Electrochemical polymerization of methyl-substituted quinolines

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Of the quinoline derivatives, only the 4-methyl-quinoline formed a polymeric film by electrochemical polymerization using acetonitrile as solvent and $LiClO_4$ or $TBA(ClO_4)$ as supporting electrolyte. The film has good mechanical properties, and its conductivity was 10^{-3}–10^{-5} S cm^{-1}.

INTRODUCTION

Electrochemical polymerization has recently attracted interest, as a synthetic method for novel conductive polymers. Conductive polymers which can be obtained by the electrochemical polymerization, include polypyrrole, polyaniline, poly(p-phenylene), and polynaphthalene[1-7]. However, few polymers produced by electrochemical polymerization are satisfactory in mechanical properties, especially flexibility. In our previous reports[7], highly conducting polymeric films that were stable to ambient conditions and had good mechanical properties, and obtained by the electrochemical copolymerization of benzo[b]thiophene with pyrrole were described. This paper reports on the electrochemical polymerization of various quinoline derivatives.

EXPERIMENTAL

Quinoline, 3-methyl-quinoline, 4-methyl-quinoline, 6-methyl-quinoline, 7-methyl-quinoline, 8-methyl-quinoline (special grade reagent) were used without further purification. Acetonitrile and benzonitrile were used after distillation. $LiClO_4$ and tetrabutyl ammonium perchlorate $(TBA(ClO_4))$ (special grade reagent) were used without further purification. Electrochemical polymerizations of quinoline derivatives were carried out in a one-compartment cell using an In–Sn oxide conducting glass (ITO) as a working electrode and a Pt plate as a counter electrode. The electrolysis cell was kept at 25°C and was flushed with dry argon to provide an inert atmosphere during the reaction. Solutions of quinoline derivatives in acetonitrile or benzonitrile were electrolysed using various supporting electrolytes. A voltage of 2–3 V between the two electrodes was applied to afford a current density of 0.1–4 mA cm^{-2}. The reduced film was obtained by electrochemical reduction or by exposing the polymeric film to gaseous ammonia for several hours. It was then washed with tetrahydrofuran in an ultrasonic cleaner. Cyclic voltammograms were performed in acetonitrile containing $LiClO_4$ using a Pt counter electrode and Ag/AgCl reference electrode. Electrochemical measurements were carried out using a potentiostat (Hokuto Denko Co Ltd HA-301 model), a function generator (Kikusui Electro. Co Ltd 4500A model) and an X-Y recorder (Graphtec WX-120 model). A universal surface geometry observation apparatus (Metricon. Co. PC-2000 model) was employed to determine the film thickness.

