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Alternation of conducting zone from propagation-control to diffusion-control at polythiophene films by solvent substitution

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Abstract

The conducting zone of polythiophene films grew under the propagation-control in acetonitrile solution at application of the positive potential to the reduced film whereas it grew under the diffusion-control when it was transferred into the propylene carbonate solution. The electrochemically polymerized film was peeled off from the electrode, and a current feeder was connected to an end of the film. The distribution of the conducting species was detected with a diode array detector through the 850 nm beam irradiated to the film. When the fully reduced film was oxidized potentiostatically in the 0.1 M LiClO₄ + acetonitrile solution, the conducting zone developed linearly with the electrolysis time at almost a constant speed. This is in accord with the theory of the propagation of the conducting zone. When the reduced film was transferred into the 0.1 M LiClO₄ + propylene carbonate solution, the conducting zone grew exhibiting a vague boundary. Quantitative analysis said that the growth obeyed at first the propagation theory and then obeyed the square root of the time, represented by diffusion of dopant ions. The diffusion coefficient was $3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. A new growth model was proposed, in which the film/solution interface was oxidized at first by the propagation mechanism and then the conducting zone was dispersed into the film center by diffusion. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Conducting polymers; Polythiophene films; Propagation of conducting zone; Diffusion of dopant ions; Penetration

1. Introduction

Conversion of redox states of electrically conducting polymers bring about large variations of conductivity, color, degree of ionic exchange, immobilization of ions, and photosensitivity [1,2]. When conducting polymers are synthesized on an electrode, these variations are well controlled by a potential application. The variations respond quite rapidly to the potential change [3–5]. They often show unusual responses such as large deviation from the Nernst plot [6,7], slow

relaxation at the conducting-to-insulation conversion [8–16], ambiguity of separating faradaic current and the charging current [17,18], and potential-dependent hysteresis [19–27].

Dynamic approach to these responses has been made by a.c. and d.c. techniques. The unusual behavior for a.c.-responses has been explained by equivalent electric circuits, typically exemplified by a transmission line model [28–31]. The more highly is improved a fitting level, the more complicated is combination of electric circuits. Then, the complication makes a physical meaning of each electric element ambiguous. In contrast, the behavior at the d.c.-mode has been explained by the propagation model [32], in which the conducting zone grows from the electrode at

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a constant speed for a potentiostatic oxidation [33–39] by use of the simulated film in which length is regarded as the thickness. In this configuration, the rate-determining step is not diffusion of doping ions but is the charge transfer kinetics at the interface between the conducting zone and the insulating zone [38,39]. The negligible effect of diffusion is ascribed to high permeability of dopant ions into the highly porous film. Change of permeability might alter the rate-determining step.

Permeability in films, generally, varies with kinds of solvents. When a film is transferred from a solvent with good permeability into a solvent with poor one, the conversion may be controlled by the slow rate of the permeation rather than the propagation rate. Since the permeation kinetics lies in diffusion, diffusion of dopant ions may be a rate-determining step. Therefore, change of solvents may be useful for examining the participation in diffusion. From a viewpoint of experimental procedure, a polythiophene film is the most preferable in that it brings about the redox reaction in various organic solvents without remarkable influence of oxygen in air. In this paper, we examine the effect of the propagation on the permeability by changing solvents. For this purpose, we determine the growth speed of the conducting zone of the reduced polythiophene film in response to an potentiostatic control by use of the previously developed photodiode array technique [37–40] when the film is transferred into a different solvent. Since the conducting zone in the film mounted on a glass plate grows in the direction of the film length rather than thickness, the grow experiment

corresponds to magnification of the film thickness (of the order of μm) to the film length (order of mm).

2. Experimental

Polythiophene films were formed on an ITO (indium–tin oxide) electrode by electropolymerization at a constant potential of 2.2 V vs a saturated calomel electrode (SCE) for 120 s in the 5°C thermostated 0.1 M (mol dm^{-3}) thiophene + 0.025 M tetra-*n*-butyl ammonium perchlorate + nitrobenzene solution at N_2 atmosphere.

