

# Complexation of Rhodium on Radiation-Grafted Acrylic Acid onto Poly(tetrafluoroethylene–perfluorovinyl ether) Copolymer Films

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**ABSTRACT:** Radiation-induced graft polymerization of acrylic acid onto poly(tetrafluoroethylene–perfluorovinyl ether) copolymer films has been prepared using  $\gamma$ -irradiation by the mutual method. The grafted copolymer rapidly complexes with rhodium ions through the carboxylic groups. The complexation process was followed by measuring the variation of the pH of aqueous  $\text{RhCl}_3$  solution of several concentrations as a function of time. Spectroscopic, electrical, optical, thermal, and diffraction measurements have been investigated. The results revealed the high stability of the ligand–metal complex formed. Thus, a practical application of the grafted copolymer in the field of rare metal waste treatment is implied. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1449–1455, 1998

**Key words:** acrylic acid; copolymer; radiation grafting; optical gap; electrical conductivity

## INTRODUCTION

Efficient ion-exchange membranes have been manufactured using grafted polymers with acrylic and methacrylic acids.<sup>1,2</sup> Polymer–metal chelate films were prepared by mixing metal salts with polymers containing functional groups such as poly(vinyl alcohol), polyamide, and poly(acrylic acid).<sup>3–5</sup> Polymer–metal complex represents a remarkably specific structure in which the central metal ions are surrounded by an enormous polymer chain.<sup>6</sup> The coordination reaction of a polymer ligand to metal ions or metal complexes are studied mainly by spectrophotometry.<sup>4–6</sup> Polymer–metal complexes have also been studied by X-ray diffractometry (XRD).<sup>7</sup> The conductivity of the polymer–metal have been investigated.<sup>4,5,8</sup> The thermal stability of grafted polyacrylic acid on some fluoropolymers has been examined.<sup>7,9,10</sup> Polymer–metal complexes have become of great interest because of their distinguished electrical

and thermal properties, use in some industrial applications,<sup>11</sup> and potential biological activity.<sup>12</sup>

The present work was designed to take advantage of the evident complexing tendency of graft copolymers toward metal ions and to explore their utilities in the field of rare metal waste treatment for the metal recovery. Therefore, the grafted poly(tetrafluoroethylene–perfluorovinyl ether) with acrylic acid, PFA-*g*-PAAc, copolymer was prepared and used as ligand for  $\text{Rh}^{3+}$  ions in solutions. The complexation route was examined by pH-metry as a function of time. The graft copolymer–metal complex was investigated by ultraviolet (UV), XRD, X-ray fluorescence (XRF) and thermogravimetric analysis (TGA) in order to probe the thermal and chemical stability of the complex bonds and structure.

## EXPERIMENTAL

### Materials

Poly(tetrafluoroethylene–perfluorovinyl ether) copolymer films (PFA) of 100  $\mu\text{m}$  thickness (Hoechst,

Germany) were used as polymeric substrates. Acrylic acid (AAc), a 99% pure product of Merck (Germany), and rhodium chloride ( $\text{RhCl}_3$ ) an AR-grade product of Koch-Light Laboratory (UK), were used as received.

### Graft Polymerization

The graft copolymers were prepared by the direct  $\gamma$ -radiation grafting of acrylic acid in distilled water (40 : 60 wt %) onto PFA films at a dose rate, 0.84 Gy/s. Mohr's salt solution (ammonium ferrous sulphate solution) (2.5 wt %) was added to reduce the homopolymerization of AAc during the radiation grafting. The obtained materials were kept in glass ampoules, which were deaerated by streaming dry nitrogen for 5 min and then sealed and subjected to 25 kGy of  $\gamma$ -radiation. The grafted films were removed; washed with hot distilled water; and finally soaked overnight in distilled water to extract any residual monomers and homopolymers, which may be occluded in the polymeric materials. The degree of grafting was determined as follows:

$$\%G = \frac{W_g - W_o}{W_o} \times 100$$

where  $W_o$  and  $W_g$  represent the weights of the initial and grafted films, respectively.

### Synthesis of the Graft Copolymer–Metal Complex

The complex formation of the grafted PFA films with PAAc were prepared by refluxing different concentrations (0.005, 0.01, 0.02, 0.05, and 0.08 wt %) of an aqueous rhodium chloride with the grafted polymer, in the form of thin films, for 2 h at 100°C and under a dry nitrogen atmosphere. The treated grafted films were then washed several times with hot distilled water and then dried under vacuum at 50°C for 24 h.