RESULTS AND DISCUSSION

When attempts were made to form a polymeric film by electrochemical polymerization of the quinoline derivatives it was difficult to obtain an appropriate combination of a supporting electrolyte with a solvent. Only the system composed of 4-methyl-quinoline as monomer, $LiClO_4$ or $TBA(ClO_4)$ as a supporting electrolyte, and acetonitrile as a solvent formed a polymeric film on the electrode. In the case of quinoline, 6-methyl-quinoline, 7-methyl-quinoline, 8-methyl-quinoline, and 4-methyl-quinoline monomers, with various supporting electrolytes and solvents used in combination, no formation of a polymeric film was found. *Figure 1* shows the relation between the conductivity and the concentration of the supporting electrolyte. The thickness of the obtained film was 2–3 μm and the conductivity was 10^{-3}–10^{-5} S cm^{-1}. The conductivity increases during first 40 min after the start of the reaction and becomes nearly constant after ≈ 2 h. No great difference was found in conductivity when different supporting electrolytes were used. In contrast, longer polymerization times and increased concentration of the supporting electrolytes gave films of relatively low conductivity. *Figure 2* shows the relation between the concentration of the supporting electrolyte and the transmittance of the films obtained. When the polymerization time was prolonged or the concentration of the supporting electrolytes was increased, the colour of the film turned deep green, accompanied by reduction in the transmittance.
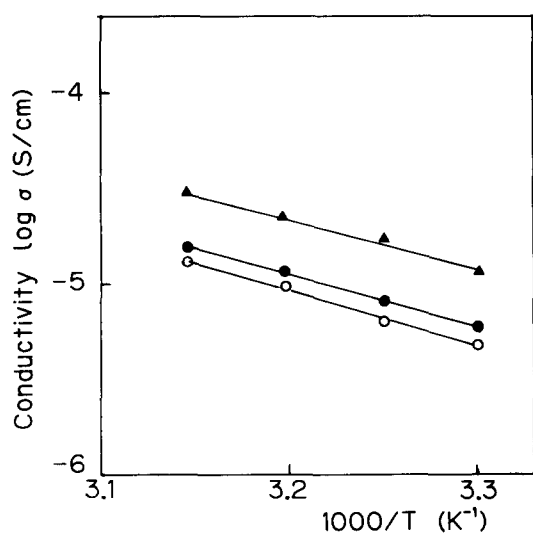
The temperature dependences of the conductivity of various concentrations of the supporting electrolyte are shown in *Figure 3*. For each supporting electrolyte, $LiClO_4$ or $TBA(ClO_4)$, a linear relationship was obtained,
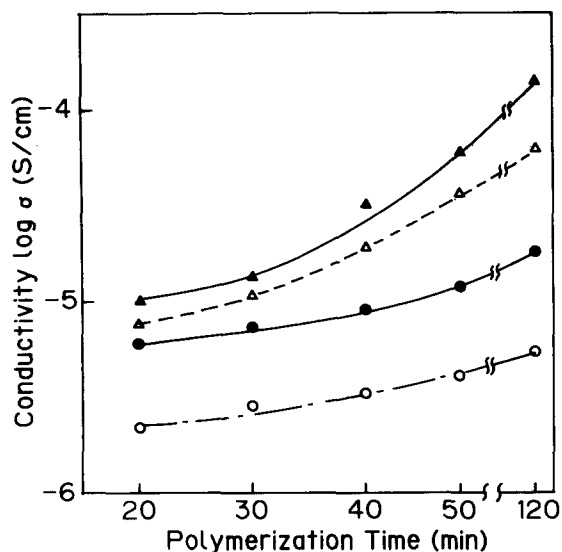
Figure 1 Dependence of the conductivity on the concentration of the supporting electrolyte in CH_3CN. $TBA(ClO_4)$: $\bigcirc$, 0.025; $\bullet$, 0.05; $\triangle$, 0.10; $\blacktriangle$, $0.15\,mol\,l^{-1}$
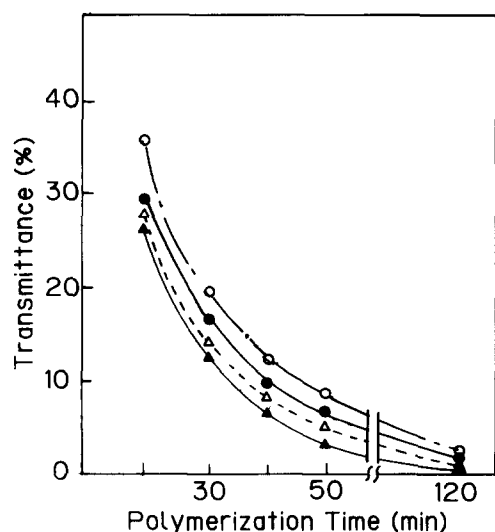

Figure 2 Dependence of the transmittance on the concentration of the supporting electrolyte in CH_3CN. $TBA(ClO_4)$: $\bigcirc$, 0.025; $\bullet$, 0.050; $\triangle$, 0.10; $\blacktriangle$, $0.15\,mol\,l^{-1}$


