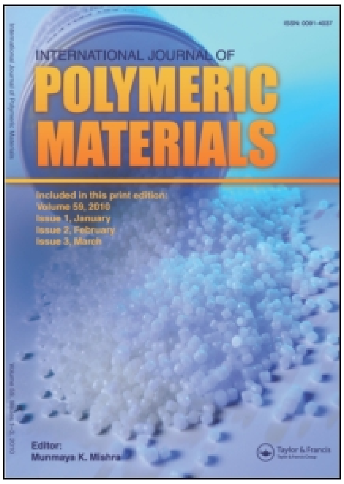

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Evolution of the Physical Properties of $FeCl_3$ Filled Polystyrene Films

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The present work investigates the effect of various filling levels (FLs) of $FeCl_3$ on the structure and physical properties of polystyrene (PS) films. X-ray diffraction scans revealed two main peaks, the amorphous and the polymerization peaks. The infrared transmission spectra depicted the main PS characterizing peaks. The direct current (dc) electrical conduction was attributed to the interpolaron charge carrier hopping. The temperature dependence of dc magnetic susceptibility exhibited Curie–Weiss behavior. The positive values of the paramagnetic Curie temperature (θ_p) indicate the predominance of a ferromagnetic exchange interaction between the magnetic centers at low temperatures, whereas the negative value of θ_p at 9% FL suggests the existence of an antiferromagnetic exchange interaction. The electron spin resonance (ESR) investigations imply the presence of isolated and aggregated Fe^{+3} ions at intermediate and higher FLs, respectively, in the polymeric matrix.

Keywords: $FeCl_3$ filled polystyrene, X-ray diffraction, infrared, electrical resistivity, magnetic susceptibility, electron spin resonance

INTRODUCTION

Since the polymerization of PS, which was achieved as early as 1839, a huge amount of research has been carried out on its physical properties and its blends [1–4]. Industrial PS is an amorphous atactic polymer not having a melting point. It has good stiffness, optical, and electrical properties; however, it has a weak point for chemical and heat resistance. PS is a perfect material in electronic technology due to its dielectric and mechanical properties and also its low cost [5]. Electronic

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packaging has continuously provided the impetus pushing for the development of new materials having a rich variety of applications. The addition of ceramic powder at low concentrations can improve the thermal properties of the polymer, whereas the adverse effects of the filler on the dielectric properties can be minimized. PS aluminum nitride composites of high thermal conductivity and low dielectric constant provide better device performance [6]. The thermal relaxation of PS close to the glass transition was discussed [7]. X-ray diffraction (XRD) studies of most amorphous polymers indicate that there is a diffraction ring at $2\theta = 19.5^\circ$ and another diffraction band with a position dependent on the size of the side groups [8]. The infrared (IR) and Raman spectra of commercial type of PS are atactic and completely amorphous [9].

A great deal of work has recently been undertaken to understand the nature of the electrical conduction and charge carriers in PS [10–13]. The conduction mechanism of $MnCl_2$ filled PS films was interpreted on the bases of interpolaron hopping model [10]. The dc electrical conductivity of pure and Fe^{+3} doped PS films has been studied at various bias field strengths [11]. The dc electrical resistivity of PS composites films containing various fractions of $NiCl_2$ and $CoCl_2$ were clarified [12].

Addition of magnetic activity to PS seems to open up vast areas of application. The magnetic susceptibility of PS composites filled with various mass fractions of Fe was discussed [13]. Moreover, PS composites containing nickel and cobalt metallic powdered were also reported [14]. An s-d type magnetic interaction was suggested between the magnetic soliton of PS and the magnetic filler in the region near the metal polymer interface [13–14].

Generally, the metal ion doped polymer represents a new class of organic materials that has high potential technological applications, Very recently, a great importance has been attached to polymer doped with rare earth and transition metal ions because of the interesting spectroscopic properties of their $4f^N$ and $3d^N$ electrons. Modifications in the physical properties of the polymer doped with transition metals of partially filled d-electron shells can be expected.

The present work is devoted to investigating the evolution of the structural, electrical, and magnetic properties of PS films filled with $FeCl_3$.

EXPERIMENTAL WORK

Sample Preparation

PS in the form of pellets of molecular weight 100,000 was obtained from the Aldrich chemical company. Metal compound $FeCl_3$ was provided in solid state. The used solvents were cyclohexanone and acetonitrile. The studied PS films filled with $FeCl_3$ were prepared by casting methods. Cyclohexanone was used to dissolve the polymer. The transition metal compound $FeCl_3$ was dissolved in acetonitrile. The polymer and the transition metal compound were cast in glass dishes and kept in a dry atmosphere at $T = 323\,K$ for one week to remove the solvent traces. Different concentrations of the filler were obtained where $W = 0.0, 0.1, 0.5, 1.0, 2.5, 5, 7.5, 9.0, 9.5, 9.9$, and 10.0 weight percent. The thickness of the films was in the range of 150 to 250 μm.

