher energy barrier. On the basis of these considerations the apparent k_{ex} values for the higher C region were estimated from the slope of the linear line in Figure 8 assuming δ = 5 Å. The values of k_{ex} were obtained to be 4.0 × 10^5 and 5.9 × 10^5 M^{-1} s^{-1} for the anodic and cathodic processes, respectively. These values are about 4 orders of magnitude smaller than the k_{ex} value for a dilute solution of *N*-methylphenothiazine in ACN (2.2 × 10^9 M^{-1} s^{-1}).[16] This means that the values of k_{ex} estimated from the data in Figure 8 are not the true activation-controlled self-exchange rate constants but reflect the rate of a segmental motion by which the neighboring redox pairs move into a proper juxtaposition in the polymer matrix. It is noted that the value of k_{ex} for the cathodic process is about 1.5 times larger than that of the anodic process. Although a detailed interpretation of this remains a future subject of study, we have speculated that there may be a difference in the favorable relative orientation between the MPT units before and after oxidation, which may stem from an electronic interaction between the redox centers.

In order to probe into the interaction between the MPT centers, we examined the change in the absorption spectra of the polymer films during electrolysis. Figure 9 compares the absorption spectra for the polyMPT and copolyMPT (f_{MPT} = 0.51) films at various electrode potentials. Upon oxidation, two distinctive absorption bands appeared at about 520 and 800 nm, the former being due to the known *N*-methylphenothiazine radical cation[6] (the spectrum for the radical cation of 3-ethyl-10-methylphenothiazine in ACN is given in Figure 9a for comparison). The latter absorption band was assigned to the dimer of the MPT radical cations based on the fact that the absorbance at 800 nm relative to that of the 520-nm band increased as the oxidation degree increased. In this dimer form two MPT radical cations presumably retain a face-to-face orientation. At an electrode potential of +0.75 V electrochemically active portions of the MPT units in the films were fully oxidized for both polyMPT and copolyMPT, wherein the ratios of the absorbance at 800 nm to that at 520 nm were 0.78 and 0.44 for polyMPT and copolyMPT, respectively. These facts imply that a face-to-face mutual orientation is favored in the oxidized films, because of the electronic interaction between the MPT radical cations, and that there is a significant difference between the homo- and copolymers in the ease for the MPT units to come into the face-to-face orientation. It is noted that the 520-nm band for the polyMPT film is considerably broad as compared with that for the copolymer, suggesting significant electronic perturbation of the MPT radical cations present in the homopolymer film. Therefore, in the initial state of the re-reduction step, as compared with that of the oxidation step, the MPT radical cations tend to be parallel, leading to an electron exchange with less motion of redox sites to attain a proper geometry for electron transfer.

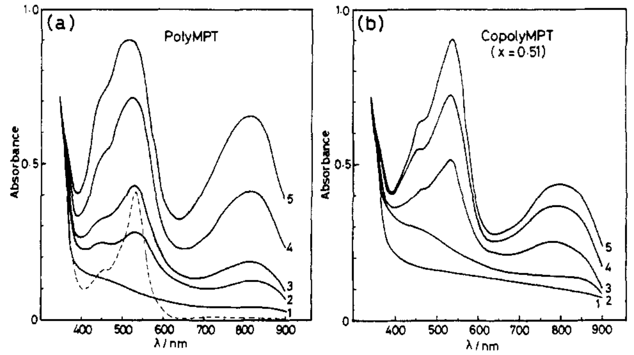


Figure 9. Absorption spectra for polyMPT (a) and copolyMPT (f_{MPT} = 0.51) (b) films on an OTE in 0.4 M $LiClO_4$/ACN at various potentials: (1) +0.1 V; (2) +0.45 V; (3) +0.5 V; (4) +0.55 V; (5) +0.75 V vs. Ag/AgCl: (---) spectrum obtained in an ACN solution of 3-ethyl-10-methylphenothiazine electrochemically oxidized at +0.75 V.

