Effect of Doping Polyacrylic Acid with Some Dopants as Studied by Different Techniques

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ABSTRACT: The molecular weight of polyacrylic acid (PAA) was determined by a viscometric method using $NaNO_3$ as solvent at 30°C. The specific electric conductivities (σ) of PAA as well as PAA doped with carbon black (CB), chromium oxide (Cr_2O_3), and cupferron with different concentrations (from 0.25 to 1 wt %) were measured at a temperature range 360–400 K. IR spectra of some polymers were determined and it was shown that when PAA was doped with 0.5 wt % CB, a C—O—C band appeared at 775–875 cm^{-1}. The positron annihilation lifetime (PAL) spectra in PAA doped with the above-mentioned dopants were measured as a function of their concentrations. It was observed that the short lifetime intensity I_1 decreased, whereas the intermediate lifetime intensity I_2, which is related to the conductivity of the material, increased with increasing the wt % of Cr_2O_3 and cupferron as well as at low concentrations of CB. These results are discussed in terms of the conducting island model. It was found that there were distinct positive relationships between σ and I_2. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 877–883, 2002; DOI 10.1002/app.10381

Key words: dopant; polyacrylic acid; positron annihilation lifetime spectroscopy; specific electric conductivity; conducting island model

INTRODUCTION

Besides their traditional use as insulators, many organic polymers have been found to possess semiconducting properties.[1] Even some polymers such as polyacetylene doped with AsF_5[2] or halogen-doped polyacetylene[3] were found to have conducting properties. Unworth et al.[4] mentioned that there are over 100 conducting polymers that have been synthesized by chemists, with a wide range of specific electrical conductivity. Many of these polymers are suitable for electronic device fabrication. Misra and Chandra[5] investigated the electric conductivity of polypyrrole and polyaniline (PAn).

The electrical properties of PAA polymer films (thickness 18.8 mm) grown by the solution growth technique have been studied.[6] The results show that the Pool–Frenkel mechanism is predominant at high temperatures, whereas the hopping mechanism may be predominant at low temperatures. Large-area (~ 0.3–1 cm^2) Schottky diodes,[7] with PAA-doped PAn and undoped PAn as P-type semiconductors sandwiched between aluminum and indium–tin oxide prepared by casting technique, exhibit a moderate rectifying behavior and low leakage current. The behavior of corrosion inhibition of iron by different polymers such as PAA was studied.[8] Hu et al.[9] reported that conducting PAn–PAA films were used as blend coat-

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ings. The conductivity of the samples is increased by two or three orders of magnitude and their thermal stability is also improved. The conduction mechanism in the interpolymer complex, resulting from the interactions between PAA and polyacrylamide, was investigated.[10] PAA divinylbenzene was doped with ferric chloride in nonaqueous medium and the effect of concentration of the dopant salt on the electrical conductivity of PAA divinylbenzene was investigated.[11]

In recent years, positron annihilation lifetime spectroscopy (PALS) has emerged as a unique tool to probe the microstructural changes in polymeric materials. By using this tool, many studies indicate that the macroscopic properties of conducting polymers are related to the positron annihilation characters. Wang and Yang[12] studied two kinds of nonmetallic conductors, fast ionic and organic, using positron annihilation. They combined their results with the measurement of the line-shape parameter, which indicated that in the fast ionic conductor the voids between microcrystals and network phases provide more transfer paths for carriers, thus leading to improved conductivity. In the organic conductor, however, the good conductivity was largely attributed to dislocated π-electrons with low momentum and to the dislocated electrons, leading to a partially occupied valence band. Peng et al.[13] measured the positron lifetime spectra in PAn as a function of their protonation level. Their results were discussed in terms of a conducting island model. Wang et al.[14] studied the effect of Li doping and γ-irradiation on the microstructure in the network of polyetherurethane (PEU) by positron annihilation lifetime spectra. It was shown that the *ortho*-positronium (*o*-Ps) lifetime and its intensity decreased with increasing the concentration of Li dopants, but the lifetime and intensity of the second component are nearly independent of the concentration of Li dopants. Wang et al.[15] studied two kinds of conducting polymers, polymeric electrolyte PEU–$LiClO_4$ and electronically conductive PAn by positron annihilation. They discussed the structure transition, doping effect, and the correlation between positron annihilation parameters and conductivity. They found that the variation of the positron annihilation parameters is sensitive to protonation level and consistent with the metal–granule island model. The electrical conductivity (at room temperature) of high-density polyethylene–carbon black (HDPE–CB) switching composites as a function of the conductivity filler (CB) content was studied by Patnaik et al.[16] using PALS. The CB imparted high conductivity to its composites, starting at a low level of loading.

