

Growth Mechanism of Transparent and Conducting Composite Films of Polyaniline

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SYNOPSIS

Composites of polyaniline (PANI) with various polymeric matrices as substrates were synthesized by means of diffusion-oxidation of aniline swollen polymeric matrices with FeCl_3 as oxidizer. The conductivity at room temperature, transmittance at 400–800 nm, stability in air, and morphology of PANI composite films depend on the polymerization time, concentration of FeCl_3 , and substrate used. A maximum conductivity at room temperature and the highest transmittance at 500–800 nm can be achieved of 10^{-1} S/cm and 70–80%, respectively. The growth mechanism of PANI composite films has been discussed.

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INTRODUCTION

Transparent and conducting thin films are useful as transparent electrodes in various electrooptical devices. In principle, the transparent conducting films in commercial use are inorganic based, i.e., thin metallic films, thin dioxide, and indium-tin oxide.¹⁻² However, some disadvantages for inorganic transparent conducting films are observed, such as high-vacuum conditions necessary for sputter-coating and evaporation of these materials. Furthermore, heating of the substrate can be a problem. In recent years, chemical oxidative polymerization and electrochemical synthesis for conducting polymers have been successfully developed to produce several transparent and conducting composites, e.g., polypyrrole-poly(vinyl chloride) (PPY-PVC),³ polypyrrole-poly(vinyl alcohol) (PPY-PVA),⁴ polypyrrole-poly(ethylene terephthalate) (PPY-PET),⁵ and polyaniline-poly(ethylene terephthalate) (PANI-PET).⁶ It has been suggested that this technique is a very good tool for obtaining transparent and conducting polymers, which might accelerate the use of conducting composites as new functional materials. However, few papers concerning growth mechanism of transparent and conducting composites have been published.

In this paper, the conductivity at room temperature, transmittance at 400–800 nm, and morphology of PANI composite films were measured as a function of polymerization time, concentration of FeCl_3 , and substrate used in order to understand the growth mechanism of PANI composite films.

EXPERIMENTAL

Polyethylene (PE), polyethylene terephthalate (PET), polyester (PER), and transparent sheet (polystyrene) with thicknesses from 40 to 250 μm were used as the polymeric matrices. The cleaned film of polymeric matrices was immersed in pure aniline monomer at room temperature for a period from 0.5 to 54 h to obtain aniline swollen polymeric matrices. The resulting film containing aniline was washed with distilled water and acetone several times and finally cleaned with filter paper. Then, it was dipped into acidic solution of FeCl_3 as oxidizing agent to obtain PANI composite films. The polymerization time, i.e., immersed time in FeCl_3 solution, and the concentration of FeCl_3 were varied depending on the required conductivity at room temperature, transmittance, and substrate used. In our experiment, polymerization time was changed from 0.5 to 28 h, while the concentration of FeCl_3 was varied from 5 to 30 wt % with a pH value from 0.15 to 1.61 depending on the concentration of FeCl_3 .

