Spectroscopic Study of Polytoluidines in the UV-Visible and IR Regions

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SYNOPSIS

Electropolymerization of o-toluidine (o-methylaniline) and m-toluidine was carried out in acidic aqueous solution, and UV-visible and IR spectra of the resulting polymer films were obtained at various electric potentials and pHs. In Na_2SO_4 aqueous solution, poly(o-toluidine) gave considerably different UV-visible spectra from polyaniline, whereas, in HCl (pH $\sim$ 0), the spectra of poly(o-toluidine) changed in the same way as polyaniline when the potential was varied. This spectral change depended also on counterion. This suggests that the intermediate state (radical cation) of poly(o-toluidine) is unstable in a neutral solution especially when a large counter ion exists, which is contrast to polyaniline. The dependency of the FT-IR spectra of poly(o-toluidine) on the potential and pH supported also the above result of UV-visible spectra. From both UV-visible and IR spectra under various conditions, it was found that o-toluidine and m-toluidine give the same polymer.

INTRODUCTION

The electrical and optical properties of polyaniline have been studied extensively with relation to electrochromic display[1-8] and electrode material of batteries.[9] The structural change of polyaniline by redox reaction has been studied by IR spectroscopy.[10-13] It has been found that polyaniline film synthesized in acidic aqueous solution shows electrochromism as the potential changes. The molecular structures of polyaniline in various oxidation steps have been proposed, where the intermediately oxidized polymer has a radical cation structure.[1] Stilwell and Park[2] have reported that there are two intermediate states, a radical cation ($\lambda_{max} \sim$ 440 nm) and delocalized free electron states ($\sim$800 nm). Furthermore, McManus et al.[1] have proposed a 2-dimensional interconversion scheme of polyaniline on varying the potential and pH.

On polytoluidines (polymethylanilines), UV-visible spectra similar to those of polyaniline have been obtained.[14-17] But relatively few researches have been done in the UV-visible and the IR regions when the potential and pH are varied. It is interesting to examine the effect of substituents on the stability of this radical, because the spectra may change due to the steric and/or electronic effects of the substituents. Besides, the pH of the aqueous solution and counterions may give some effects on the spectra. In this paper, absorption spectra of poly(o-toluidine) and poly(m-toluidine) were obtained in the UV-visible and the IR regions when the potential and pH were varied, and compared with those of polyaniline.

EXPERIMENTAL

On a gold-coated quartz plate, toluidines were polymerized electrolytically in aqueous system in nitrogen atmosphere. Typically, oxidative polymerization was done in 1.0M HCl solution containing 0.5M monomer at a constant potential of +0.75 V (vs. Ag–AgCl) using a potentiostat (Nikko NPOT 2501). Polyaniline and poly(o-toluidine) films were obtained in 15–20 min for UV-visible measurements, whereas, for the samples for FT-IR measurements, it took about three times longer because thicker films were needed for IR measurements. The current

density was 100–400 μA/cm^2 in the both cases. The polymerization reaction of m-toluidine was slower, so that it took ca. 45 min in the case of UV-visible measurements.
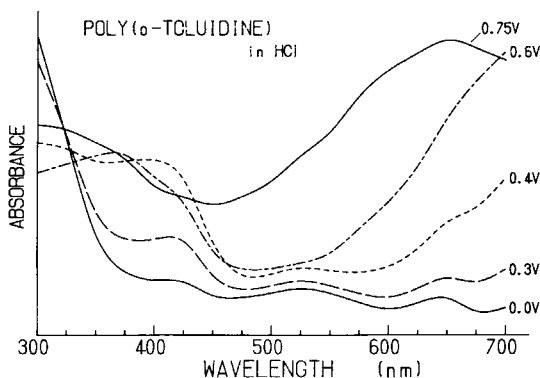
After polymerization reaction, the polymer film was reduced at 0.0 V vs. Ag–AgCl for 30 min, and rinsed with 0.1M HCl. Then it was transferred into a solution which did not contain the monomer, and it was used for measurements of UV and visible absorption *in situ* at various potentials and pHs. All of these operations were carried out in nitrogen atmosphere because the polymers are oxidized by exposure to air.