### UV-Vis Spectrophotometry

UV-vis spectrophotometric measurements were carried out over the 200–900 nm wavelength range using a model  $\lambda 3\beta$  Perkin–Elmer instrument.

### X-ray Fluorescence Spectroscopy

XRF (hnu, pc ORTEC 6110 TEFA, Tube Excited Fluorescence Analyzer System, USA) was used to

confirm the existence of metal complex, which may be formed in the graft copolymer.

### X-ray Diffraction

XRD measurements were conducted on grafted samples and those complexed with  $\text{Rh}^{3+}$  ions. The diffractograms were obtained using Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ , at 40 kV and 30 mA) generated by a PW 1390 Philips apparatus.

### Electrical and Optical Conductivity

Measurements of electrical conductivity were carried out using a specially designed cell equipped with two probe electrodes. The measurements were carried out at room temperature (303 K). A Keithly 616 digital electrometer was used for current measurements at a certain applied voltage, 200 V.

The optical absorption is measured by Uvikon 860 Koutron at room temperature in the range from 200 to 900 nm of UV-VIS radiation.

### Thermogravimetry

TGA was carried out in a dynamic atmosphere of pure nitrogen gas by means of a Shimadzu DSC 50 analyzer (Japan) with a heating rate of 20°C/min.

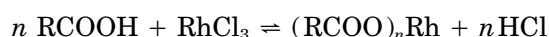
## RESULTS AND DISCUSSION

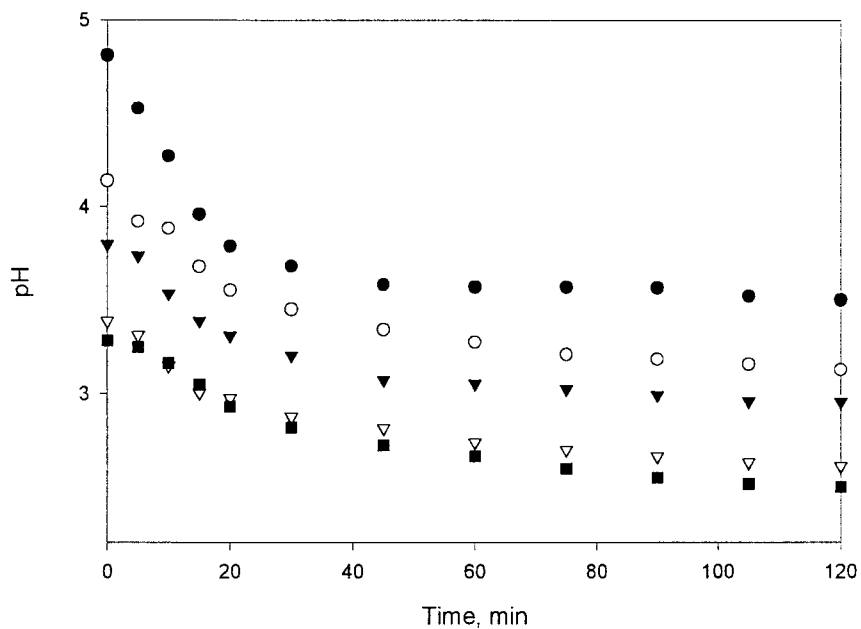
### Graft Copolymer Complexation with Rhodium Ions

#### *PH Measurements*

Figure 1 shows the medium pH as a function of the time of reaction for the PFA-*g*-PAAc films and  $\text{Rh}^{3+}$  ion solution of different concentrations. It can be seen that the acidity of the medium increases with the cation concentration ( $\text{Rh}^{3+}$ ). The decrease in the pH is due to the replacement of  $\text{H}^+$  ion on the carboxylic groups of the grafted layer of poly(acrylic acid) by the rhodium ions. The initial value of the pH decreases until it reaches a constant value after approximately 20 min.