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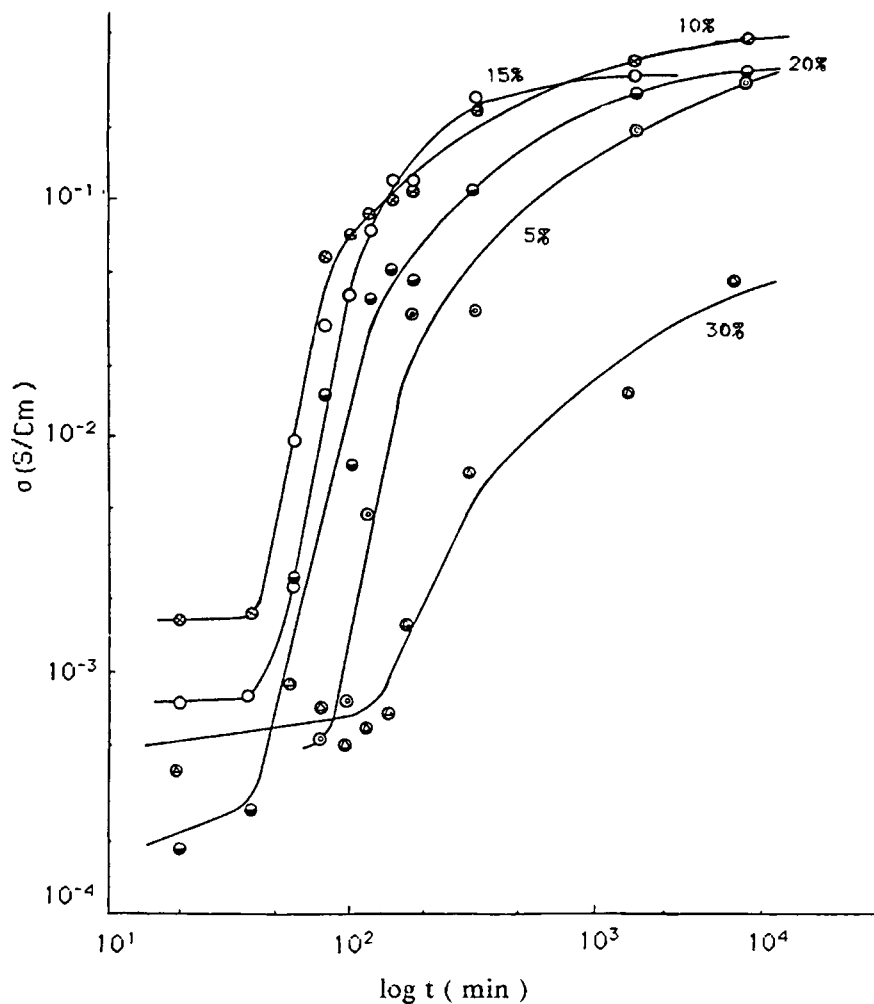


Figure 1 The relationship between the conductivity at room temperature and the polymerization time for PANI-PE composite films at different concentrations of FeCl_3 . Swollen time in aniline monomer is about 46 h; concentration of FeCl_3 : (1) 15 wt %; (2) 10 wt %; (3) 20 wt %; (4) 5 wt %; (5) 30 wt %.

The obtained PANI composite films were dried in a silica gel desiccator at room temperature. The conductivity of PANI composite films at room tem-

perature was measured by a four-probe method. UV-vis absorption and transmittance spectra of composite films at 400–800 nm were measured by a

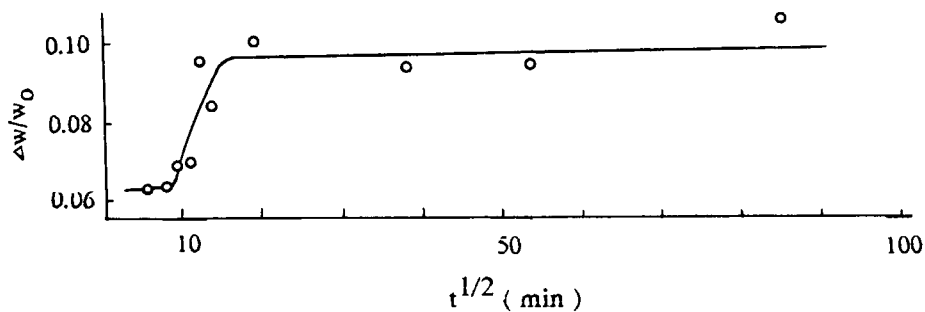


Figure 2 The ratio of enhanced weight of PANI-PE composite film to PE polymeric matrix vs. square polymerization time. A $32 \mu\text{m}$ thickness of PE film was immersed in aniline monomer for 45 h; then, it was polymerized in 15 wt % of FeCl_3 solution.