The films were 0.3 μm thick, which was evaluated from an atomic force microscope, Nanoscope III (Digital Instruments, USA). The films were immersed in distilled water for 24 h to be reduced chemically to the neutral state. The reduction would be completed, partly because of disappearance of absorption bands due to bipolaron states and partly because of negligible dependence of the time on the oxidation rate. When the film-coated electrode was dipped into water, the film was detached from the electrode, floating in the water as a self-standing film. The film was scooped up on a glass plate and cut into a rectangle ($2 \times 6 \text{ mm}^2$). A half part of the ITO-coated glass plate was immersed in sulfuric acid in order to dissolve ITO. A part ($2 \times 1 \text{ mm}^2$) of an end of the film was sandwiched between a bent platinum plate and the half ITO-coated glass plate so that part $2 \times 5 \text{ mm}^2$ was set on the ITO-free glass plate, as shown in Fig. 1. The ITO and the platinum functioned as a current feeder to the film. We have called this film-electrode assembly a film-

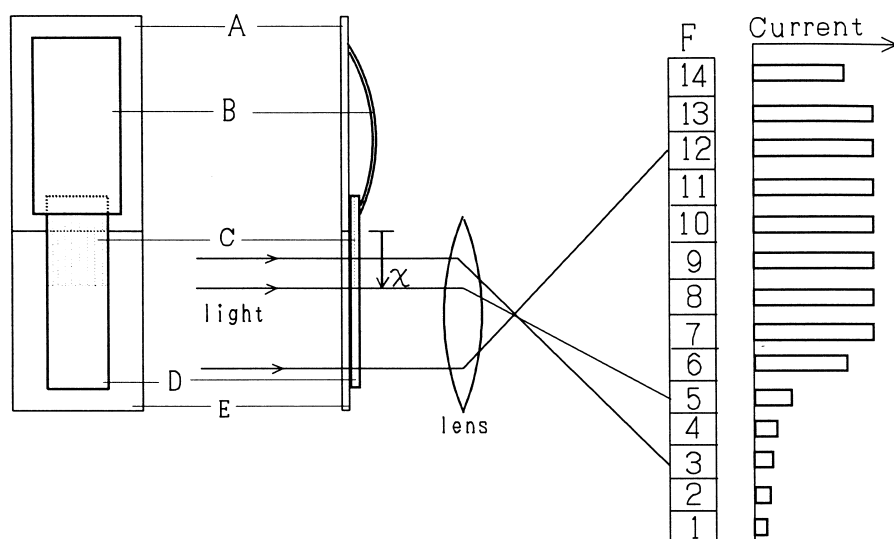


Fig. 1. Illustration of the spectrochemical cell: (A) ITO electrode, (B) platinum plate, (C) conducting domain of polythiophene, (D) insulating domain of polythiophene, (E) glass plate, (F) photodiode array detector.

simulated unit, because the film length (5 mm) is regarded as film thickness (usually 1 μm) for conventional experiments. In this assembly, spatial variation of the conducting and the insulating species may occur in the direction of the film length, whereas ion transport associated with the redox reaction occurs in the direction of the film thickness.

The apparatus of measuring concentration distribution in the direction of the film length was composed of the film-simulated unit in a rectangular quartz cell ($1 \times 1 \text{ cm}^2$), a monochromatic light beam (850 nm), and the photodiode array with 14 elements, S2311-35Q (Hamamatsu Photonics, Japan). The arrangement and the details were described previously [37,40,41]. The spatial resolution was 0.36 mm, which was provided by the separation of closest neighboring diodes and magnification with the lens. Photocurrent signals from each element of the photodiode array were converted numerically to the

absorbance, and were regarded as the dimensionless concentration of the oxidized (conducting) species at an assigned position in the film. A relation between the absorbance and the dimensionless concentration of the oxidized species was determined by an X-ray microanalyzer, IS-300 (Oxford Instruments K.K., UK). The reference electrode was a SCE and the counter electrode was a platinum plate.