The results suggest that the lower rate in the case of higher concentration is due to the release of layer amounts of HCl, which develops the following reversible reaction:<sup>13</sup>





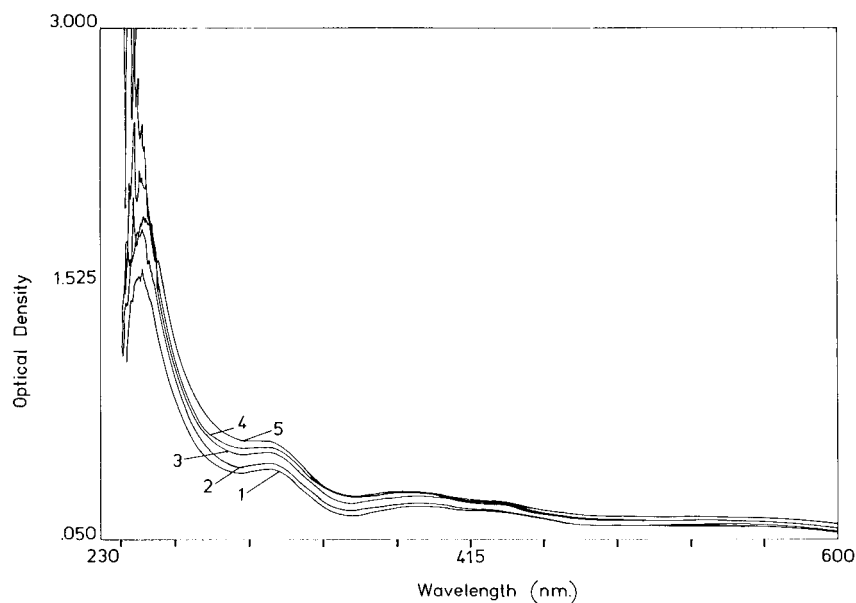
**Figure 1** Time-pH relationship of the PFA-g-PAAc films for various  $\text{Rh}^{3+}$  ion concentrations (wt %): (●) 0.005, (○) 0.01, (▼) 0.02, (▽) 0.05, and (■) 0.08.

where R is the grafted layer in the polymeric materials.

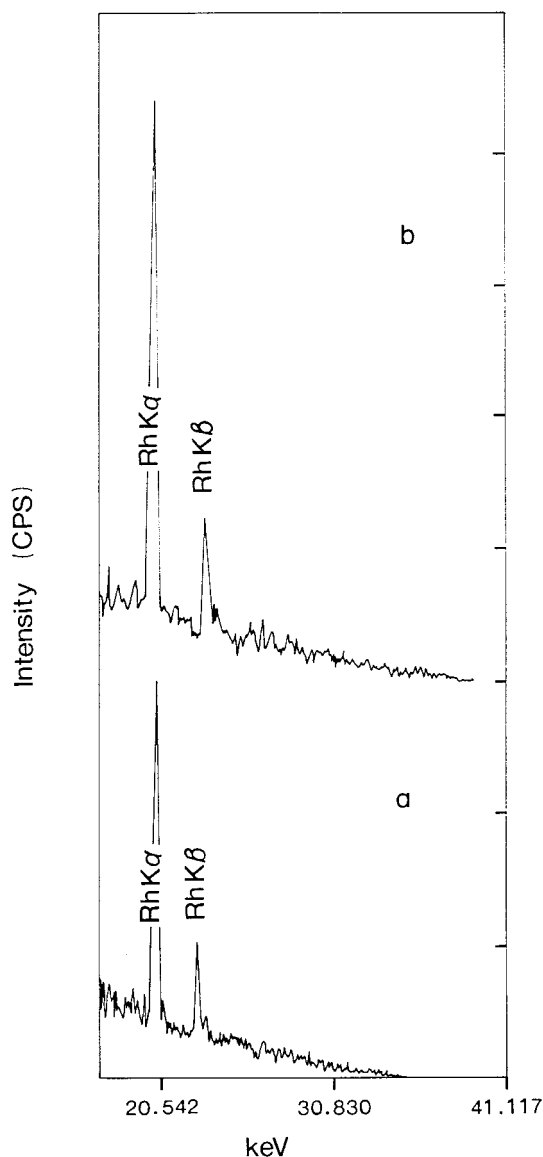
#### Optical Density Measurements

Figure 2 shows the variation in the optical density with wavelength (nm) for the graft copolymer-metal complex with  $\text{Rh}^{3+}$  ion, under various con-

centrations of  $\text{Rh}^{3+}$  ions. The band characteristic of the metal complex occurs at 313.5 nm (cf. Fig. 2). Meanwhile, the band characteristic of the carbonyl group of the polyacrylic acid shifts to 251 nm due to complexation of metal ions with polyacrylic acid graft chains. It has been found that the optical density of the color-transparent PFA-g-



**Figure 2** UV spectra of PFA-g-PAAc films treated with different  $\text{Rh}^{3+}$  ion concentrations (wt %): (1) 0.005, (2) 0.01, (3) 0.02, (4) 0.05, and (5) 0.08.