In the FT-IR measurements, a Jasco FT/IR-8000 spectrometer and a microscope accessory of reflection type were used. The sample on a plate was treated with a solution of desired pH at a constant potential, dried in nitrogen, and immediately used for measurement in air.
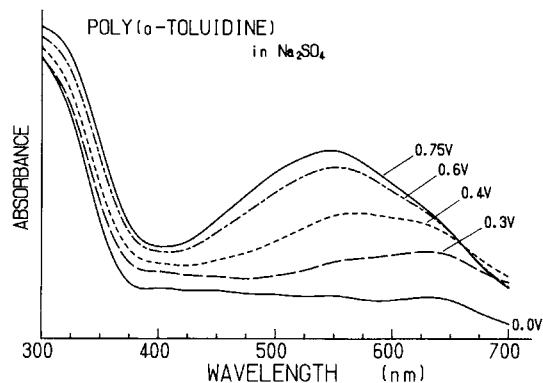
RESULTS AND DISCUSSION

UV-Visible Spectra

Figures 1 and 2 show the UV and visible spectra of poly(o-toluidine) film in 1.0M HCl (pH $\sim$ 0.3), and in 1.0M Na$_2$SO$_4$ aqueous solution (pH $\sim$ 5), respectively. In the spectrum in HCl (Fig. 1), the reduced poly(o-toluidine) ($-0.2–+0.2$ V vs. Ag–AgCl) gave no absorption in the visible region, and the intermediately oxidized polymer ($\sim$ 0.4 V) gave a peak at ca. 400 nm as well as another absorption in the near IR region. By further oxidation up to 0.75 V, the absorption of this peak decreased. This

Figure 2   UV-visible spectra of poly(o-toluidine) film in 1M Na$_2$SO$_4$ solution.

change of the spectrum is very similar to that of polyaniline (Fig. 3).

In the spectra of poly(o-toluidine) in Na$_2$SO$_4$ solution (Fig. 2), no peak appeared at 400 nm in the intermediately oxidized form (0.4 V), which is in contrast to the spectra of polyaniline in Na$_2$SO$_4$ solution (Fig. 4).

This difference can be discussed on the basis of the proposed mechanism of oxidation and reduction of polyaniline (Fig. 5). The reduced polyaniline [light yellow, Fig. 5(a)] is oxidized through one or two intermediate states [λ_{max} $\sim$ 400 nm, Figs. 5(b) and 5(c)] to the oxidized form [Fig. 5(d)], which is green in the acidic solution and red in the neutral solution. In the case of poly(o-toluidine), the present result indicates that the intermediate state (radical cation) in the neutral solution is unstable, probably because its structure is difficult to be planar due to steric hindrance by methyl group at the ortho position as shown in Figure 6.

Figure 1   UV-visible spectra of poly(o-toluidine) film in 1M HCl solution. Electric potentials vs. Ag/AgCl are shown on the right-hand side.
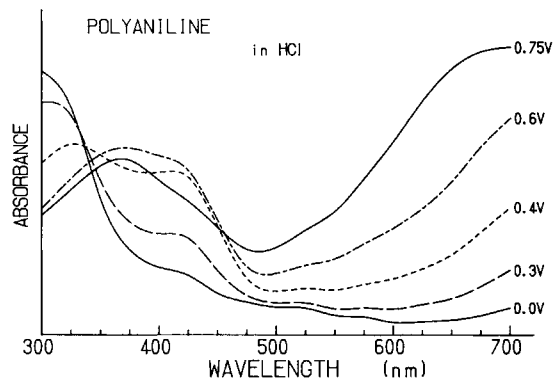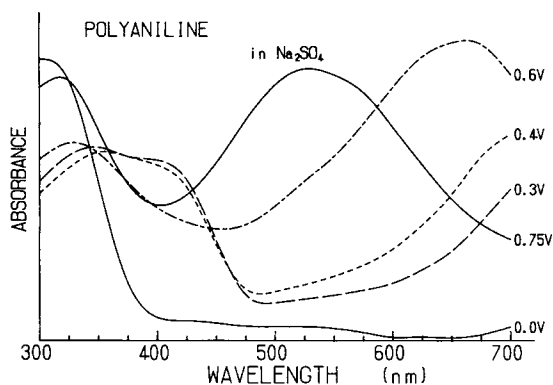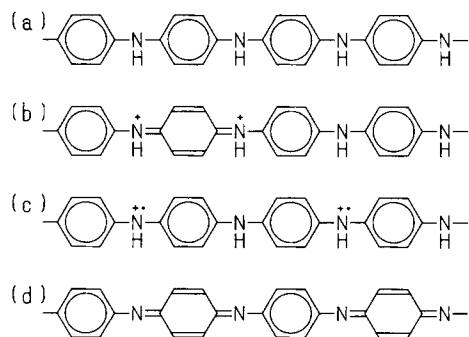

Figure 3   UV-visible spectra of polyaniline film in 1M HCl solution.

Figure 4 UV-visible spectra of polyaniline film in $1M$ Na_2SO_4 solution.