Tools of Analysis

XRD scans were carried out using a Siemens type F diffractometer with Cu Kα radiation and LiF monochromator. An IR spectrophotometer (Perkin Elmer 883) was used for measuring the IR spectra of the different films at room temperature in the wavenumber range 4000–600 cm^{-1}. Here we shall present the IR spectra in the range 2000–600 cm^{-1}, in which the main characterizing spectral features were found. The electrical resistivity was measured by standard technique using insulation tester (type TM 14) and autoranging multimeter (Keithley 175 A) of accuracy ±0.2% [15]. The dc magnetic susceptibility was measured, in the temperature range of 90 to 280 K, using a Faraday pendulum balance [16]. The accuracy of the measurements was better than ±3.5%. ESR spectra were recorded on a JOEL spectro-photometer (Type JES - FE2XG) at frequency 9.45 GHz using 1,1-diphenyl 2-pieryhydrazyl (DPPH) as calibrant.

RESULTS AND DISCUSSION

X-ray Diffraction

Figure 1 depicts the XRD scans for PS films filled with various mass fractions of $FeCl_3$. The observed spectrum characterizing the virgin sample showed two main peaks at $2\theta \approx 19.5^\circ$ and 10°. The first peak, which is the most intense one, is the amorphous peak and it corresponds to the average Van der Waals distances [17–19]. Most workers believe that the chains in amorphous linear polymers are approximately parallel to one another leading to a value of d (distance between neighbors) of about 4.5–5.0 Å [17]. This value characterizes the mean distance between non-bonded atoms. The second peak at $2\theta \approx 10^\circ$ is the larger distance, polymerization peak that may be attributed to the intermolecular backbone-backbone correlation and also may be dependent on the size of the side group that corresponds to an approximately hexagonal ordering of the molecular chains [19].

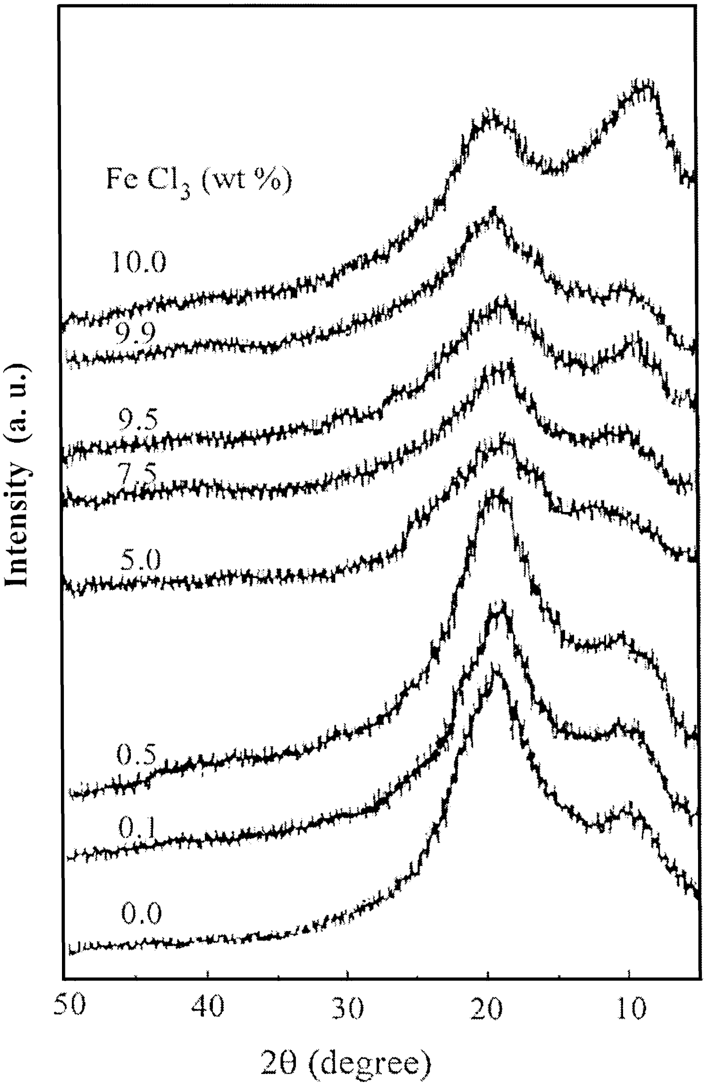

FIGURE 1 XRD scans of PS filled with various mass fractions of $FeCl_3$.

IR Spectroscopy

The IR transmission spectra for polystyrene $-(CH_2)-(CH\ (C_6H_5))-$ are shown in Figure 2. The main PS characterizing peaks are observed. The aromatic ring (C_6H_5) gives a rise to the group of bands above 3010 cm^{-1} (i.e., 3030 cm^{-1}), which is not shown here. Aromatics