The concentration dependence of D_{ap} in the present study qualitatively agrees with the results reported by Murray and co-workers on the electron transport between Os(III/II) complex redox sites in copolymer films electrochemically prepared from $[Os(2,2'\text{-}bpy)_2(4\text{-}pyNHCOCH{=}CHPh)_2]^{2+}$ and the corresponding Ru complex comonomer.[17] They reported that the value of D_{ap} increased from about 1 × 10^{-10} to 1.3 × 10^{-9} cm^2/s when the value of C for the Os(III/II) pair increased from approximately 6 × 10^{-4} to 1.2 × 10^{-3} mol/cm^3. Buttry and Anson have reported a similar dependence of D_{ap} on the concentration of the $Co(bpy)_3^{2+}$ complex ionically bound to Nafion coatings on graphite electrodes.[18] These two studies found that the value of D_{ap} for polymer films increased with an increase in the concentration of redox species in the films. Oyama et al.[19-21] and Anson et al.[22,23] have investigated the dependence of D_{ap} on the concentration of ionic redox species electrostatically bound by polyelectrolyte films. They reported that, in contrast to the above two cases,[17,18] the D_{ap} values decreased with the increase in C, presumably because of the ionic cross-linking of the polyelectrolyte by ionic redox species with multicharges.

The k_{ex} values estimated in the present study may be compared to those reported on viologens covalently linked to polymer films.[25] Oyama and co-workers studied the electrode kinetics of a poly(xylylviologen)–poly(*p*-styrenesulfonate) polyion complex film attached on a graphite surface and estimated the D_{ap} values to be 1 × 10^{-9} cm^2/s for a film with a concentration of 1.1 × 10^{-4} mol/cm^3.[25] Bookbinder and Wrighton have reported the value of D_{ap} = 3 × 10^{-10} cm^2/s for a siloxane type of viologen polymer film directly anchored to an electrode surface.[26] In these studies the values of k_{ex} were estimated to be on the order of 10^5–10^6 M^{-1} s^{-1}. More recently, Bard and co-workers estimated the k_{ex} value to be >10^6 M^{-1} s^{-1} for a polymer film with viologens covalently anchored to the polymer backbone by simultaneous electrochemical and electron spin resonance techniques.[27] All these k_{ex} values in polymer films are much smaller than that in homogeneous solutions of methylviologen ($>10^8$ M^{-1} s^{-1}).[27] This is attributed to the fact that, even though the redox species are close enough, they cannot necessarily achieve a proper juxtaposition for electron transfer because of their attachment to the polymer chains; i.e., the configurational constraints of the polymer would limit the mutual orientation of neighboring redox sites. Since this would involve an ordering process with an entropy loss, an exothermic interaction between redox centers, if any, may significantly favor the mutual orientation that would in turn favor electron exchanges.

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Twisted Intramolecular Charge-Transfer Phenomenon as a Fluorescence Probe of Microenvironment. Effect of Polymer Concentration on Local Viscosity and Microscopic Polarity around a Polymer Chain of Poly(methyl methacrylate)

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ABSTRACT: A 4-(*N,N*-dimethylamino)benzoate group showing a twisted intramolecular charge transfer (TICT) was bonded to a poly(methyl methacrylate) side chain and the effects of polymer environment on fluorescence were investigated in ethyl acetate. The temperature dependence of the fluorescence behavior indicated restricted side chain rotation and reduced solvation in the polymer even under dilute conditions. With increasing polymer concentration, the TICT emission showed a blue-shift and decreased intensity up to a polymer concentration of 70%. Above this concentration, the activation energy to form the TICT state suddenly increased. The twisting motion of the dimethylamino group required a free volume of 5.4 cm^3/mol, which was in good agreement with the activation volume obtained from pressure effects on the TICT phenomenon. The TICT phenomenon is shown to be sensitive to both local polarity and local viscosity of the surroundings so that the TICT chromophore is expected to be a candidate for a fluorescence probe in polymer property studies.

Introduction

Fluorescence methods, such as steady-state fluorescence spectroscopy, excited-state decay analysis, time-resolved fluorescence spectroscopy, and fluorescence depolarization have been shown to be quite effective in the investigation of the microscopic environment around a chromophore. A number of studies have been reported on the use of excimer or exciplex formation in polymeric systems to examine local segment mobility, phase separation, or polymer compatibility.[1] The fluorescence depolarization method has been widely used to monitor molecular motion in polymers, molecular aggregates, and biological systems.[2]

A series of derivatives of 4-(*N,N*-dimethylamino)benzonitrile (DMABN) or 4-(*N,N*-dimethylamino)benzoate exhibits characteristic fluorescence spectra in polar solvents, showing two emission bands (dual fluorescence)