Figure 6 Structure of polytoluidine, showing the steric hindrance of methyl group and counterion.

shown in Figure 10(b). This corresponds to the result of UV-visible spectra.

The positions of the first pair of redox peaks (lower potential) in Figure 10(a) agree approximately with those of the peaks in Figure 10(b). On the other hand, the second pair of peaks (higher potential) in Figure 10(a) disappeared in Figure 10(b), which may be related to the result of Wei et al.[17] that the positions of the second pair of peaks shift to the lower potential as the pH becomes higher, because a proton is involved in the second redox reaction.

Figure 11(a) shows the absorbance as a function of potential at the wavelength of 400 nm for data taken when the potential was varied upward and downward, and Figure 11(b) shows its differential curve with respect to time. The potentials at the steepest gradient $(d(\mathrm{Abs})/dt)$ agree approximately with the peaks in the cyclic voltammograms [Fig. 10(a)]. When the polymer was oxidized, the speed of the change of absorbance was almost independent of the sweep rate of potential in the range of 25–100 mV/s. When it was reduced, the change of absorbance was retarded when the sweep rate was high. This means that reduction is slower than oxidation.

The spectra were also affected by electrolyte. Figure 7 shows the difference between the anions of Cl^- and SO_4^{2-} under the condition of $V = 0.40$ V. In the case of KCl (pH 6.1), a weak peak appeared at ca. 400 nm. This suggests that the radical cation is more unstable when a larger counter ion exists.
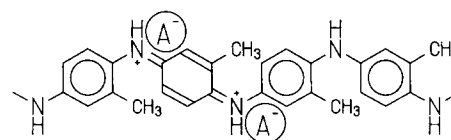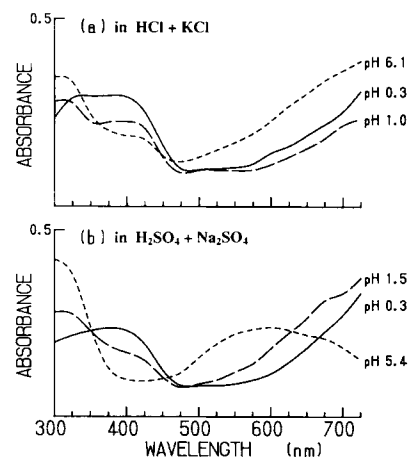
Poly(m-toluidine) showed almost the same spectra as poly(o-toluidine) at pH 0 (Fig. 8) and pH 6 (Fig. 9). This strongly suggests that the same polymers are formed from the two monomers.

In summary, the intermediately oxidized state is unstable under the condition that there is a substituent group at the ortho position with respect to the —NH— group, and the pH of the solution is high, especially when a large counter ion exists.

Figures 10(a) and 10(b) show the cyclic voltammograms in HCl and in Na_2SO_4 solution, respectively. Oxidation and reduction of polytoluidine proceed by two steps in HCl as shown in Figure 10(a), while they proceed by 1 step in Na_2SO_4 as

Figure 5 Structure of polyaniline: (a) leuco form; (b) doubly protonated emeraldine form; (c) radical cation; (d) quinoid form.

Figure 7 Dependence of spectra of poly(o-toluidine) on electrolyte: (a) in mixture of HCl and KCl; (b) in mixture of H_2SO_4 and Na_2SO_4. Potential: 0.40 V vs. Ag/AgCl.
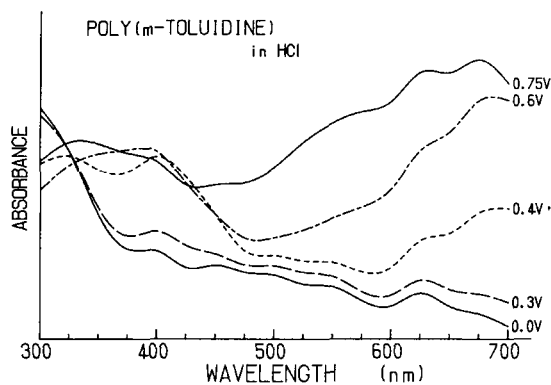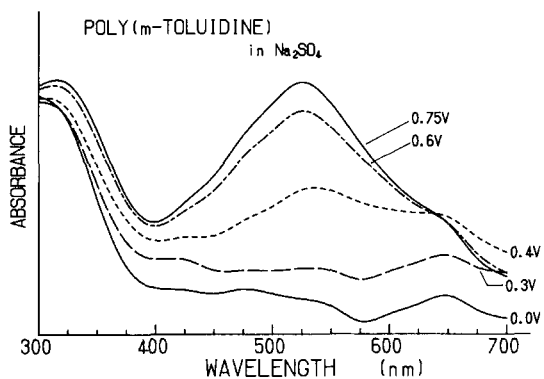
**Figure 8** UV-visible spectra of poly(*m*-toluidine) film in 1*M* HCl solution.