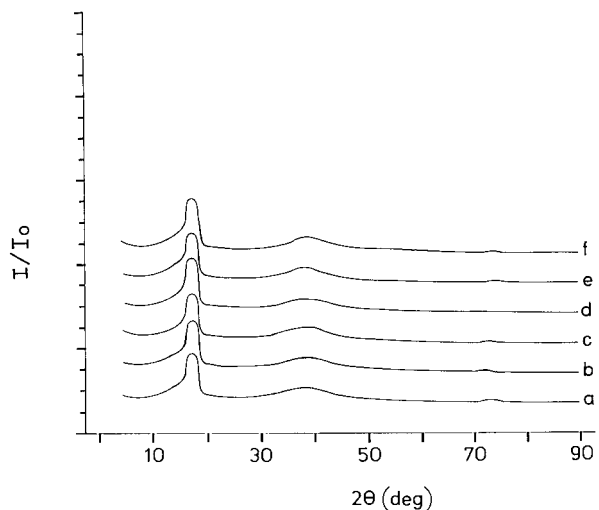
**Figure 3** X-ray fluorescence of grafted PFA copolymer treated with (a) 0.05 wt %  $\text{Rh}^{3+}$  solution and (b) 0.08 wt %  $\text{Rh}^{3+}$  solution.

PAAc metal complex of  $\text{Rh}^{3+}$  ions increases with an increase in the metal ion concentration in the grafted poly(acrylic acid) chains,<sup>4,5,9</sup> as shown in Figure 2.

#### Stability of Graft Copolymer- $\text{Rh}^{3+}$ Complexes

##### XRF Measurements

Figure 3 shows the intensity (cps) as a function of energy (keV) for PFA-*g*-PAAc-Rh complex films. It can be seen that the peaks of  $\text{Rh}^{3+}$  chelated in the grafted films appears at 20.21 keV for  $K_{\alpha}$  and 23.23 keV for  $K_{\beta}$ .

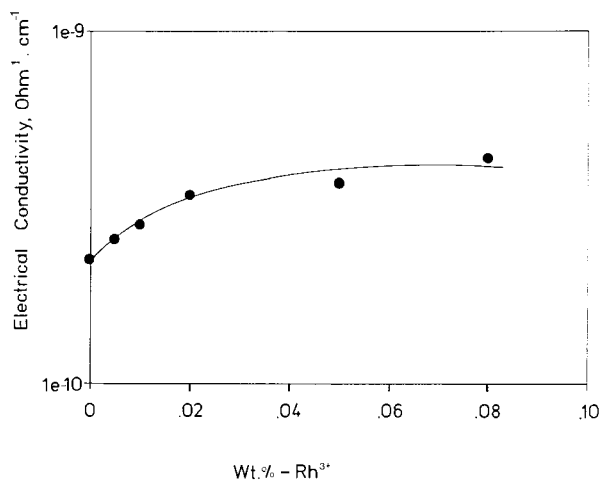


**Figure 4** X-ray diffraction patterns of grafted copolymers treated with various  $\text{Rh}^{3+}$  solutions (wt %): (a) 0.00, (b) 0.005, (c) 0.01, (d) 0.02, (e) 0.05, and (f) 0.08.

The results indicate that the higher the concentration of  $\text{Rh}^{3+}$  ion introduced to the grafted layer of films, the higher the intensity of the  $K_{\alpha}$  or  $K_{\beta}$  of  $\text{Rh}^{3+}$  ion acquired during the diffusion process of metal in the grafted chains.

##### XRD Investigation

XRD measurements were carried out on the grafted PFA and those treated with rhodium chloride solution. Figure 4 shows XRD diffractograms of grafted copolymer and their complexed one with various concentrations of  $\text{Rh}^{3+}$  ions. The results display a one-and-the-same diffraction pattern constituting a single peak at  $2\theta = 17.9^{\circ}$  ( $d = 4.96$



**Figure 5** Electrical conductivity of grafted films as a function of  $\text{Rh}^{3+}$  ion concentrations.

Å) for all of the tested materials. Thus, the complexed  $\text{Rh}^{3+}$  ions do not result in either formation of a crystalline structure<sup>5</sup> or a change to the trunk polymer structure.<sup>4,7</sup>

These results indicate that neither the trunk polymer nor the grafted one and nor graft copolymer metal complex has a strongly crystalline structure.