Figure 3 Dependence of the conductivity on the temperature of the polymeric film obtained in various supporting electrolytes in CH_3CN. $TBA(ClO_4)$: $\bigcirc$, $0.025\,mol\,l^{-1}$ 50 min; $\bullet$, $0.050\,mol\,l^{-1}$ 40 min. $LiClO_4$: $\blacktriangle$, $0.30\,mol\,l^{-1}$ 60 min

enabling activation energies to be determined. The activation energy for the systems using $LiClO_4$ as a supporting electrolyte was 30 meV, and that for those using $TBA(ClO_4)$ was 52 meV. These values are near to those found for other general conductive polymers. *Figure 4* shows cyclic voltammograms of a typical *ca.* 5 μm thick film of poly(4-methyl-quinoline)-ClO_4^- attached to an ITO electrode in acetonitrile containing $0.4\,mol\,l^{-1}$ $LiClO_4$. The peaks are not perfectly symmetrical about the E value, probably resulting from the difference in the background currents plus some kinetic limitations in the redox reaction. Further, the peaks are quite broad and it is not clear to what extent the broadening is due to repulsive interactions between the electroactive sites and/or the electrochemical non-equivalence of the sites. The peak oxidation current values (I_p) vary with sweep rate (V) between $14.5\,mV\,s^{-1}$ and $87\,mV\,s^{-1}$, as expected, for a surface attached species. *Figure 5* shows relation between logarithmic plot of I_p in the oxidation reaction and sweep rate (V). From the plot the relationship $I_p \propto V^{0.46}$ was determined. When I_p is in linear proportion to V, electric charge transfer from an electrode to a polymer coating the electrode is the reaction-rate determining step. On the other hand, when I_p is proportional

E (Volt vs Ag/AgCl)
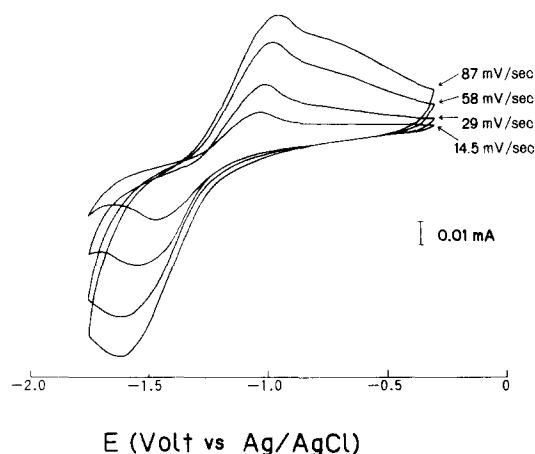
Figure 4 Cyclic voltammograms of [ITO] poly(4-methyl-quinoline) film in $LiClO_4/CH_3CN$ solution
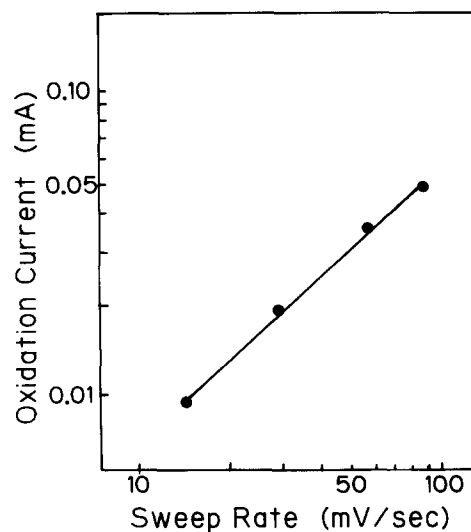
Figure 5 Plot of I_p vs. V for [ITO] poly(4-methyl-quinoline) in CH_3CN
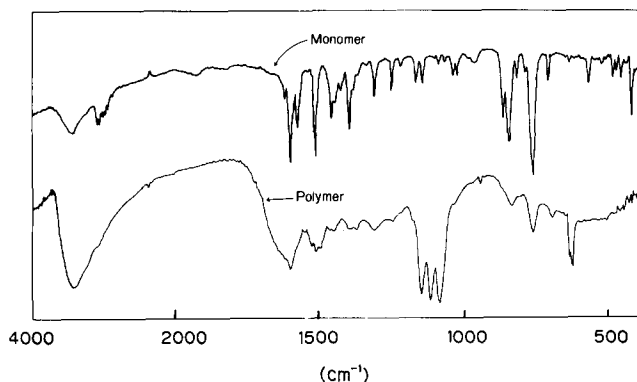
Figure 6 The i.r. spectra of the monomer and the polymer films

