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Conducting Polymer Composites of Polythiophene and Polyacrylamide

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A conducting composite of polythiophene (PTh) with polyacrylamide (PAA) as the insulating matrix was prepared via electrochemical methods. The change in the conductivity of composites was analyzed as a function of the percent composition of the insulating component. The characterization of the composite was done by FTIR, SEM, and TGA studies. Conductivity and solubility studies together with spectroscopic methods reveal that a chemical interaction between the polymers exists.

Keywords: polyacrylamide, polythiophene, electrochemical polymerization

INTRODUCTION

In the last decade, various electrically conductive polymers have been extensively studied. Among them a considerable number of works on polyheterocylic polymers such as polypyrrole, polythiophene, and polyaniline were noticed because of their important advantages. These polymers are relatively stable under ambient conditions and can be conveniently synthesized via electropolymerization [1–3]. The most successful way of forming composites was found to be the

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electropolymerization of the conducting component on an electrode coated with the insulating polymer. Among these, the electrochemically polymerized composites of thiophene have attained much attention due to their flexibility, ease of doping, and good conductivity. As the host polymers, polyacrylonitrile [4], polyethyleneadipate [5], and polyacrylamide [6] were used. The detailed analysis of electrochemical behavior of PTh and derivative films under different conditions was reported [7–20]. Earlier, the present authors had investigated the electrochemical polymerization of pyrrole on a surface coated with polyacrylamide [21].

In order to obtain PTh-PAA film, three different electrochemical methods were used. These methods are explained in detail in the following section.

EXPERIMENTAL

Preparation of PAA-PTh Polymer Blends

Several electrolysis conditions were applied during the polymer blend preparation. These conditions are summarized in Table 1.

In the first group experiments, PTh-PAA composites were prepared by the electrochemical polymerization of thiophene onto a PAA precoated electrode at a constant potential of +2.36 volt versus $Ag^o/Ag^+(10^{-2}$ M). The remaining components of the electrolysis cell were Pt foil (2 cm^2) working and counter electrodes and a Luggin capillary (Ag^o/Ag^+ 10^{-2} M) reference electrode. It is well known that

TABLE 1 Electrolysis Conditions of PTh-PAA Blends

Sample code	Polymer or monomer	Electrode coating method or electrolysis condition	Polymer or monomer	Electrode coating method or electrolysis condition
A	Catholyte PAA	Dip coated (in CH_3CN)	Th and dip coated electrode	$E_{pot.} = +2.36$ (in CH_3CN)
B	Catholyte PTh	$E_{pot.} = +2.25$ V (in CH_3CN)	AA (added to Th containing electrolysis cell Step 1)	$E_{pot.} = -2.25$ V (in CH_2Cl_2)
C	AA and Th together	$E_{pot.} = +2.25$ V (in CH_3CN) $E_{pot.} = -2.25$ V (in CH_2Cl_2)		

polyacrylamide is soluble in water. Therefore, polyacrylamide was dissolved in doubly destilled water (1%) and used for dipcoating the Pt electrodes. The coated electrode was placed in the electrolysis cell. 10^{-3} M monomer was introduced into the electrolysis cell. All the polymerization was carried out at room temperature. The cathode compartment of the electrolysis cell was purged with N_2 throughout the polymerization. Acetonitrile was used as the polymerization solvent, and tetrabutylammonium fluoroborate (TBAFB) as the supporting electrolyte. The oxidation peak potential of thiophene was determined on the coated polyacrylamide Pt electrode (Figure 1b). In order to overcome the resistance caused by the insulating film, the synthesis of PTh on a precoated electrode was done at +2.36 / V VS $Ag^o/AgBF_4$. The reason may be that the oxide layer was not completely formed at the anodic step because of the coverage of the surface with the oxidation products and at the same time, if the quantity of PAA on the electrodes surface level is more than 66%, polymerization of thiophene is not possible. When the electrolysis started, the monomers diffuse through the film towards the electrode surface and form a polymeric film between the polyacrylamide and the electrode surface. The color of the PTh blend was greenish black. After electrolysis, the anode was removed from the cell and immersed in water and acetonitrile for quick washing process, and dried. The weight percent of polythiophene in the composite was determined by weighing the electrodes