3. Results and discussion

When the potential was stepped from -0.3 V vs SCE to various values, E , more positive than 1.0 V vs SCE at the dark-red reduced film, the blue conducting zone grew from the electrode to the end of the film, exhibiting a well-defined boundary between the conducting zone and the insulating zone. Quantitative results can be seen in the time-variation of the absorbance, A , at the 14 diodes, as shown in Fig. 2. Curves for *ca.* $E < 1.6 \text{ V}$ vs SCE [Fig. 2(A)] consist of three sectioned lines; no response at the initial stage ($A = 0.12$), the constant increase in A , and the saturated absorbance at the final stage ($A = 0.51$). The well-sectioned variation suggests that the film should take locally either the conducting state or the insulating state. The delay time of the absorbance ($A = 0.12$) at the initial stage has a linear relation with the distance x (see Fig. 1) between a given position of the film and the electrode|| film interface. The linearity demonstrates that the conducting front reaches successive positions (x) on the film at a constant speed. The constant speed is also supported by the linear increase in A at each position of the second stage in Fig. 2(A). As E became more positive [cf. Fig. 2(A) with Fig. 2(B)], neither the linearity nor the constant speed was lost. In contrast, the

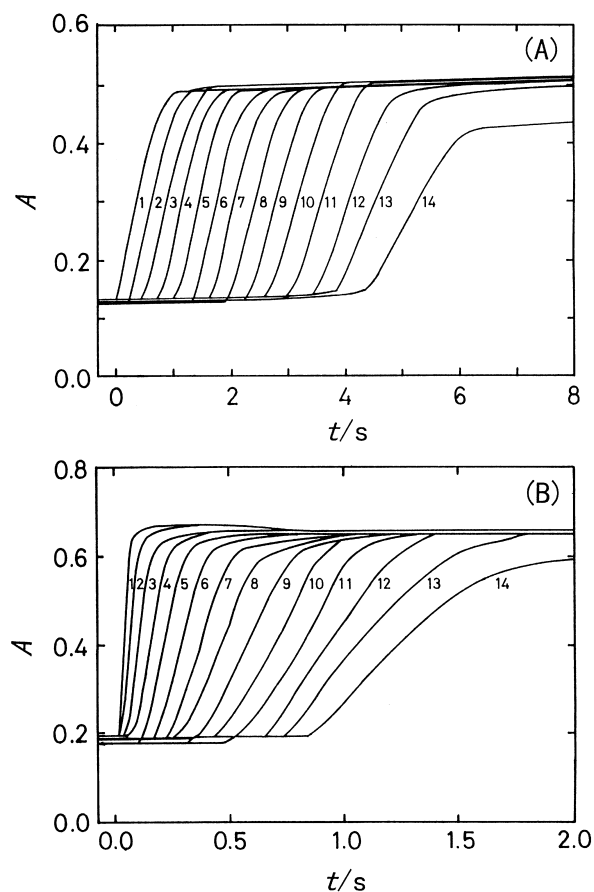


Fig. 2. Variation of absorbance at the 14 segments of the film when the potential was stepped from -0.3 to (A) 1.0 and (B) 2.4 V vs SCE in $1.0 \text{ M LiClO}_4 + \text{acetonitrile}$ solution. Each diode is numbered in series from the side of the electrode. The curve at the 14th segment was deformed by edge effects.

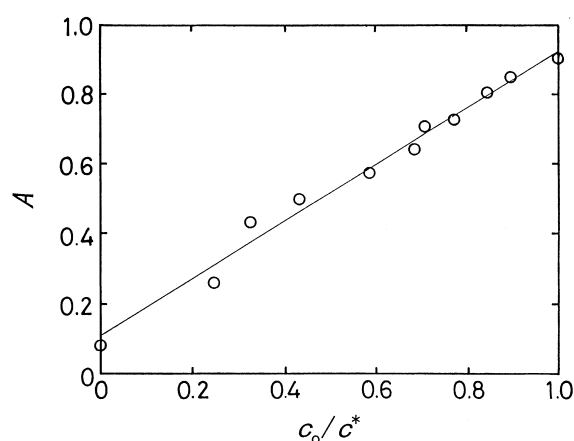


Fig. 3. Plots of the absorbance A at 850 nm against the normalized concentration c_0/c^* of the oxidized species, determined by the X-ray microanalyzer.