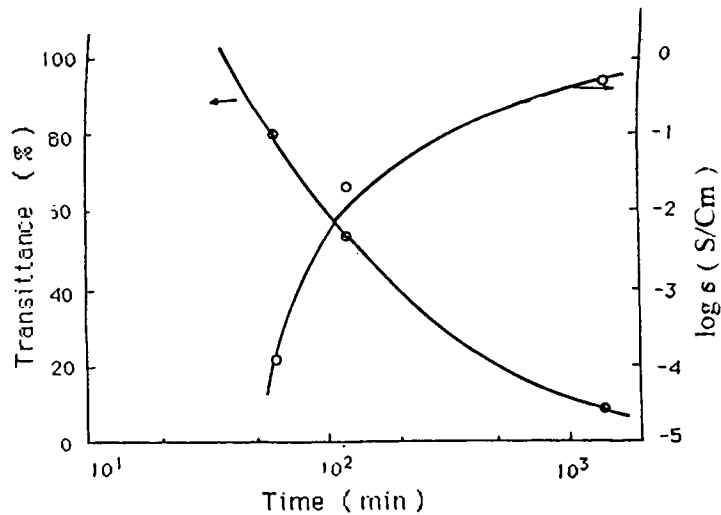


Figure 3 Dependence of the conductivity and the transmittance of PANI-PE composite films with the polymerization time. PE film was immersed in aniline monomer for 54 h; then, it was polymerized in 5 wt % of FeCl_3 .

NanoSPEC/10 microspectrophotometer. Scanning electron microscopy (SEM) of composite films was examined by a Hitachi S-530 scanning electron microscope.

1. Relation between Conductivity and Polymerization Time

A typical relationship between the conductivity of PANI-PE composite films at room temperature and the polymerization time for different concentrations of FeCl_3 is shown in Figure 1. As one can see, all

curves of $\log \sigma$ vs. $\log t$ can be regarded in three parts (A, B, and C). In the A region, conductivity is almost independent of the polymerization time and its magnitude is about 10^{-4} to 10^{-3} S/cm, which is called the "introduced regime." In the B region, conductivity rapidly increases with increase of the polymerization time, which is called the "growth region." In the C region, however, conductivity slowly increases with increase in polymerization time and a saturation phenomenon is observed, which is called the "saturated region," and its conductivity can reach 10^{-2} – 10^{-1} S/cm depending on the concentra-

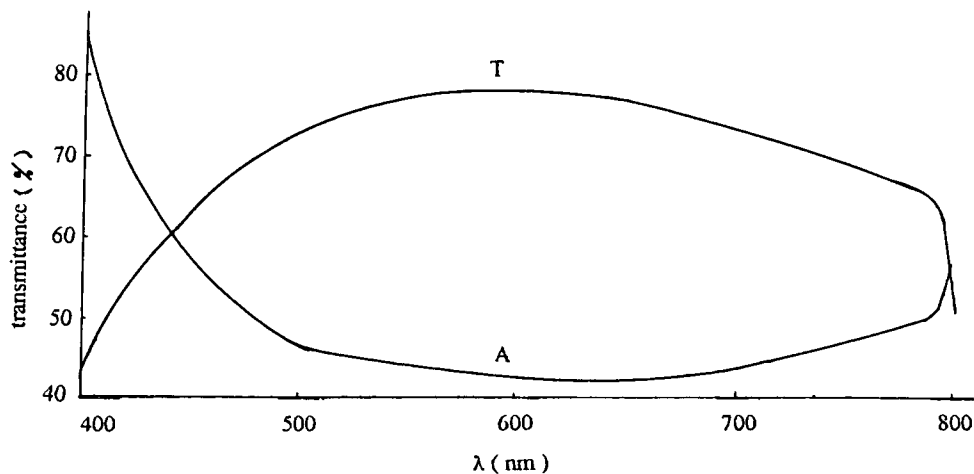


Figure 4 Absorption and transmittance of PANI-PE composite films at 400–800 nm. PE film was immersed in aniline monomer for 45 h; then, it was polymerized in 5 wt % of FeCl_3 for 60 min.