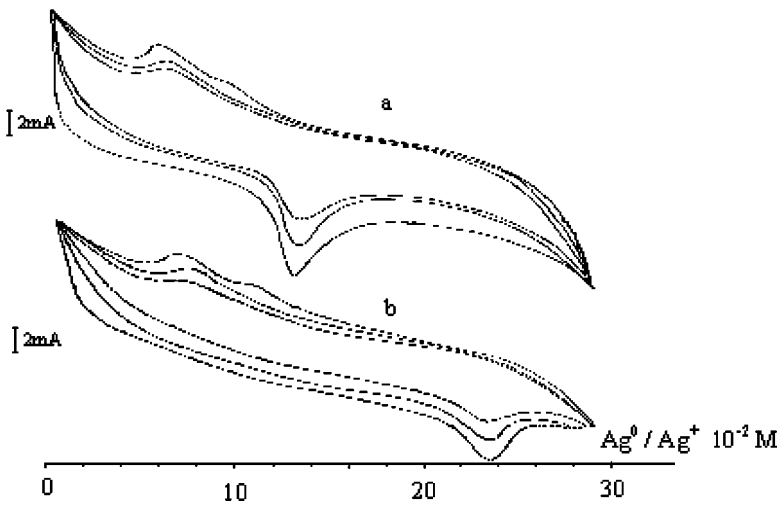


FIGURE 1 The cyclic voltammograms of thiophene, (a) on bare Pt electrode and (b) on PAA coated electrode.

TABLE 2 The Conductivities of Thiophene and Acrylamide Polymer Composites in First Group Experiments

PTh (Wt%)	PAA (Wt%)	Conductivity (S/cm)
94.4	5.6	1.15×10^{-4}
90.0	10.0	2.00×10^{-4}
79.0	21.0	1.15×10^{-5}
75.0	25.0	1.25×10^{-5}
65.0	35.0	2.15×10^{-6}
55.0	45.0	6.15×10^{-7}
50.0	50.0	4.90×10^{-7}
34	66.0	3.25×10^{-7}

before and after the polymerization. The blends were prepared by varying the PTh and PAA contents (sample A). As a consequence of incorporation of PTh component in the blends, the conductivity increased (Table 2). The conductivity of composite films obtained by the first electrolysis method is shown in Table 2.

In the second approach, first the oxidation peak potential of thiophene (+2.25 V) was applied where the working electrode was Pt anode and the solvent was acetonitrile. As soon as the film reached a certain thickness (20–30 μm), acrylamide monomer was added to the system. After the addition of acrylamide to the cell, the potential was reversed to the $E_{p,c}$ of the acrylamide (sample B). The films could easily be peeled off from the electrode surface. The conductivity of composite films obtained by the second electrolysis method is shown in Table 3.

TABLE 3 The Conductivities of Thiophene and Acrylamide Polymer Composites in Second Group Experiments

PTh (Wt%)	PAA (Wt%)	Conductivity (S/cm)
97	3	2.25×10^{-4}
93	7	2.15×10^{-4}
80	20	1.85×10^{-5}
75	25	1.65×10^{-5}
64	36	2.75×10^{-6}
55	45	7.50×10^{-7}
34	66	5.25×10^{-7}
25	75	3.15×10^{-7}
10	90	7.50×10^{-8}
2	98	2.25×10^{-10}

In the third group experiments, thiophene was polymerized at the oxidation potential in acetonitrile until conducting polymer electrode films were formed on the surface of the Pt electrode. As soon as the film reached a certain thickness (35 μm) the electrochemically coated electrode was removed and immersed in another electrolysis cell. This new cell contained acrylamide monomer and the solvent was acetonitrile-CH_2CI_2 (%10 v/v). The polymerization potential was the $E_{p,a}$ of acrylamide (samples C). The film on the electrode surface was peeled off for further gravimetric, conductivity, thermal (Figure 2), and FTIR (Figure 3), and SEM (Figure 4) analyses. The conductivity of composite films obtained by the third electrolysis method is shown in Table 4. PTh film has an oxidation peak at +1.46 V on the anodic sweep and the corresponding reduction peak at +0.60 V on the cathodic sweep (Figure 1).