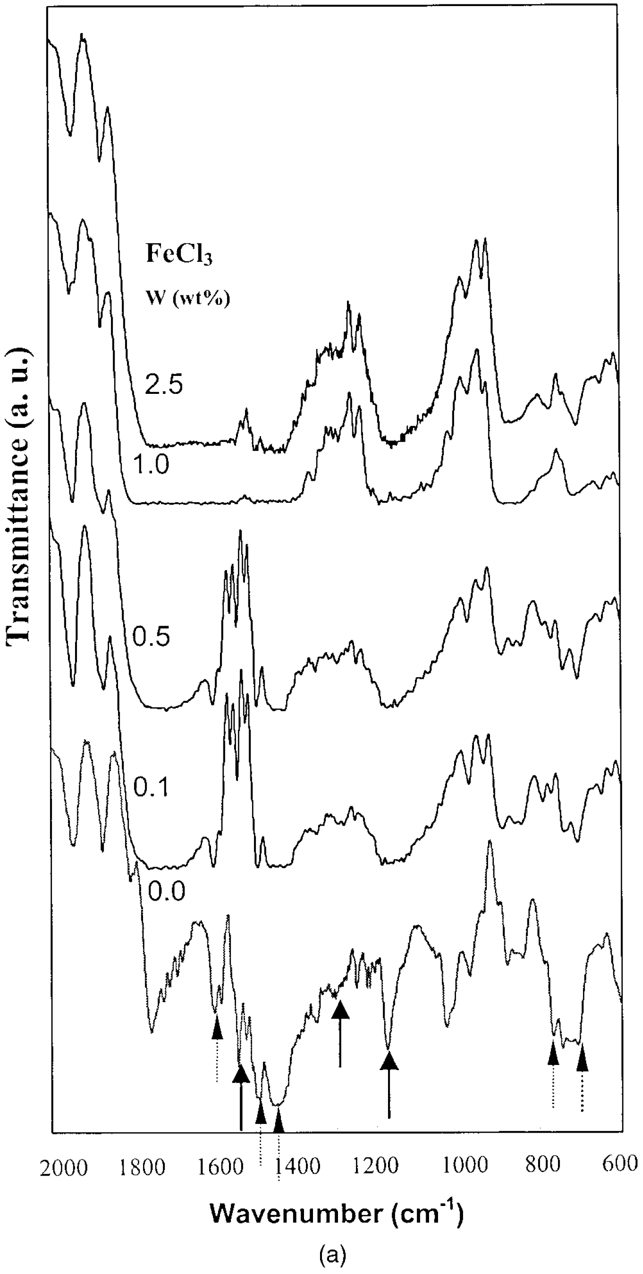

FIGURE 2 IR transmission spectra of PS filled with various mass fractions of $FeCl_3$.

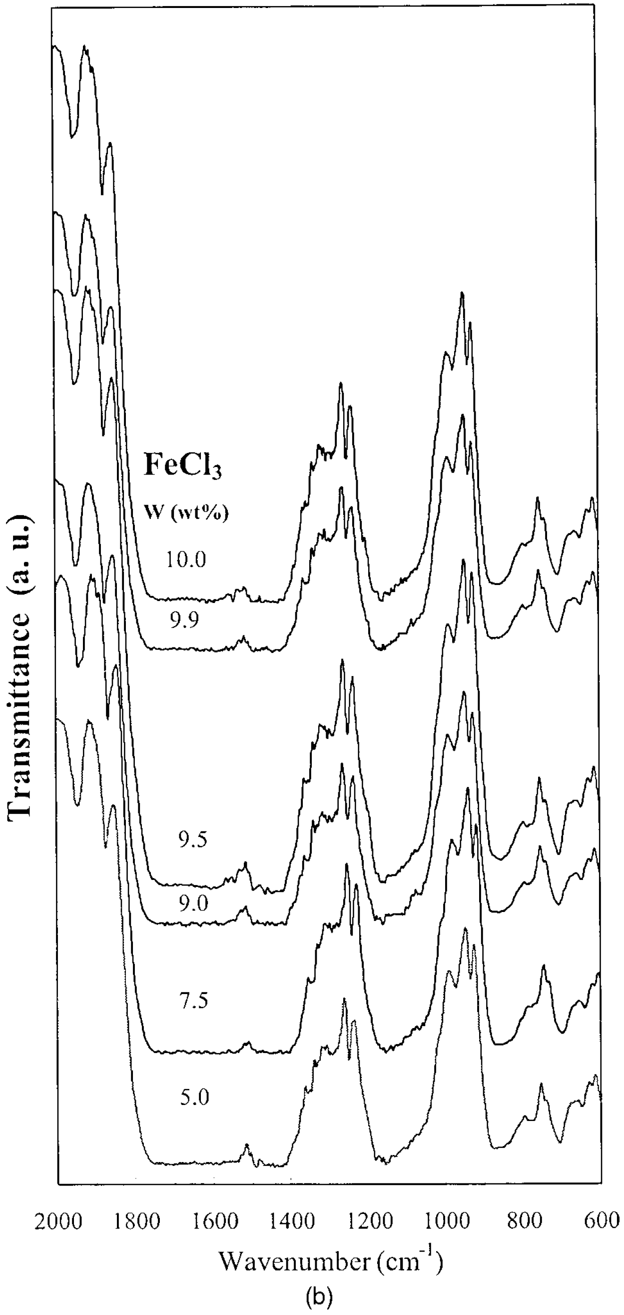

FIGURE 2 Continued.

display a distinctive double bond C=C stretching at about 1600 cm^{-1} [20], which in combination with unsaturated C−H stretching above 3000 cm^{-1} identify polymers containing aromatics. The C−C stretching mode of phenyl rings at 1480 cm^{-1} and the C−H out of plane deformation modes of monosubstituted phenyl rings at 765 and 695 cm^{-1} are noticed [20–21]. The IR transmission decreases with increasing doping content in the whole frequency range studied. This could be due to free or weekly bound charge carriers [21]. The peaks at 1530, 1275, and 1180 cm^{-1} (solid arrows) are interesting because Shacklette et al. [22–23] found dopant-induced peaks at exactly the same wavenumbers in AsF_5-doped polyparaphenylene (PPP). These peaks were also found in doped polyacetylene (PA) [24] and $FeCl_3$-doped PPP [21]. However, Kuivalainen et al. [21] and Fincher et al. [24] stated that these modes of vibrations are not due to specific vibration of the dopant molecules but are intrinsic vibrations of the polymer chain. According to Kuivalainen et al. [21], the mode at 1275 cm^{-1}, which also appears at 1298 cm^{-1} according to Racovics et al. [25], is related to the deformations of the benzene ring structure that is typical of the polaron and bipolaron defect states [26–27].