Table I Influence of Polymeric Matrix on the Maximum Conductivity of PANI Composite Films

Polymeric Matrix	σ (S/cm)			
Concentration of FeCl_3 (wt %)	6	10	15	20
PE	2.2×10^{-1}	1.9×10^{-1}	2.1×10^{-1}	1.6×10^{-1}
PER	5.3×10^{-2}	5.1×10^{-2}	5.4×10^{-2}	2.7×10^{-2}
PET	4.7×10^{-2}	5.2×10^{-2}	6.0×10^{-2}	6.2×10^{-2}
Transparent sheet	2.4×10^{-2}	1.4×10^{-2}	1.1×10^{-2}	1.3×10^{-3}

tion of FeCl_3 and substrate used. Similar behavior for the PANI composite with other polymeric matrices used in this paper is observed. Moreover, the

ratio of $\Delta w/w_0$, in which $\Delta w = w - w_0$, and w and w_0 are total weight of the PANI-PE composite films and PE substrate, respectively, can be plotted to $t^{1/2}$

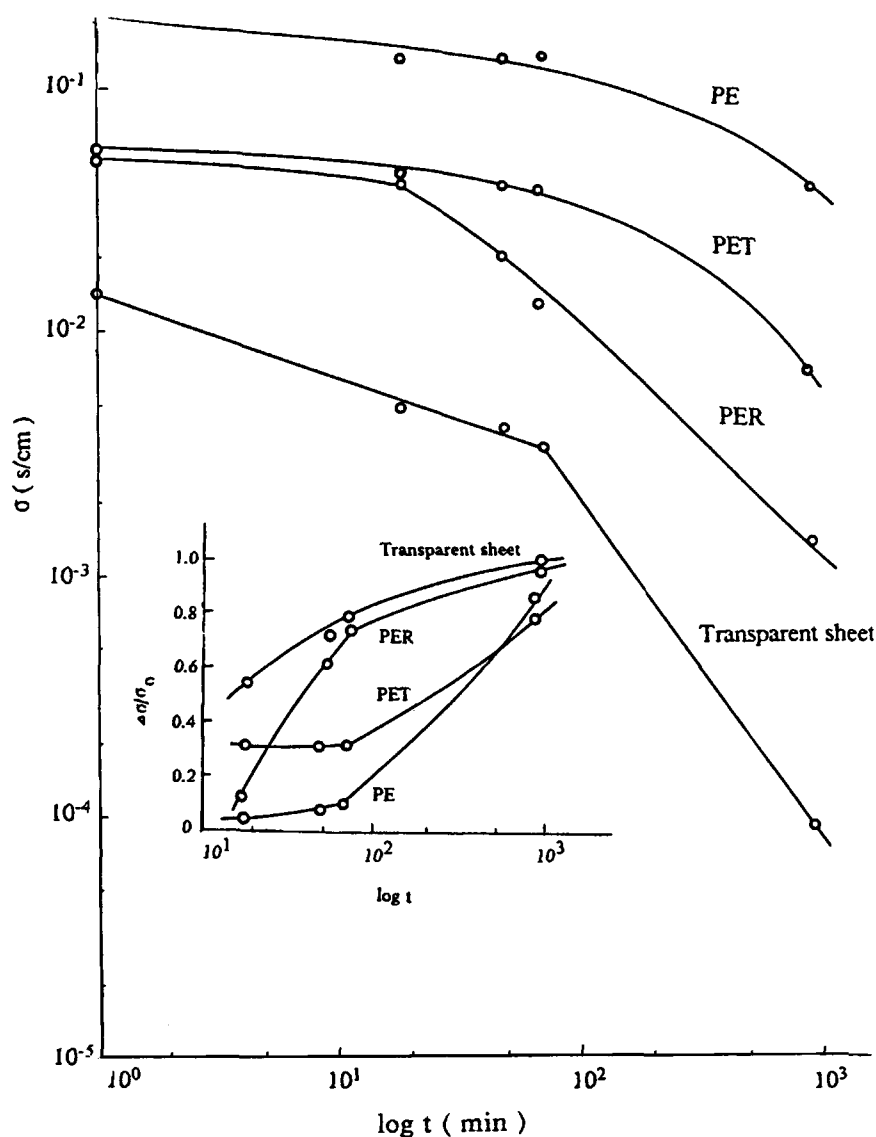


Figure 5 The stability of PANI composite films with different polymeric matrices as substrate. Polymeric matrix was immersed in aniline monomer for 54 h; then, it was polymerized in 10 wt % concentration of FeCl_3 for 28 h.