The conductivities of the polymer blends were measured by a four-probe technique. IR (Mattson 1000), thermal DSC (Setaram 131), and TGA (Shimadzu) and SEM (Jeol JSM 840A) analyses characterized the polymers.

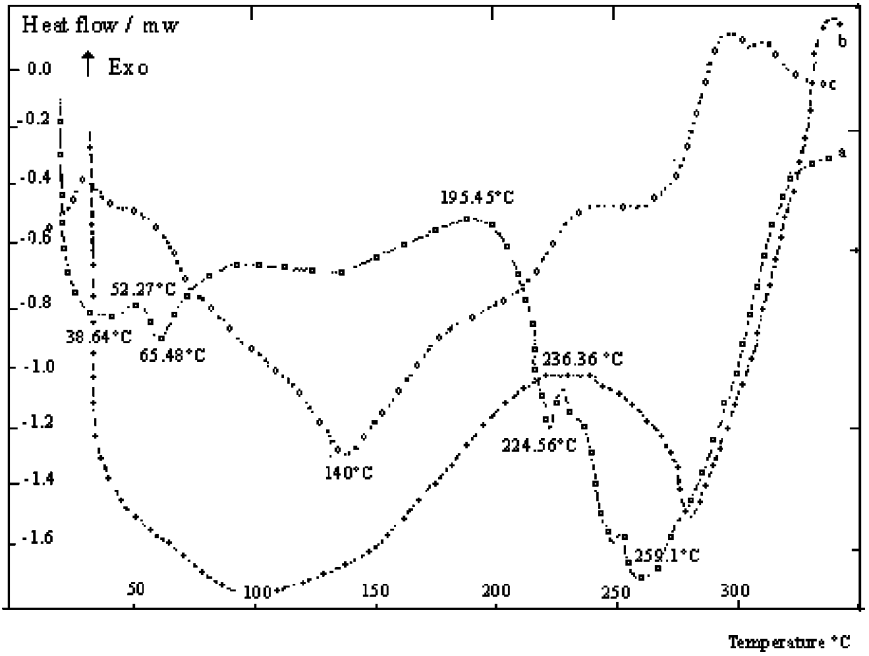


FIGURE 2 DSC thermogram of: (a) polyacrylamide, (b) polythiophene, (c) PTh-PAA composite film.

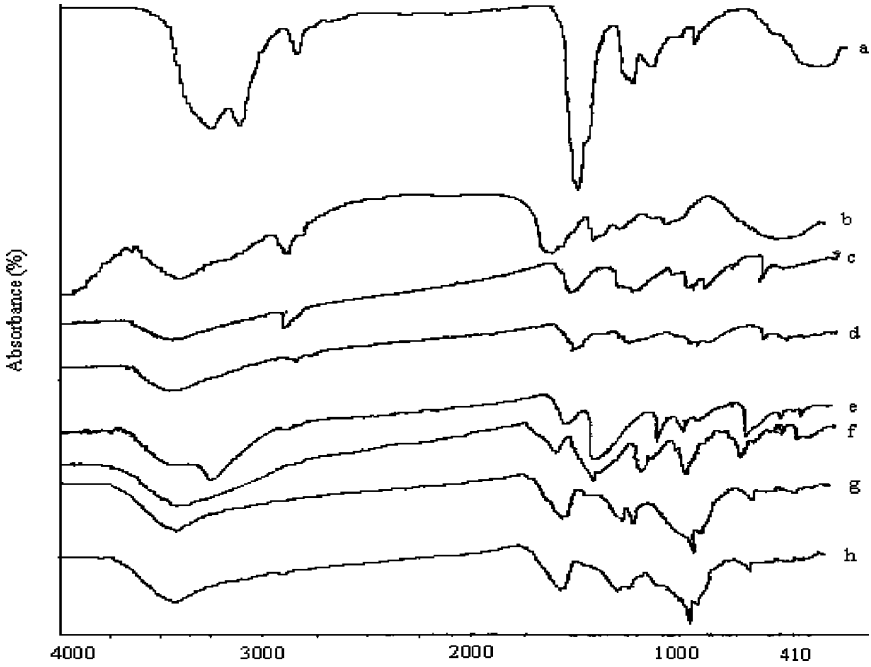


FIGURE 3 IR spectra of PTh-PAA films (a) 100% PAA, (b) 66.65% PAA–33.35% PTh, (c) 45.03% PAA–54.97% PTh, (d) 36.71% PAA–64.29% PTh, (e) 26.08% PAA–73.92% PTh, (f) 19.35% PAA–81.65% PTh, (g) 10.25% PAA–89.75% PTh, (h) 100% PTh.