DC Electrical Conduction

The dc electrical resistivity (ρ) was measured in the temperature range 293 to 390 K for PS filled with $FeCl_3$. The double bond C=C and the deformation in the benzene ring detected by the IR analysis, may evidence the formation of polarons and/or bipolarons in the polymeric matrix. Therefore, the present results can be discussed on the basis of the Kuivalainen et al. [21] modified interpolaron hopping model, in which the conduction is attributed to a phonon-assisted charge carrier hopping between polaron and/or bipolaron bound states in the polymer, According to this model the electrical resistivity can be expressed as

$$\rho = [\mathrm{kT}/\mathrm{A_1 e^2}\gamma(\mathrm{T})(\mathrm{R_0}^2/\zeta)] \cdot [(\mathrm{Y_p} + \mathrm{Y_{bp}})^2/\mathrm{Y_p Y_{bp}}] \exp(2\mathrm{B_1 R_0}/\zeta) \qquad (1)$$

where $A_1 = 0.45$, $B_1 = 1.39$, Y_p and Y_{bp} are the concentration of polarons and bipolarons, respectively; $R_0 = (3/4\pi\ C_{imp})^{1/3}$ is the typical separation between impurities whose concentration is C_{imp}, $\zeta = (\zeta_{\parallel}\zeta_{\perp}^2)^{1/3}$ is the average decay length of a polaron and bipolaron wave function, $\zeta_{\parallel}$ and $\zeta_{\perp}$ are the decay lengths parallel and perpendicular to the polymer chain, respectively. The electronic transition rate between polaron and bipolaron states can be expressed as

$$\gamma(\mathrm{T}) = \gamma_0(\mathrm{T}/300\,\mathrm{K})^{n+1} \qquad (2)$$

where n is a constant ~10, and the prefactor, $\gamma_0 = 1.2 \times 10^{17}\ \mathrm{s}^{-1}$, was estimated by Kivelson [28]. Using a computer-aided program, the order of magnitude of ρ in the present work was adjusted with the impurity concentration C_{imp}, which actually was the fitting parameter. The parameters $\zeta_{\|} = 1.06\,\mathrm{nm}$ and $\zeta_{\perp} = 0.22\,\mathrm{nm}$ [29], depend on the interchain resonance energy and the interchain distance. Taking $Y_p = Y_{bp}$ for simplicity, which is an acceptable approximation [30], and using Eqs. 1 and 2, the values of the hopping distance R_0 can be obtained. Figure 3 reveals a linear temperature dependence to R_0 for various FLs, indicating that the conduction mechanism is dominated by interpolaron hopping model [21]. The FL dependence of $\log\rho$ measured (and R_0 calculated) at 348 K are shown in Figure 4. Minimum values of $\log\rho$ (and R_0) are observed at 1 and 9% FLs, whereas maxima are observed at 0.1, 5, and 9.9% FLs. This indicates that the FL affects the distribution of the hopping sites.

DC Magnetic Susceptibility

The dc magnetic susceptibility (χ) of PS films filled with various mass fractions of $FeCl_3$ was measured in the temperature range 90–280 K. The temperature dependence of the reciprocal of magnetic susceptibility is plotted in Figure 5. These plots are linear and obey Curie-Weiss law

$$\chi = C/(T - \theta_p) \tag{3}$$

where C is Curie constant and θ_p is the paramagnetic Curie temperature. The values of θ_p for various FLs were calculated from Eq. 3, and were plotted in Figure 6. The observed positive values of θ_p indicate the predominance of a ferromagnetic exchange interaction between the magnetic centers at low temperatures. On the other hand, a negative value of θ_p noticed at W = 9%, suggests the presence of an antiferromagnetic exchange interaction between the magnetic centers at low temperatures. A critical FL (W = 9%) was found at which θ_p changed its sign. The obtained Curie–Weiss behavior implies that the energy band diagram of the present filled PS system is characterized by magnetic localized energy states [31]. Moreover, the effective paramagnetic moment (μ_{eff}) was calculated at T = 100 K, using Eq. 4:

$$\mu_{\mathrm{eff}} = 2.828[\chi_m(T - \theta_p)]^{1/2} \tag{4}$$

where χ_m is the molar susceptibility of the filled polymer. The obtained values of μ_{eff} were plotted as a function of the FL in Figure 7.