Table 1 Mechanical properties of poly(4-methyl-quinoline) films prepared in various supporting electrolytes in CH_3CN

Supporting electrolyte $(mol\,l^{-1})$	Tensile strength $(N\,mm^{-2})$	Elongation at break (%)	Young's modulus $(N\,mm^{-2}) \times 10^{-2}$
$LiClO_4$ (0.05)	18.4	6.5	13.2
$TBA(ClO_4)$ (0.05)	24.8	8.2	20.3

to $V^{0.5}$, diffusion of electrons or ion pairs (ClO_4^- for this experiment) within the formed film is the rate-determining step. Accordingly, the above relation between I_p and V suggests that the rate of the oxidation–reduction between the electrodes is determined by the diffusion of ClO_4^- within the poly(4-methyl-quinoline) film.

Figure 6 shows the infra-red (i.r.) spectra of the monomer and the polymer. Though the structure of the poly(4-methyl-quinoline) has not been completely elucidated yet, the strong i.r. absorption bands representing the CH stretching vibration ($2900\,cm^{-1}$) and the CH deformation vibration ($1380\,cm^{-1}$, $1460\,cm^{-1}$) due to the CH_3 group of the monomer disappear from the i.r. spectrum of the polymer. This fact suggests that the methyl group linked to a naphthylizine ring participates in the polymerization reaction. *Table 1* shows the mechanical properties of poly(4-methyl-quinoline) film prepared with various supporting electrolytes in aceto-
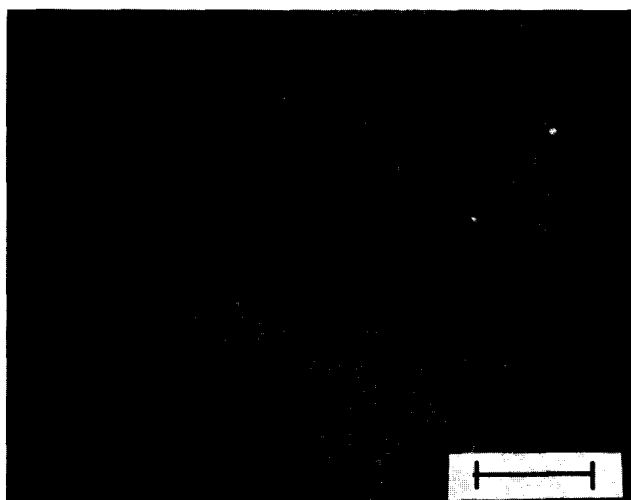

Figure 7 Scanning electron micrograph of the poly(4-methyl-quinoline)–ClO_4^-. Bar = 2 μm

nitrile. In general, a polymeric film obtained by electrochemical polymerization has a very rough surface and is brittle[5-7]. However, the films obtained here have good mechanical properties. The scanning electron micrograph of the poly(4-methyl-quinoline) surface is shown in *Figure 7*. It is clearly seen that the film is compact and has an even surface. In summary, conducting films with enhanced mechanical properties can be obtained by the electrochemical polymerization of 4-methyl-quinoline. A detailed discussion of the polymer structure and conduction mechanism will be reported elsewhere.

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