#### Electrical Conductivity Measurements

Figure 5 shows a semilogarithmic relationship between the electrical conductivity of the untreated and treated grafted copolymer metal complex as a function of  $\text{Rh}^{3+}$  ions concentration. It can be seen that, at first, the electrical conductivity increases with an increase of the concentration of metal ion up to 0.02 wt %, and it tends to almost level off. The grafted PFA copolymer metal complex of rhodium obtained at the highest metal concentration (0.02 wt %) possessed electrical conductivity in the range of  $10^{-10} \Omega^{-1} \text{cm}^{-1}$ , which may warrant its application in the field of semi-

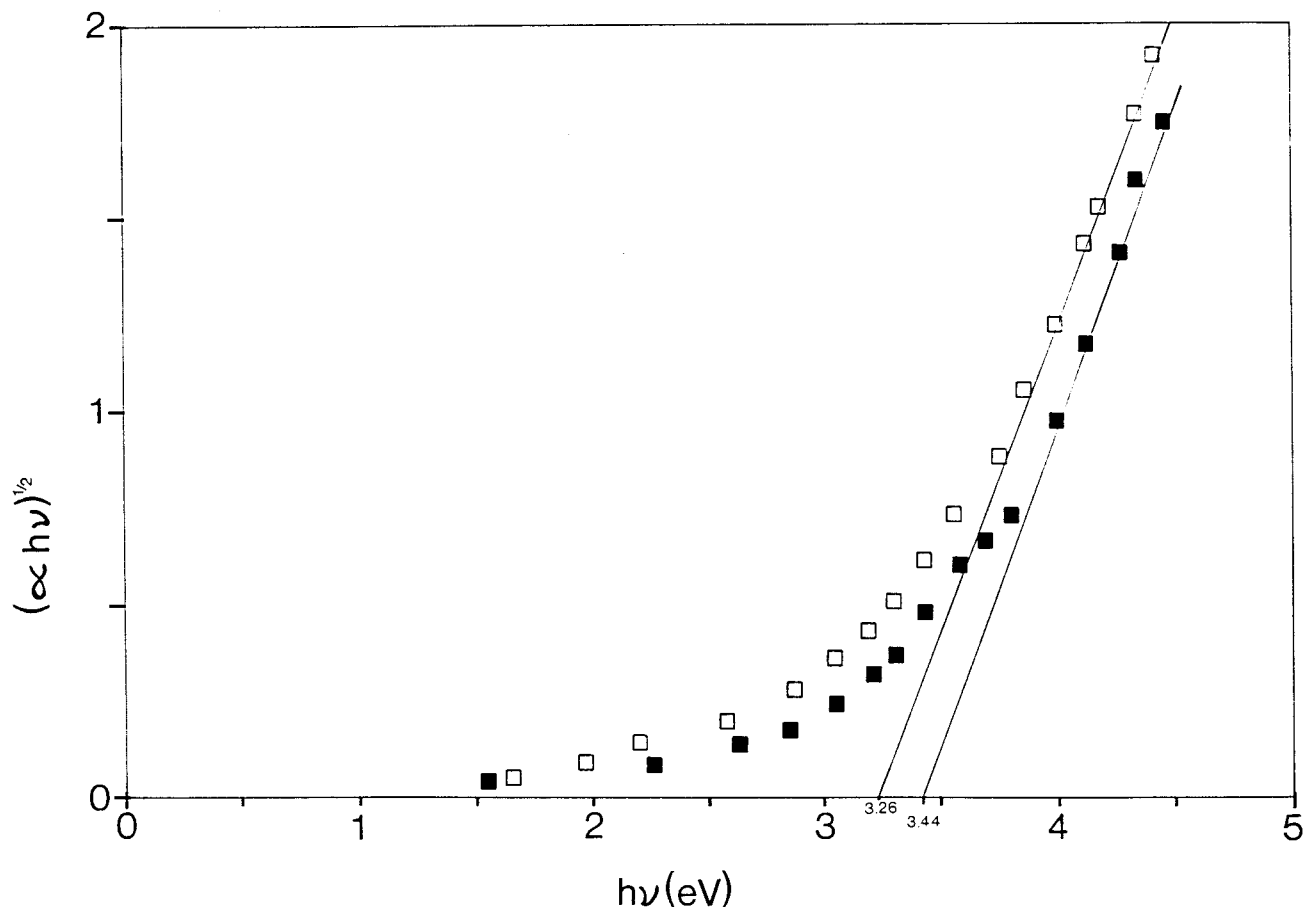
conducting materials.<sup>14</sup> Moreover, the electrical conductivity of polymeric substrates depends mainly on the presence of the high density of free ions with high mobility and the existence of low-molecular-mass impurities in the film.<sup>3,15</sup>