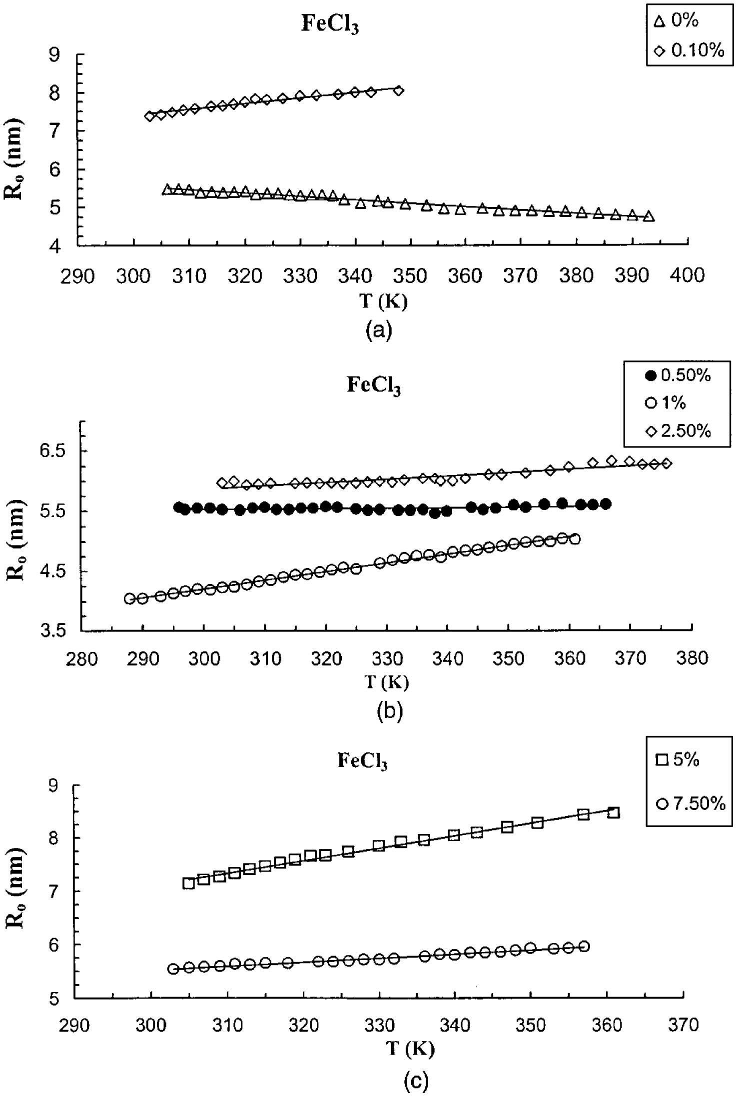

FIGURE 3 The temperature dependence of R_0 for variously filled PS.

The significant values of μ_{eff} indicate that the present filler generally increases the magnetic response of PS. The non-monotonic behavior of the FL dependence of μ_{eff} clarifies that the present system does not obey the magnetic dilution mechanism [13,31]. The decrease in the μ_{eff} at light doping content (i.e., at 0.1 and 0.5% FL) may be due to the

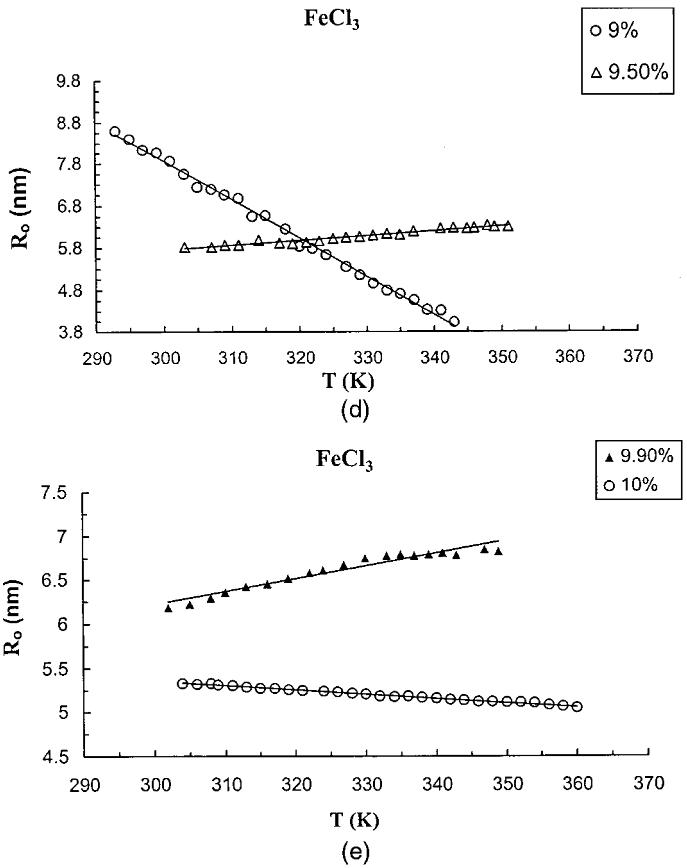

FIGURE 3 Continued.

formation of spinless bipolarons [21,32]. It is remarkable that the order of magnitude of μ_{eff} confirms the trivalent state of Fe^{+3}. From the electrical conduction studies, it is clear that the minimum value of both log ρ and R_0 at 9% FL can be correlated with the negative value of θ_p noticed at the same FL.