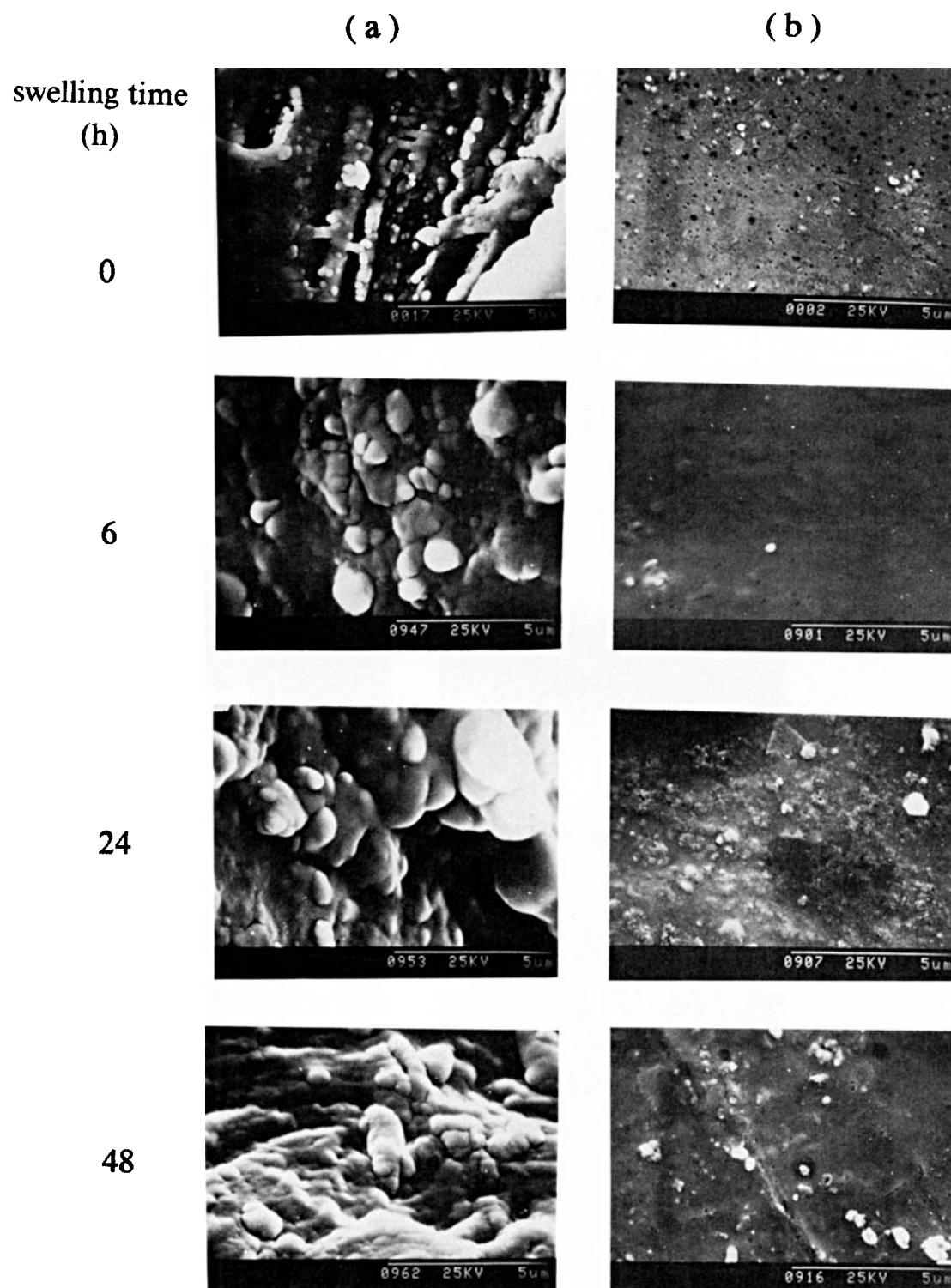


Figure 6 Morphology of PANI-PE composite films. (A) Effect of swelling time in aniline monomer on the morphology of aniline swollen PE film: (a) across section; (b) on surface. (B) Effect of polymerization time in FeCl_3 solution on the morphology of PANI-PE composite films.