#### Optical Gap Measurements

The optical gap ( $E_o$ ) for the investigated films was determined from the Tauc formula, as follows<sup>16</sup>:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_o)$$

where  $\alpha$  is the absorption coefficient,  $h\nu$  is the energy, and  $A$  is a constant. By plotting  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  and then extrapolating the straight line to  $\alpha = 0$ , one gets the optical energy gap  $E_o$  for each  $\text{Rh}^{3+}$  ion concentration chelated to the grafted film, as shown in Figure 6. The value of  $E_o$  for different  $\text{Rh}^{3+}$  ion concentrations are listed in Table I. It can be seen that the value of the optical energy gap decreases slightly with an in-



**Figure 6** Variation of  $(\alpha h\nu)^{1/2}$  with  $h\nu$  for grafted PFA (■) blank and (□) treated with  $\text{Rh}^{3+}$  ions 0.005%, at 42% grafting.

**Table I Optical Conductivity for PFA-g-PAAc and its Grafted Copolymer of Rhodium Complex at 42% Grafting**

No.	Sample	RhCl <sub>3</sub> (%)	G (%)	Optical Energy Gap $E_o$ (eV)
1	PFA-g-PAAc	0.00	42	3.44
2	PFA-g-PAAc-Rh	0.005	42	3.26
3	PFA-g-PAAc-Rh	0.01	42	3.23
4	PFA-g-PAAc-Rh	0.02	42	3.21
5	PFA-g-PAAc-Rh	0.05	42	3.18
6	PFA-g-PAAc-Rh	0.08	42	3.12

crease in the rhodium concentration in the initial aqueous solution. The results are in good agreement with the general rule formulated by Yoffe and Regel.<sup>17</sup> The slight lowering of the optical gap could be rationalized through the effect of the Rh<sup>3+</sup> ion, which decreases the optical energy  $E_o$ , leading to an increase in the transportation of electrons to the conduction band and, consequently, to an increase in the conductivity of the films. It has also been shown that the electrical properties depend on the kind of metal ion included in the grafted copolymers.

#### Thermogravimetric

Table II illustrates the thermal stability of the original PFA, PFA-g-PAAc, and grafted copolymer films containing various concentrations of Rh<sup>3+</sup> ions. The data summarized in Table II indicates that the trunk polymer, PFA, is stable up to 300°C. The grafted PFA films brought about a marked decrease in the thermal stability of the films due to the faster rate of degradation of the grafted chains of poly(acrylic acid).<sup>9</sup> On the other hand, the introduction of Rh<sup>3+</sup> ions, through the grafted layer during the chelation process, may increase the rate of degradation of graft copolymer chains. This is in good agreement with the behavior of an analogous treatment of PVA with ZnCl<sub>2</sub>

**Table II Thermogravimetric Analysis of the Grafted Copolymer Complexed with Rh<sup>3+</sup> Ions at 42% Grafting**

Polymer	Rh <sup>3+</sup> (%)	Weight Loss (%)	
		200°C	300°C
PFA	0.00	0.00	0.00
PFA-g-PAAc	0.00	2.20	6.96
PFA-g-PAAc-Rh	0.005	2.15	7.50
PFA-g-PAAc-Rh	0.08	2.04	14.00

in which the metal helps in oxidative degradation of poly(vinyl alcohol).<sup>18</sup>

#### CONCLUSION

The extent of complexation of rhodium with the grafted copolymer film increases with the grafting yield. The detectable decrease in the pH of RhCl<sub>3</sub> solution during the reaction reflects the strong ligand–metal affinity. The XRD patterns for grafted copolymer with and without Rh<sup>3+</sup> ions show similar amorphous structures. Thus, the Rh<sup>3+</sup> bonding to the copolymer is specific and stable so that no separate Rh<sup>3+</sup> bulk phases were allowed to form. The strong ligand–metal grafted bonding can be further concluded from the observed metal-induced changes to the thermal, electrical, and optical properties of the copolymer. The treatment of grafted copolymer with metal leads to oxidative degradation of copolymer–metal complex with an elevating temperature above 200°C.

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