Figure 12 shows the absorbance of poly(*o*-tolu-idine) at 400 nm as a function of pH under coexistence of SO_4^{2-} in the solution. The radical cation form is converted to oxidized form as pH is raised to 0.3–1.5, i.e., the radical cation form exists only when pH is lower than 2.

Infrared Spectra

Figure 13 shows FT-IR spectra of poly(*o*-toluidine) treated in HCl or Na_2SO_4 aqueous solutions at various potentials. In the wavenumber region of 1610–1480 cm^{-1}, two to three absorption peaks appeared due to the vibrations of benzene or quinoid type ring. The reduced polymer treated in HCl (pH 0.1) [Fig. 13(c)] showed peaks at 1610, 1585, and 1495 cm^{-1} and this is very similar to that treated in Na_2SO_4 (pH 5.5) [Fig. 13(f)]. This indicates that the protonation does not affect the spectra of reduced poly(*o*-toluidine). This is true also for polyaniline


**Figure 9** UV-visible spectra of poly(*m*-toluidine) film in 1*M* Na_2SO_4 solution.
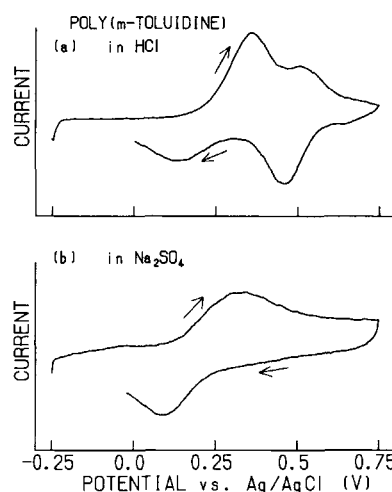
Figure 10 Cyclic voltammograms of poly(*m*-toluidine) film: (a) in HCl solution; (b) in Na_2SO_4 solution. Sweep rate: 100 mV/s.

[Figs. 14(c) and 14(f)], which has also been reported by Harada et al.[12]

On the contrary, when the polymer was oxidized intermediately at 0.40 V vs. Ag/AgCl, the spectrum for HCl solution is different from that for Na_2SO_4 solution. The spectrum (Na_2SO_4, 0.40 V) [Fig. 13(e)] is rather similar to that of reduced polymer [Fig. 13(f)]. The peak at 1590–1585 cm^{-1} has been
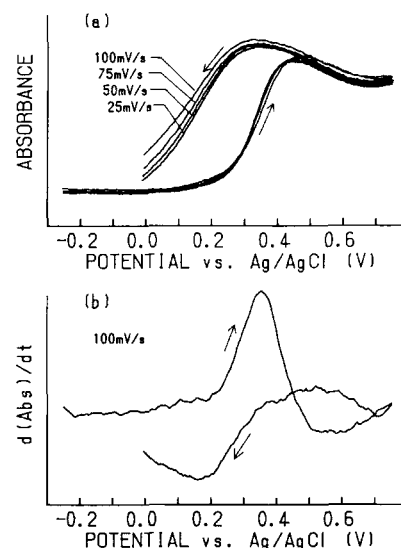

Figure 11 (a) Absorbance of poly(*o*-toluidine) at 400 nm as a function of potential. Sweep rate of potential: 100–25 mV/s. Electrolyte: HCl. (b) Its differentiated curve with respect to time.
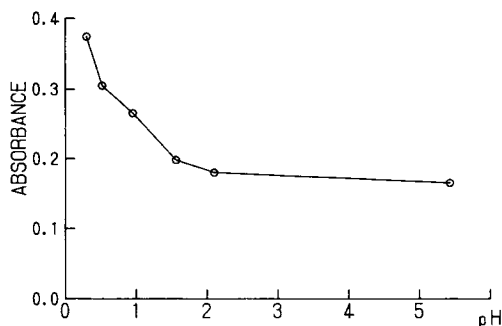
Figure 12 Absorbance of poly(o-toluidine) at 400 nm as a function of pH. Potential: 0.4 V; Electrolyte: H_2SO_4 + Na_2SO_4.

assigned to the ring stretching of the radical cation [Fig. 5(c)] and the quinoid form [Fig. 5(d)] by means of isotopic substitution of polyaniline.[12] The peak intensity at this wavenumber increased as the poly(o-toluidine) was oxidized until +0.4 V vs. Ag/AgCl in HCl solution, while it did not increase in Na_2SO_4 solution. This implies that the radical cation was formed by oxidation only in HCl.