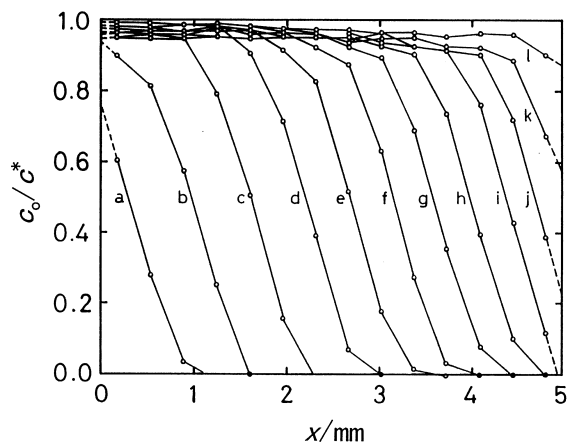


Fig. 4. Concentration distribution curves of the conducting species in the film at times; $t =$ (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, (f) 3.0, (g) 3.5, (h) 4.0, (i) 4.5, (j) 5.0, (k) 5.5 and (l) 6.0 s for $E = 1.0$ V vs SCE. They were created from combination of Fig. 1(A) and 3.

growth rate decreased probably owing to IR-drop effects in the film.

Absorbance of visible light often shows complicated variations with electrode potentials [42]. We obtained a relation of the absorbance at 850 nm with the molar ratio of the conducting species by measuring molar ratio of chlorine to sulfur of the polythiophene film using the X-ray microanalyzer. The measurement was made at various oxidation levels of the film. The calibrated plot in Fig. 3 shows almost a linear relation. By the use of calibration curve, we converted the time-variation of the absorbance at various positions into the distribution of the concentration of the oxidized species at various electrolysis times, as shown in Fig. 4. The drastic change of the profiles supports the for-

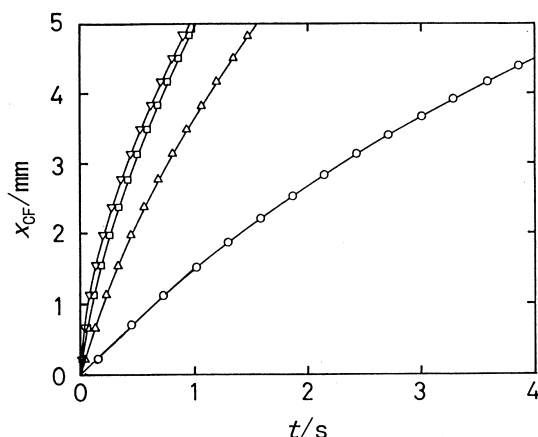


Fig. 5. Time-variations of the position of the conducting front x_{CF} for potentials $E = 1.0$ (○), 1.2 (△), 1.6 (□) and 2.4 (▽) V vs SCE.

mation of the well-defined boundary between the conducting and insulating zone. The change is steeper than the polypyrrole system [37,40], probably because polythiophene is oxidized directly to a bipolaron without taking a polaron state owing to the highly ordered state of polymer chains [43].