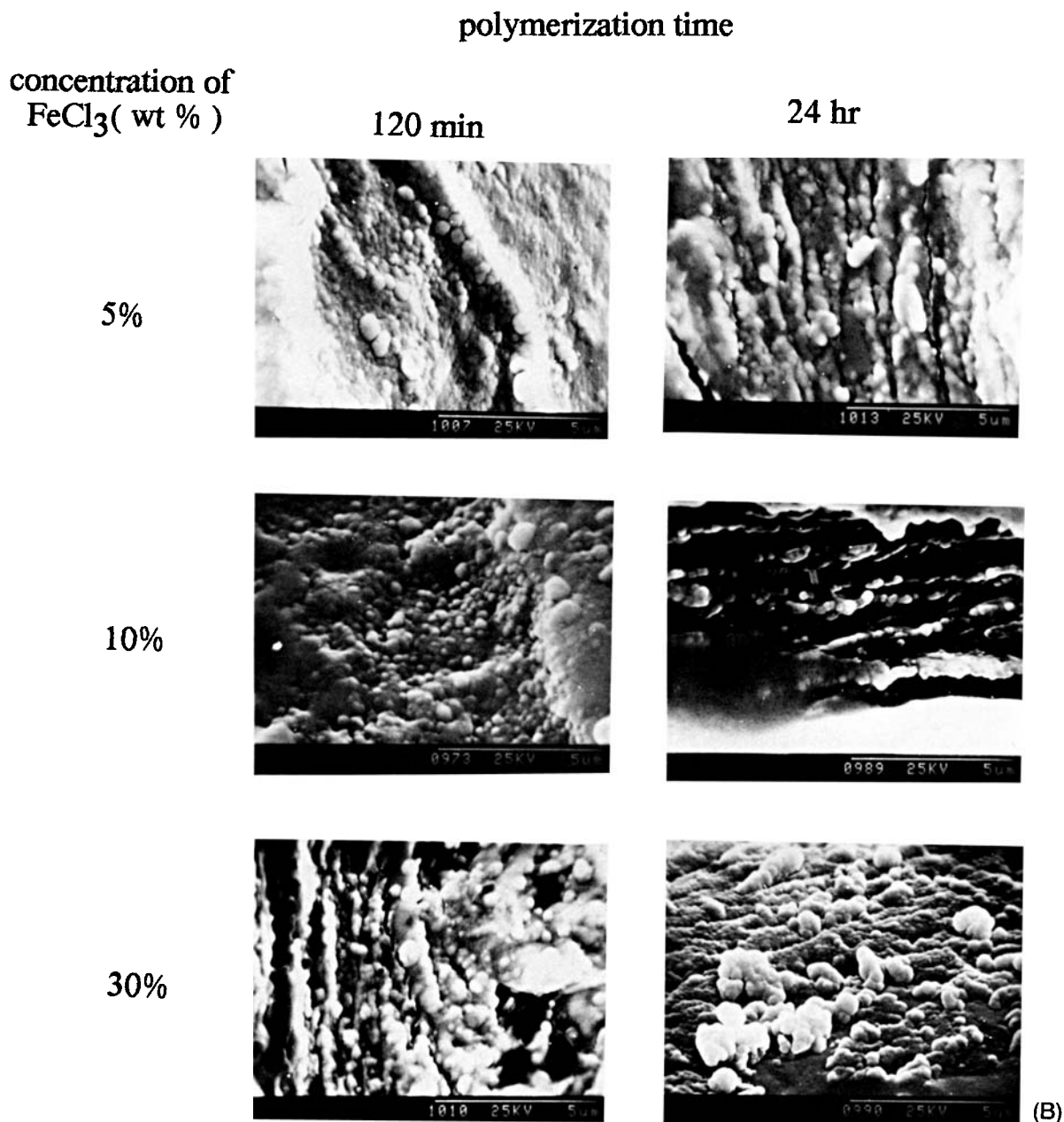


Figure 6 (continued from the previous page)

as shown in Figure 2. In the growth regime (B), as Figure 2 shows, w/w_0 is proportional to $t^{1/2}$. This shows that the weight of PANI in the composite occurs approximately under a Fickian condition as⁷

$$w_t/w = 4/\pi^{1/2}(D_t/l^2)^{1/2}$$

where w_t is the total amount of PANI in the PE film after an infinite time; l , the thickness of the PE film; and D , a diffusion coefficient. For a 32 μm PE film, according to Figure 2, the factor of saturated PANI in PE was estimated to be 10%. Therefore,

the diffusion coefficient of FeCl₃ in aniline-swollen PE film was calculated to be about $8.96 \times 10^{-15} \text{ m}^2/\text{S}$, which is consistent with results obtained by Li et al.⁵ and indicates the growth region was controlled by diffusion processes. In the saturated region, the saturated phenomenon of conductivity might be due to the absorbed aniline monomer in polymeric matrices being totally polymerized. This suggests that the conductivity of PANI composite films is controlled mainly by the amount of PANI in the composite films.

2. Relation between Transmittance and Polymerization Time

It is shown that the transmittance decreases with increase of the polymerization time; on the other hand, the conductivity increases with increase of the polymerization time, as shown in Figure 3. This result suggests that the required polymerization time for given concentration of FeCl_3 can be found if a PANI composite film with high conductivity and transparency is needed. For example, a 70–80% transmittance of PANI–PE composite polymerized in 5 wt % of FeCl_3 for 60 min was obtained as shown in Figure 4. As discussed before, the conductivity and transparency of PANI composite films were controlled by both the concentration of FeCl_3 and polymerization time. Thus, to meet required conductivity and transparency of PANI composite films, an optimal concentration of FeCl_3 and polymerization time for