RESULTS AND DISCUSSION

Thermal Analysis of Polyacrylamide

In the thermogravimetry analysis of polyacrylamide, there exists about 10.52% weight loss at 216°C and 23.25% loss at 280°C and 35% loss at 345°C (Figure 5). The glass transition temperature of PAA is 165°C [22]. On the other hand, in the thermogravimetry analysis of the polythiophene (sample A), there exits about 16.85% weight loss at 287°C and 21.45% loss at 600°C and 50% loss at 680°C (Figure 6). The thermogravimetry analysis results of PTh-PAA (sample C) are different than those of PAA $\notin$ PTh (sample B) (Figure 7). There exist mainly three weight loss steps. Upon heating of the sample up to 278°C the weight loss was 16%, then upon continuing heating up to 500°C the total loss had reached 34%. Afterward, the authors further heated the sample up to 700°C, and it

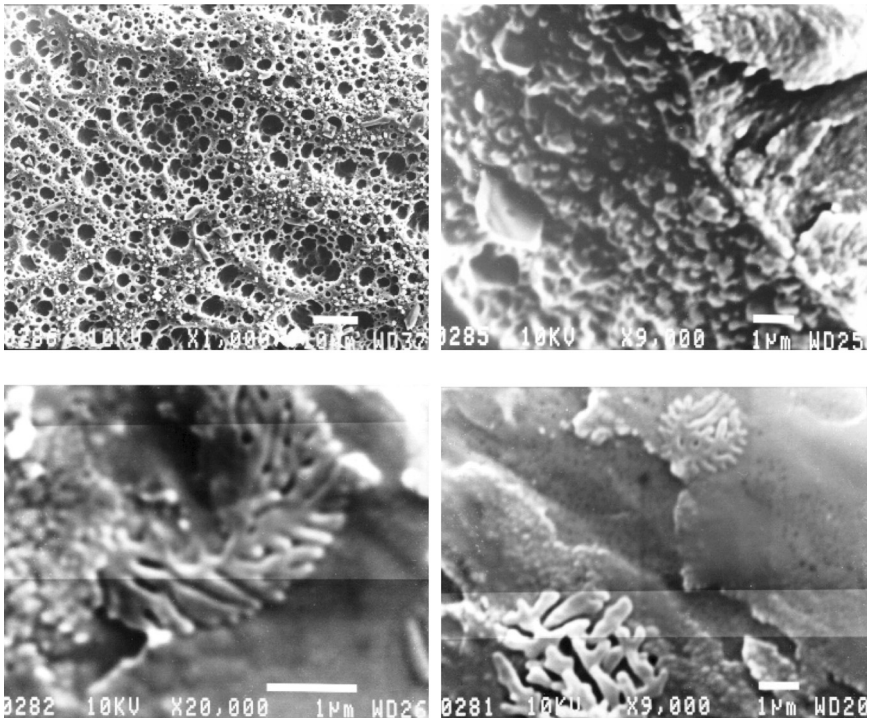


FIGURE 4 SEM pictures of (a) PTh solution side, (b) PTh-PAA film electrode side, (c) PTh-PAA film solution side, (d) PTh-PAA film solution side of washed film.

was observed that at that temperature the total loss had reached 87%. The main sharp weight loss was observed between 600°C and 800°C (Figure 2).

TABLE 4 The Conductivities of Thiophene and Acrylamide Polymer Composites in Third Group Experiments

PTh (Wt%)	PAA (Wt%)	Conductivity (S/cm)
0.00	100	3.6×10^{-10}
33.35	66.65	8.5×10^{-8}
54.97	45.03	1.5×10^{-6}
64.29	36.71	3.6×10^{-5}
73.92	26.08	7.3×10^{-5}
81.65	19.35	2.4×10^{-4}
89.75	10.25	7.5×10^{-4}
100	0.00	1.2×10^{-3}