In this work, polyacrylic acid was prepared and doped with different concentrations of carbon black, chromium oxide, and cupferron (0.25, 0.5, 0.75, and 1 wt %) to increase its specific electric conductivity. The lowest σ of the polymer obtained was $10^{-11}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, whereas that of the undoped polymer was $10^{-16}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. The relation between log σ and $1/T$ was found to be linear. This was typical of the relation of semiconductors. Also, we used PALS to study the effect of dopants on the microstructure of polymers, and tried to establish a correlation between the conductivity and lifetime parameters.

EXPERIMENTAL

Polymerization of Acrylic Acid

Acrylic acid (68.6 mL) was poured into a round-bottom flask. Benzoyl peroxide (1 g) and chloroform (100 mL) were added and heated at 70°C for 0.5 h. Part of the solution was poured in a petri dish to form a thin film of the polymer (thickness, 1 mm) without any additive. Samples of the polymer with different dopants (0.25, 0.5, 0.75, and 1 wt %) of CB, Cr_2O_3, and cupferron were made using the other part of the solution.

Measurement of Molecular Weight of PAA

The number-average molecular weight $\overline{M}_n$ of PAA was found to be 720 from viscosity measurement, using a solution of $NaNO_3$ as solvent at 30°C and Ubbelohde[17] viscometer. The relation for $\overline{M}_n$ for PAA is:

$$[\eta] = 6.8 \times 10^{-4}[M_n]^{0.66} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity.

Measurement of Specific Electric Conductivity

The specific electrical conductivity (σ) of thin films of the polymers was measured by the method mentioned by Eley and Parfitt.[18,19] The thin film (diameter, 1 cm; thickness, 1 mm) was tightly adjusted between the plates of two copper electrodes of an electric cell. The cell was put in an electric furnace that was connected to a thermocouple for measuring the temperature. The electric cell was also connected to a 12-V battery and an electrometer, forming an electric circuit. σ

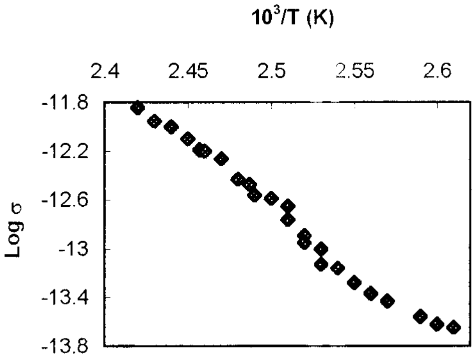

Figure 1 Plot of log σ versus $10^3/T$ for PAA.

was measured either directly by the electrometer or from the measurements of the voltage and the electric current passing through the cell. Accordingly, the relation between σ of the used polymer can be determined at different temperatures.

Measurements of Positron Annihilation Lifetime Spectroscopy

The PAL measurements were performed for PAA and with dopants of CB, Cr_2O_3, and cupferron by detecting the prompt γ-ray (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from the ^{22}Na radioisotope and the annihilation γ-rays (0.511 MeV). All PAL spectra were recorded in air at room temperature ($\sim$ 25°C) using a fast–fast coincidence system with a lifetime resolution 230 ps. A 20-μCi ^{22}Na positron source was deposited on Kapton foil, then sandwiched between two similar pieces of the sample. Each spectrum contained one million counts. All of the PAL spectra obtained were analyzed by finite-term lifetime analysis using the PATFIT program.[20] It was found that three lifetime components gave the reasonable standard deviations and the best χ^2 (1.1). The shortest lifetime τ_1 of 0.125 ns is the lifetime of *para*-positronium (*p*-Ps) constraint; the intermediate lifetime τ_2 of 0.3–0.4 ns is the lifetime of free positron; and the longest lifetime τ_3 of 2–4 ns is attributed to the *o*-Ps annihilation.