Compared with the spectra of polyaniline (Fig. 14), poly(o-toluidine) gave considerably different spectra from polyaniline only when they were treated in Na_2SO_4 solution at 0.40 V. This may correspond to the result in UV-visible study, in which the radical cation form of polytoluidine is unstable in Na_2SO_4 solution.
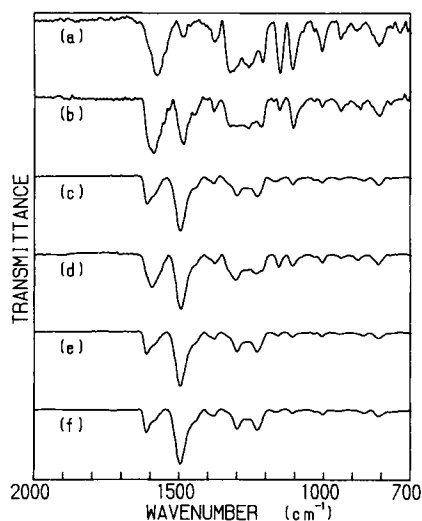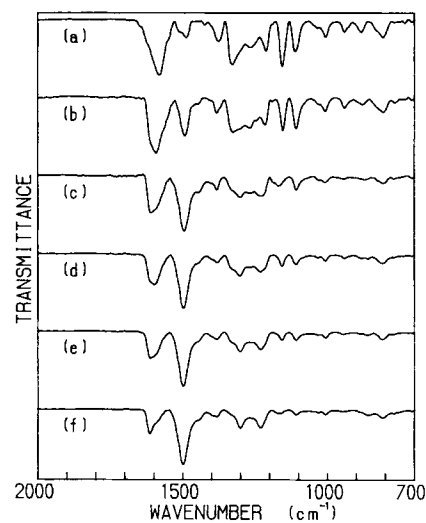

Figure 13 FT-IR spectra of poly(o-toluidine). Electrolyte and potential vs. Ag/AgCl are: (a) HCl, 0.75 V; (b) HCl, 0.40 V; (c) HCl, −0.15 V; (d) Na_2SO_4, 0.75 V; (e) Na_2SO_4, 0.40 V; (f) Na_2SO_4, −0.25 V.
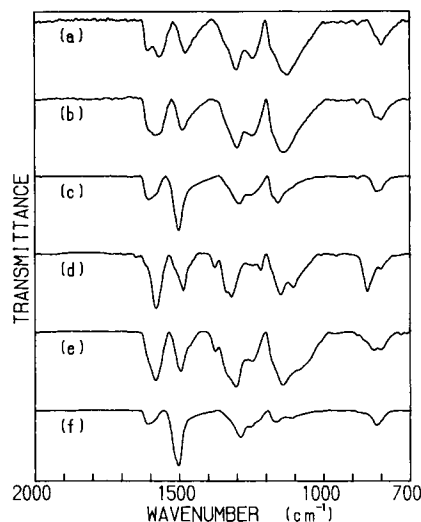
Figure 14 FT-IR spectra of polyaniline. Conditions are same as Figure 13.

As the pH was raised at a constant potential of 0.40 V, the intensity ratio of the peaks at 1610–1580 and 1500–1490 cm^{-1} changed greatly at pH 1.0–1.5 and pH 3.9–5.7. This implies that structural change of poly(o-toluidine) such as deprotonation and reduction occurred in these pH regions.

Figure 15 shows the FT-IR spectra of poly(m-toluidine) taken in various conditions. By comparison with poly(o-toluidine) (Fig. 13), the two polymers gave essentially the same IR spectra in every condition, which strongly suggests again that the two polymers are identical.

Figure 15 FT-IR spectra of poly(m-toluidine). Conditions are same as Figure 13.

Stability of conducting polytoluidine has been reported by Clark and Yang,[14] who concluded that the steric effect of methyl group causes the unstability of the radical cation form.

Polytoluidine treated in KCl solution gave different spectra from that treated in Na_2SO_4 solution even when the pH was the same. Rather, the former spectrum at 0.40 V had a strong peak at 1590 cm^{-1} (ring stretching of radical cation and quinoid forms), which is the same tendency as the spectrum for HCl. This result of FT-IR is also consistent with the result of UV-visible spectra where the structure of the polymer depends on not only pH, but also the counterion.

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