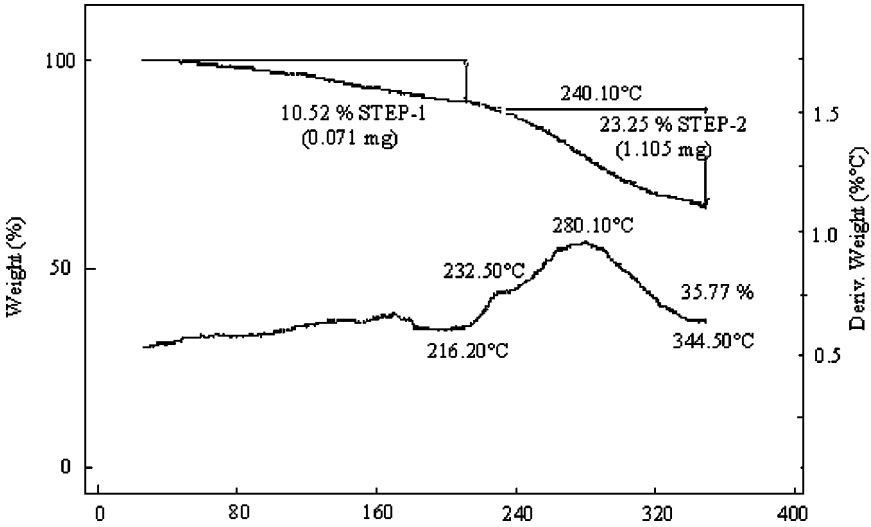


FIGURE 5 TGA thermogram of polyacrylamide.

IR Analysis of PTh-PAA Films

IR analyses of PTh-PAA blends were carried out using KBr pellets prepared at room temperature. Pure PAA IR absorption peaks are 1660 cm^{-1} (C=O stretching). 3240–3345 cm^{-1} (N–H stretching) and

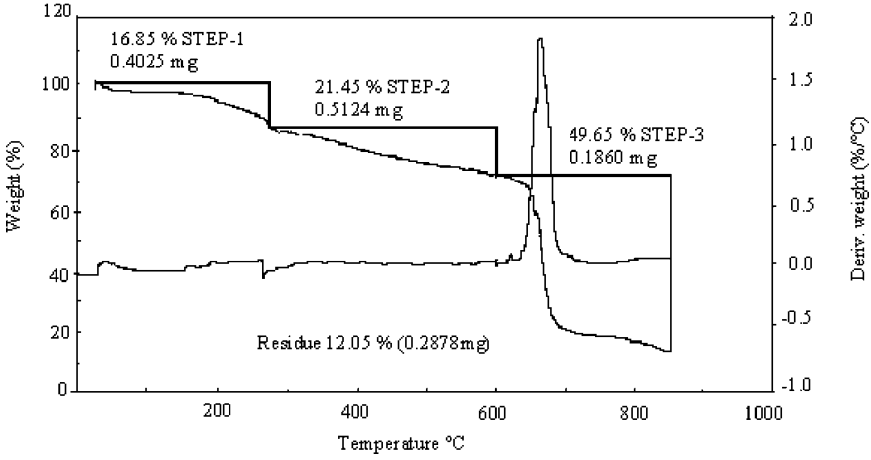


FIGURE 6 TGA thermogram of polythiophene.

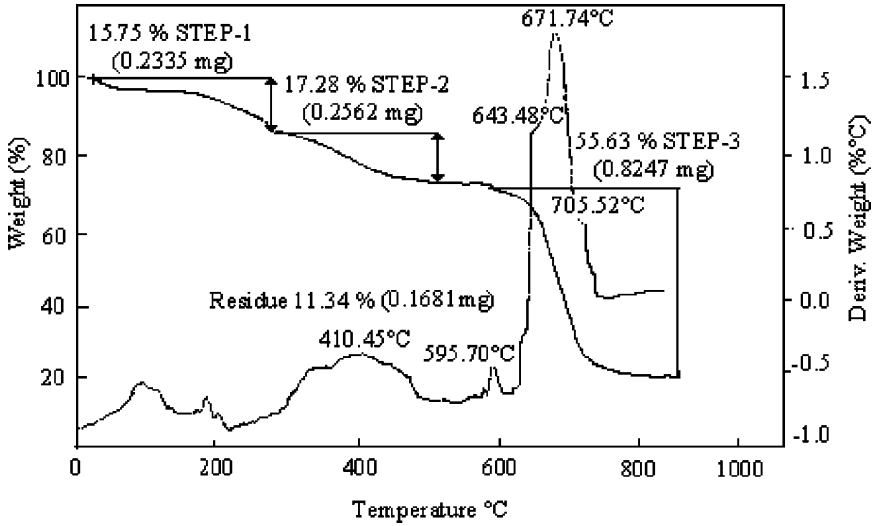


FIGURE 7 TGA thermogram of PTh-PAA composite film.