Electron Spin Resonance Measurements

The ESR spectra, measured at room temperature, for PS films filled with various mass fractions of $FeCl_3$ are depicted in Figure 8. Pure PS has an unresolved complicated spectral line due to the hyperfine interaction. For an intermediate concentration of $FeCl_3$ and at 5%

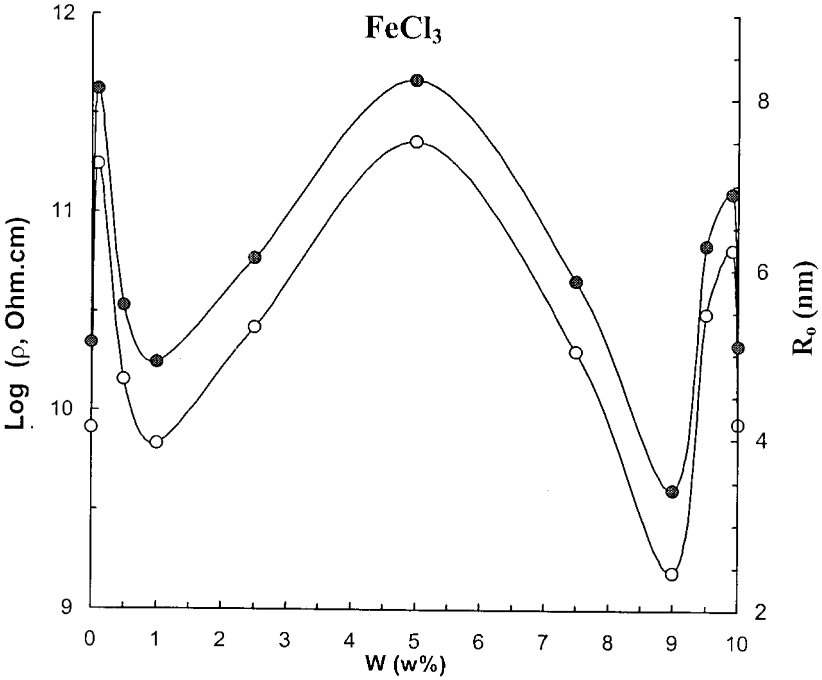

FIGURE 4 The FL dependence of (○) Log ρ and (●) R_0 at 348 K.

FL, the spectrum possesses unresolved five lines in the higher part of the magnetic field (3600–4600 gauss), which can be attributed to the fine structure suggesting the presence of isolated Fe^{+3} ions. The dipolar spin–spin coupling, the spin orbit coupling, and the internal electric field within Fe^{+3} clusters can explain this fine structure. The net result of the aforementioned three energy perturbations can be considered as zero field splitting because they produce an energy level shift in the absence of an external field. Generally, if there are n parallel spins, there will be n equally spaced resonances in the ESR spectrum [33].

Briefly, the unresolved five lines in the ESR spectrum at the higher part of the magnetic field can be attributed to the fine structure of Fe^{+3} ions, which have the electronic configuration $3d^5$ of five parallel spins. However, there is no common Fe isotope with nuclear spin $I \neq 0$, so there could be no hyperfine splitting due to the filler [34]. With increasing concentration of Fe^{+3} and at 7.5% FL, the unresolved five lines became vague. At 9.5% FL, a broad and deformed

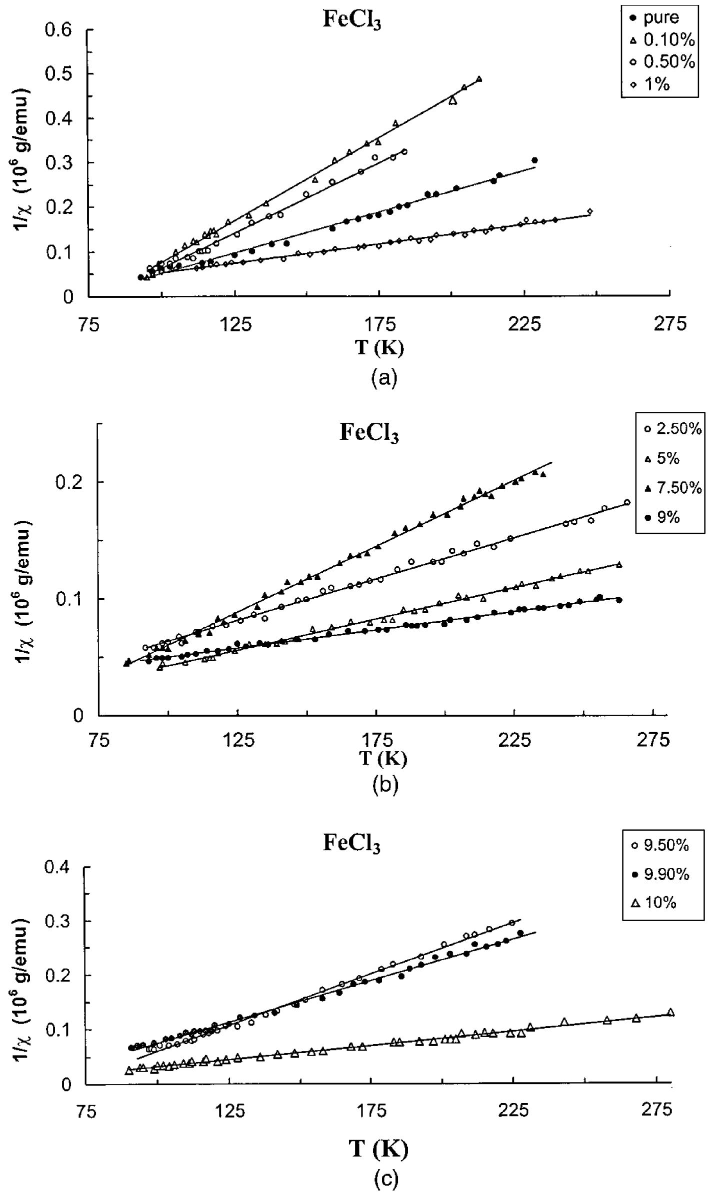

FIGURE 5 The temperature dependence of the reciprocal magnetic susceptibility for variously filled PS.