PANI composite should be chosen. For PANI–PE composite films, the optimum concentration of FeCl_3 and the polymerization time are 10–20 wt % and 100–400 min, respectively. For a given concentration of FeCl_3 and polymerization time, it was noted that the conductivity of PANI composite films depends on the properties of the polymeric matrices used, as shown in Table I. The highest conductivity was observed for PANI composite with PE film as substrate. This may be associated with morphology because a granular morphology with pinholes was observed for PE film, which allows aniline monomer to diffuse into PE films. Moreover, the PANI–PE composite film was more stable in air compared with other substrates as shown in Figure 5.

3. Morphology

A typical morphology of PANI–PE composite films is shown in Figure 6. A granular morphology for both the surface and across the section of PE film

itself was observed as shown in Figure 6(A). However, many pinholes on the surface of the PE film were found. It is very interesting to find that these pinholes gradually disappeared with increasing swelling time of the PE film in the aniline monomer. In addition, the diameter of granules increases with increase of swelling time. A similar phenomenon for other polymeric matrices used was also observed. These results suggested that polymeric matrices used in this paper can be swollen by the aniline monomer, which is a very important procedure for growing transparent and conducting composites of PANI. Furthermore, the cross section of PANI–PE composite films was similar to that of aniline-swollen PE film and was independent of the concentration of FeCl_3 used, as shown in Figure 6(B). This indicates that the morphology of PANI–PE composite films was controlled by the morphology of aniline-swollen PE film. However, the diameter of granules of PANI–PE composite films increases with increase of the concentration of FeCl_3 and the polymerization time.

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