2750–2790 cm^{-1} (–CH_2-stretching) (Figure 3a). Polyacrylamides display one stretching band in the carbonyl region. The incorporation of PTh affects the IR spectrum (Figure 3b–g). For example, as 33% PTh was incorporated into the matrix, the absorption peaks of PAA at 3240 cm^{-1} and 2750 cm^{-1} decreased considerably (Figure 3b). The bands around 1672 cm^{-1} and 1635 cm^{-1} are due to amide-I (C=Stretching) and amide-II (NH bending) of the amide group of PAA. The peaks in 1700–1000 cm^{-1} region were broadened. Both washed and unwashed films have 1780–1720 cm^{-1} region a for thiophene ring and a 1780–1720 cm^{-1} asymmetric and symmetric carbonyl. The C–N stretching band appears at 1380 cm^{-1}, but the absorption peaks are decreased (Figure 3e–g). The strongest band at 1080 cm^{-1} stands for BF_4 dopant ion (Figure 3f).

DSC Analysis of PTh-PAA Films

In DSC analyses, pure PAA has an exothermic peak at 259°C (Figure 2a). Under the same conditions, PTh has thermal changes between 270°C and 380°C (Figure 2b). In DSC thermograms of PTh-PAA film, there exist three endothermic shoulders between 200°C and 300°C. The film has another endothermic peak at 375°C (Figure 2c). In the PTh-PAA film an exothermic wide peak was observed between 70°C and 150°C (Figure 2c). The PTh-PAA composition above

300°C was stable up to 350°C. Such behavior was not observed for either PTh or PAA homopolymers.

SEM Analysis of PTh-PAA Films

SEM analyses reveal some morphological differences between the films. The solution side of pure PTh film show hemispheres (cauliflower-like) on the surface (Figure 4a). The electrode sides and solution sides of the electrolytic composites PTh-PAA films have different appearances (Figure 4b–c). Obvious difference could be detected between the micrographs of electrolytic film and that of the film washed with acetonitrile-CH_2CI_2 (Figure 4d). In earlier reports, that difference was explained by a model [22].

As explained previously, blends of PAA with PTh at different percentages for each component (Table 2) were prepared. In the blends, the PTh content ranged from 33% to 90%. Pure PTh and PAA were used as the reference points. The conductivity of pure PTh film was measured as 1.2×10^{-3} S cm^{-1} by the four probe method. As the PTh incorporated into the matrix increased, the conductivity of the blend also increased (PAA conductivity 10^{-10} S cm^{-1}). For instance, incorporation of 33% PTh increased the conductivity to the order of 10^{-8} S cm^{-1}, involvement of 55% PTh increased the conductivity to 10^{-6} S cm^{-1}. Up to 74% PTh contribution, the conductivity increased but then almost a plateau was observed, where the conductivity stayed about 10^{-4} S cm^{-1}.

CONCLUSIONS

The conductivity behavior of electrochemically obtained polymers was investigated. It was clearly observed that although the films formed on the surface of the electrodes, their conductivity was sufficient to apply a desired polymerization potential. At least, this was solid evidence of the presence of conductive films that themselves behave as the electrodes. Because the polymerization rate of Th is faster than that of acrylamide, the appropriate ratio of concentration of monomers was chosen to give a chance to the acrylamide to interact with PTh oligomers that were formed immediately on the electrode surface. The conductivity change of films obtained by the first and second methods is significantly lower as compared to films obtained by the third approach. The reason for this behavior may be due to the solubility of the intermediate species in acetonitrile and/or a strong adherence of the products to the electrode surface. The electrochemically obtained polymers by the third electrolysis method were multilayered composites

that although the multilayers increased the conductivity did not change.

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