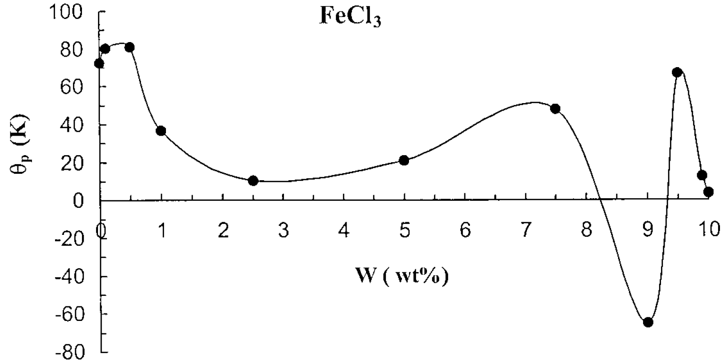

FIGURE 6 The FL dependence of θ_p.

signal was noticed where the individual lines characterizing the whole proceeding spectrum have almost disappeared. This suggests the absence of isolated Fe^{+3} and the presence of $Fe^{+3} - Fe^{+3}$ exchange interaction leading to the existence of aggregated Fe^{+3} [10,35–36]. At higher FLs, 9.9 and 10%, the spectra take the shape of incomplete deformed signal confirming the aggregated forms of Fe^{+3} due to proximity of iron ions and the absence of isolated Fe^{+3}. Consequently, the ESR investigations imply the formation of Fe^{+3} clusters in the polymeric matrix. The FL dependence of g factor of the ESR signal

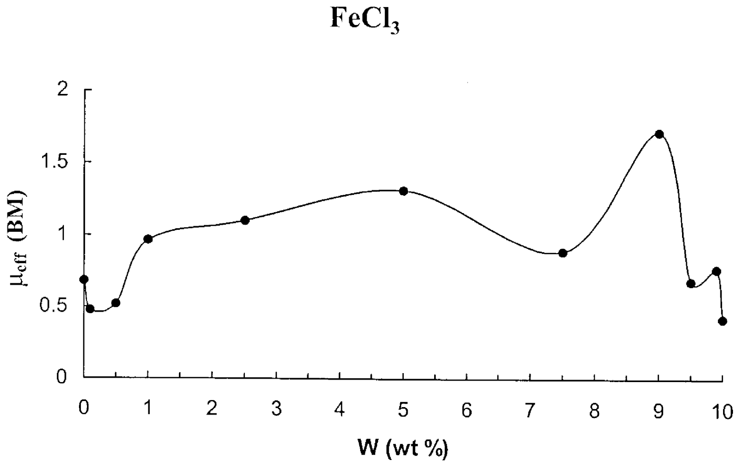

FIGURE 7 The FL dependence of μ_{eff} at 100 K.

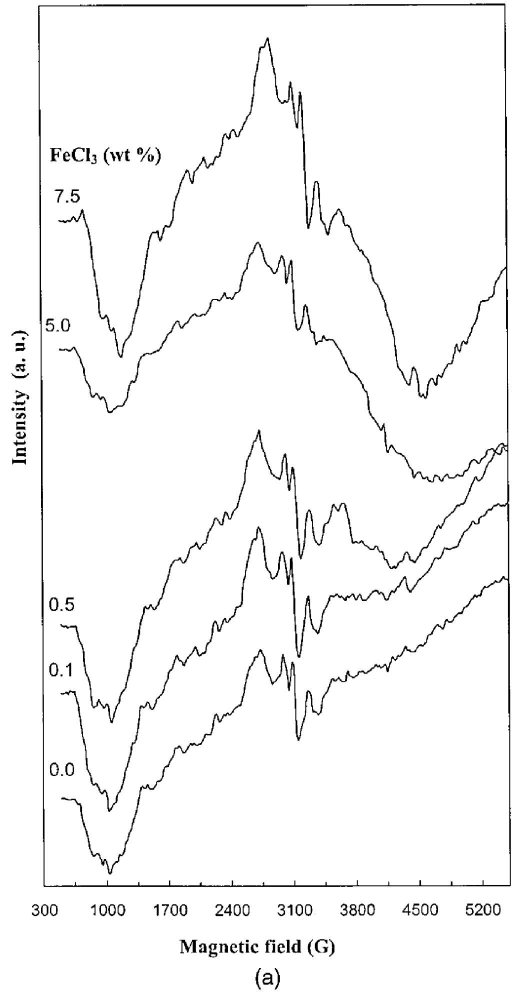

FIGURE 8 The ESR spectra of PS filled with various mass fractions of $FeCl_3$.

is depicted in Figure 9. This dependence has a behavior that generally agrees with the FL dependence of μ_{eff} shown in Figure 7. The landé g factor in this study has values that differ from the g factor for a free electron of 2.0023. In some cases considerably different g factors values between about 0.2 and 8 have reported [33]. This can be attributed to one of the following two important points: (a) The internal crystal field of the sample is weak or (b) the paramagnetic electron is well shielded from the field. In this case the orbital