Fig. 5 shows time-variation of the position of the conducting front, x_{CF} , which is defined by the extrapolation of the steepest part of the curves in Fig. 4 at $c_0/c^* = 0$. The variation within a short distance ($x_{CF} < 1.5$ mm) tends to a proportional relation, indicating the growth at a constant speed. The curve becomes a concave for a long time probably because a participation of ohmic drop of the potential in the film. This is in accord with the observation that the linear domain decreased with an increase in the potential. Fig. 6 shows plots of logarithmic values of the averaged propagation speed \bar{u} against E at two concentrations of LiClO_4 . There was no appreciable difference in the concentrations of LiClO_4 . Therefore, transport of LiClO_4 is not a rate-determining step. The plot for $E < 1.6$ V vs SCE has a linear relation with E . Since the speed is proportional to the current, it can be expressed by a Tafel relation [39]:

$$\ln u = \frac{\alpha n F}{RT} E + \text{const} \quad (1)$$

where α is the transfer coefficient of the electrode reaction. The slope of the linearity gives $\alpha n = 0.06$, which is smaller than the value for polyaniline in the sulfuric acid [39]. Since no physical meaning of αn has been well-defined, we do not pursue this value. Values of instantaneous speed at $t = 0$ with E also leveled off at $E > 2.0$ V vs SCE. As E became positive, a domain of x_{CF} for the straight line in Fig. 5 got so narrow that values of u could be determined to be smaller.

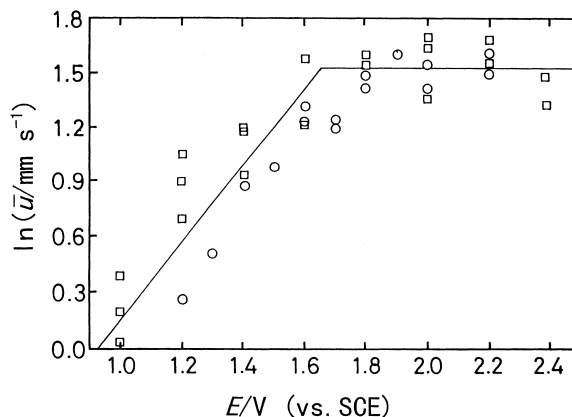


Fig. 6. Logarithmic plot of \bar{u} against E , measured in acetonitrile solutions containing 0.1 M LiClO_4 (○) and 1.0 M LiClO_4 (□).

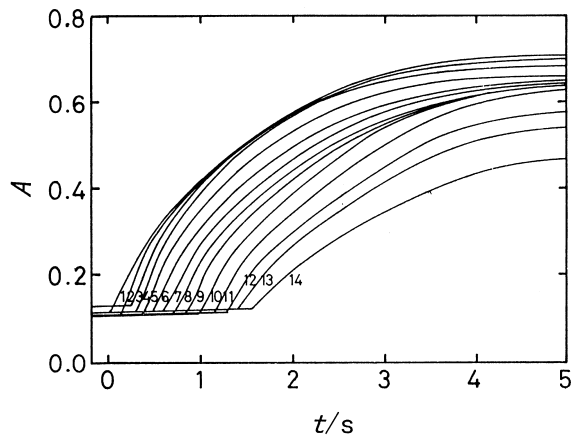


Fig. 7. Variations of absorbance at 14 segments of the film when the film was transferred into the 1.0 M LiClO_4 + propylene carbonate solution and potential was stepped from -0.3 to 2.2 V vs SCE.

The film prepared in the acetonitrile solution was transferred into the cell which included 1.0 M LiClO_4 + propylene carbonate solution. When the oxidation potential was applied to the end of the sufficiently reduced film, the conducting domain was viewed to grow gradually without any clear boundary. The variations of A were composed of the two domains: no response at the initial stage, and a rapid rise at $t = t_0$ followed by a smooth increase in time, as shown in Fig. 7. Some intersections of the curves mention a vague boundary. Fig. 8 shows variation of the distance, x , with t_0 . The plots at a short distance fall on a straight line, suggesting the control of the propagation model. Extrapolation of the plot to $x = 0$ gives no-zero value. Therefore, there is a delay of the growth

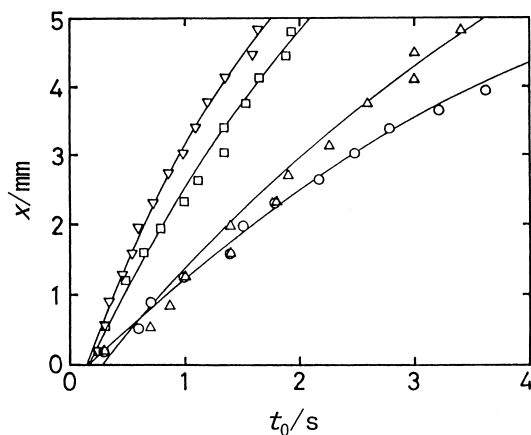


Fig. 8. Plots of the distance x of a given location against the rising time, t_0 , for $E = 1.2$ (O), 1.6 (Δ), 2.0 (\square) and 2.4 (∇) V vs SCE.

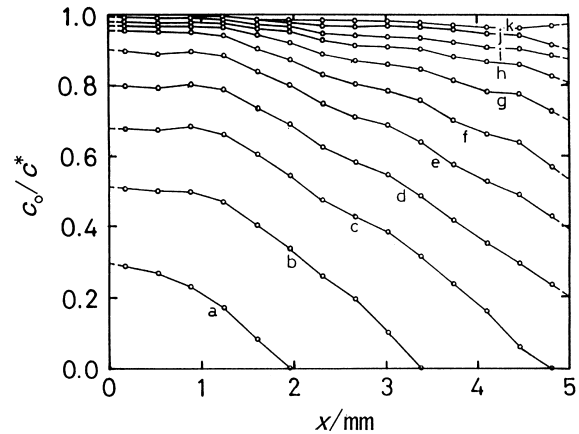


Fig. 9. Concentration distribution curves of the conducting species in the film at times: $t =$ (a) 0.5 , (b) 1.0 , (c) 1.5 , (d) 2.0 , (e) 2.5 , (f) 3.0 , (g) 3.5 , (h) 4.0 , (i) 4.5 , (j) 5.0 and (k) 6.0 s when the film was transferred into the 1.0 M LiClO_4 + propylene carbonate solution and potential was stepped from -0.3 to 2.2 V vs SCE.

of the conducting zone. The delay seems to be a feature of polythiophene films [44]. From combination of Fig. 3 and curves similar to Fig. 7, concentration distribution was obtained and plotted in Fig. 9 at various times. The variations are much smoother than those in Fig. 4, indicating dispersion of the conducting species.

Fig. 10 shows plot of c_0/c^* against $\sqrt{t-t_0}/h$, where h is the film thickness ($0.3 \mu\text{m}$). The linear variation indicates a diffusional contribution after t_0 . We applied the conventional expression for chronocoulometry to the variation in Fig. 10. The time integral of the Cottrell equation is given by

$$q = 2nFc^*\sqrt{Dt/\pi} \quad (2)$$

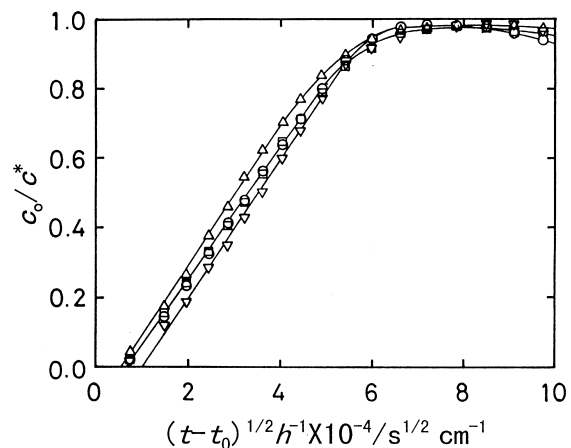


Fig. 10. Variation of c_0/c^* with $\sqrt{t-t_0}/h$, at $E = 2.2$ V vs SCE for $x = 0.18$ (O), 1.60 (Δ), 3.02 (\square) and 4.82 (∇) mm.

where D is the diffusion coefficient of the dopant ion. Letting the available diffusion length be h , we can express the total charge density as $q_0 = nFc^*h$. Then c_0/c^* is expressed by

$$c_0/c^* = 2\sqrt{Dt}/\sqrt{\pi h}. \quad (3)$$

The slope in Fig. 10 gives $D = 3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. Unfortunately, this analysis includes inconsistency in that a concept of the finite diffusion with h has been mixed with that of the infinite diffusion represented by the Cottrell equation. However, it has been demonstrated [45] that only the Cottrell term is predominant so far as we are concerned with values of c_0/c^* except for very close to unity.