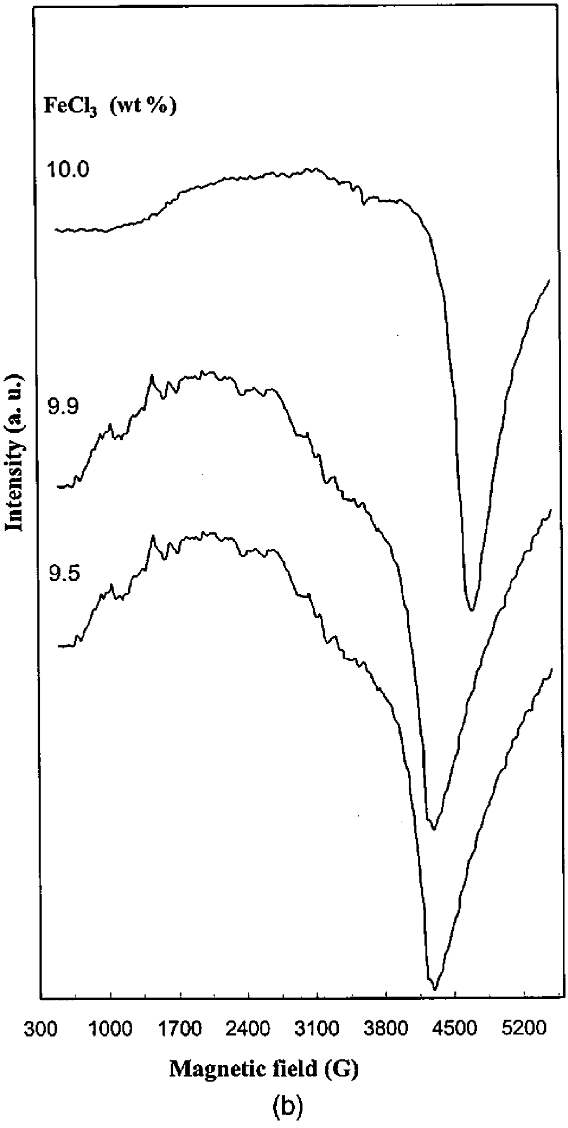

FIGURE 8 Continued.

angular momentum (L) and the spin angular momentum (S) couple to produce a resultant (J), which itself precesses about the applied magnetic field, giving rise to g values, which differ from that of a free electron and are not easily predictable theoretically [33].

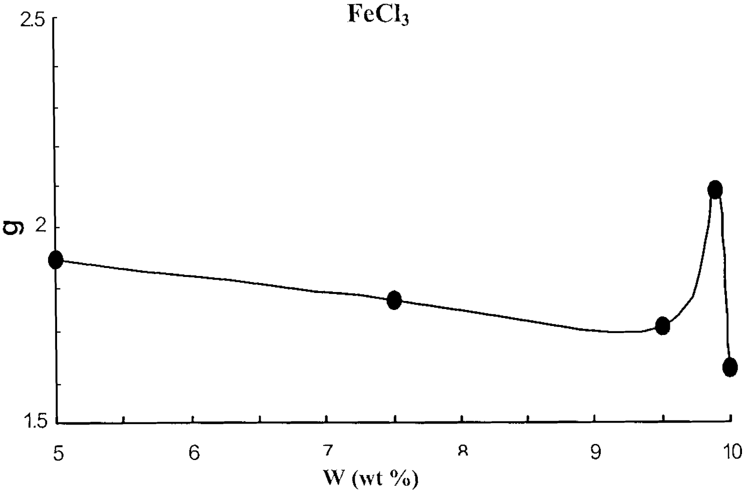

FIGURE 9 The FL dependence of the g values.

CONCLUSION

The XRD studies revealed two main characteristic peaks, the amorphous peak at 2θ ≈ 19.5° and the polymerization peak at ≈10°. The main PS characterizing peaks were confirmed by IR transmission spectra. Aromatic C=C stretching at $\approx 1600\,\text{cm}^{-1}$ and the peaks at 1530, 1275, and $1180\,\text{cm}^{-1}$ can be considered as an evidence of the existence of polaron and/or bipolaron defect states. The dc electrical conduction measurements were explored using a modified interpolaron hopping model. A linear temperature dependence of the hopping distance R_0 for various FLs was noticed. The FL dependence of log ρ and R_0 indicated that the $FeCl_3$ filler affected the distribution of the hopping sites. The temperature dependence of the reciprocal magnetic susceptibility implied that χ obeys Curie–Weiss law. The present filled PS system was characterized by magnetic localized energy states. The positive values of the paramagnetic Curie temperature θ_p indicate the predominance of a ferromagnetic exchange interaction between the magnetic centers at low temperatures, whereas the negative value of θ_p at $W = 9\%$ suggests the existence of an antiferromagnetic exchange interaction. The ESR spectra of intermediate FLs of $FeCl_3$ possess unresolved five lines, which are attributed to the fine structure indicating the presence isolated Fe^{+3}. The disappearance of these lines at higher FLS suggests the presence of aggregated Fe^{+3} and the absence of isolated Fe^{+3} implying the formation of Fe^{+3} clusters in the polymeric matrix.

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