Fig. 10 supports the diffusion-control whereas Fig. 8 does the propagation-control. This discrepancy may be explained by the following model. The solvent (propylene carbonate) and the dopant ion can penetrate into only a surface domain of the film immediately after the film transfer. Then the penetrated surface part can be converted into the conducting species, obeying the propagation model. Thus the conducting zone grows in the restricted portion (the surface), as illustrated in Fig. 11(A). As the dopant ion penetrates toward the film/glass interface for a long time, the conducting zone grows downward [Fig. 11(B)], of which rate is controlled by penetration. Since the penetration is ascribed to diffusion, the long time variation obeys diffusion.

The film used for obtaining the data of Fig. 7 was immersed into 1.0 M LiClO_4 + propylene carbonate for 7.5 h in the spectroelectrochemical cell after the film was re-reduced sufficiently in the distilled water. It was transferred to the photochemical cell which contained the same solution. The absorbance–times curves responding to the potential step showed the propagation-like behavior rather than the diffusion behavior, as seen in sharper variations of Fig. 12 than those of Fig. 7. The immersion of the film for a long time may make the dopant penetrate sufficiently in the whole film. When comparing the averaged propagation speed

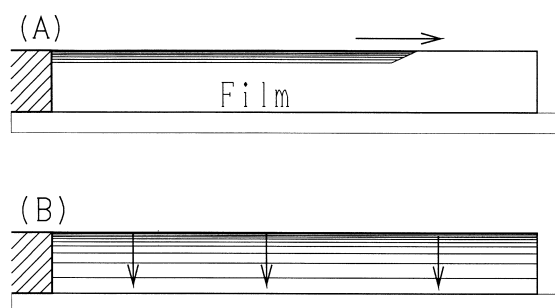


Fig. 11. Illustration of the propagation-diffusion mechanism at a short time (A) and a long time (B).

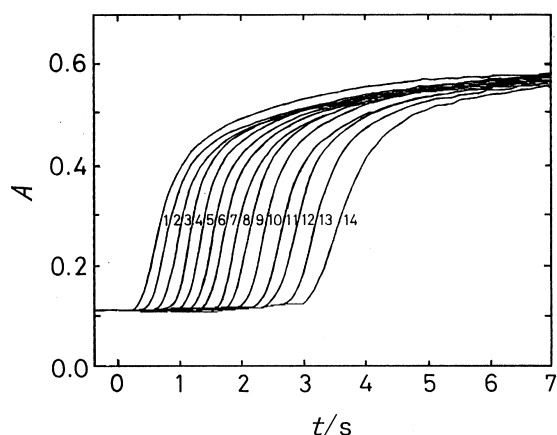


Fig. 12. Variations of absorbance at 14 segments of the film when the film was transferred into the 1.0 M LiClO_4 + propylene carbonate solution, retained in the solution for 7.5 h, and potential was stepped from -0.3 to 2.0 V vs SCE.

in propylene carbonate with that in acetonitrile in Fig. 6, propylene carbonate retards the conversion rate.

In conclusion, the substitution of acetonitrile into propylene carbonate altered the rate-determining step at first from the propagation-control to the diffusion-control and then lead to the slower diffusion-control. A diffusing species for the conversion is the dopant ion from the conventional concept. The dopant ion and its concentration were invariant whereas solvents were exchanged. Thus, the diffusion may be ascribed to an exchange rate of the solvent rather than a concentration gradients of the dopant ion. From the fact that propylene carbonate is mixed with acetonitrile at arbitrary ratio, the exchange rate may be responsible for the diffusion-control.

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