RESULTS AND DISCUSSION

Specific Electric Conductivity Results

The specific electric conductivity of plain PAA having a high molecular weight was found to be on the order of 10^{-16} Ω^{-1} cm^{-1} at room temperature. However, when PAA was doped with 0.25 wt % CB, it was found that σ rises to 10^{-12} Ω^{-1} cm^{-1} at a temperature of 120°C. Figures 1 and 2 show a relation between log σ and $10^3/T$ for the insulating PAA and when it was doped with different concentrations of CB at temperature range 360–400 K, respectively. It was found that, when the concentration of CB was increased to 1 wt %, σ increased to 10^{-11} Ω^{-1} cm^{-1} at 116°C. The CB aggregates introduced an additional physical and chemical crosslinking to the matrix (serving as obstacles against the segmental motion); thus, the mobility of the polymer molecules diminishes. The dielectric loss increase with increasing the volume fraction of CB corresponds to the increase in the conductivity of the composites. These relations are almost linear, as is typical of the relation to semiconductors.[21] The relation between the voltage V (in volts) and the electric current I (n amperes) was also linear, that is, it is an ohmic relation showing that the electron transfer from the valance band to the conduction band was smooth, like that which occurs in metals. Figure 3 is an example showing a linear relation between I and V for PAA doped with 0.5 wt % CB at T = 121°C. Nearly the same results were obtained in the case when PAA was doped with Cr_2O_3 (Fig. 4) because Cr_2O_3 may form chelated compounds with the polymer, which act as electron donors, and increase σ to 10^{-10} Ω^{-1} cm^{-1}.

In the case of PAA doped with cupferron, σ was found to be in the range 10^{-11}–10^{-9} Ω^{-1} cm^{-1}. Also, log σ versus $10^3/T$ was linear (Fig. 5), which indicated that PAA doped with cupferron is a semiconductor. Most probably, cupferron forms a complex with PAA through the OH group of the

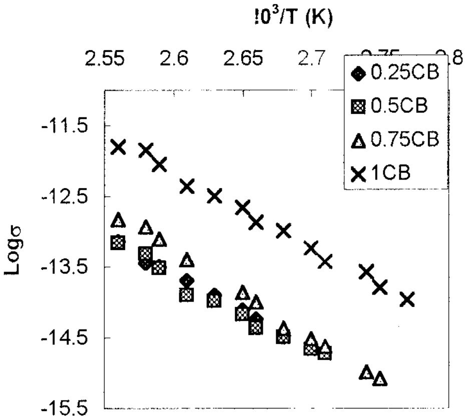

Figure 2 Plot of log σ versus $10^3/T$ for PAA doped with carbon black.

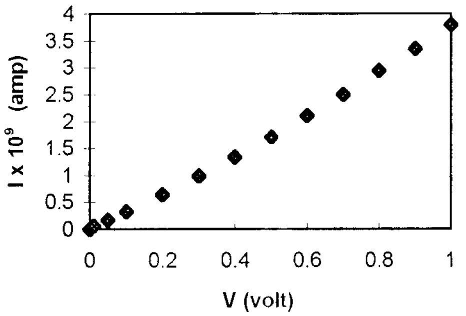

Figure 3 Plot of V versus I for PAA doped with 0.5 wt % CB.

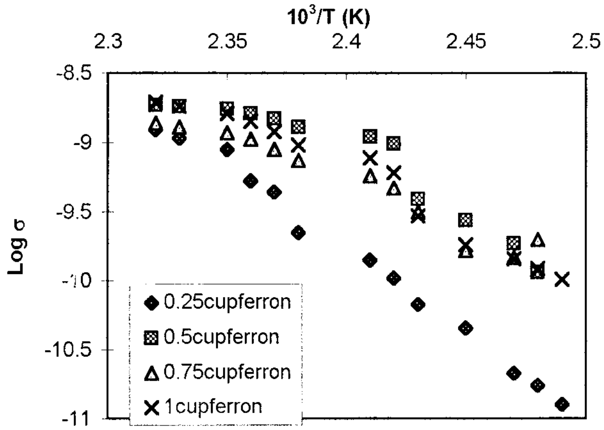

Figure 5 Plot of log σ versus $10^3/T$ for PAA doped with cupferron.

hydroxyl amine, the nitroso group in the cupferron, and the OH group of PAA. This kind of complex increased σ.

The variation of log σ of PAA doped with CB, Cr_2O_3, and cupferron at room temperature with wt % of dopants is shown in Figure 6. The plain PAA has a conductivity of 1.23×10^{-16}. However, when PAA is doped with these additives, it was found that σ increases to 1.13×10^{-11}. It is obvious that there is a transition from insulator to semiconductor.

IR Results

The structure of the prepared polymers was detected by IR. Figures 7 and 8 show the IR spectra for PAA in the absence of dopants and after treatment with 0.5 wt % CB, respectively. It was shown that, when PAA was doped with CB, a C—O—C band appears at 775–875 cm^{-1}. This means that carbon in the form of CB is easily oxidized and linked to the polymer. However, it was mentioned that CB was present inside the polymer in the form of granules at the interface between the polymer and CB.[22] However, there may be some sort of linkage.

Positron Annihilation Lifetime Results

Positron annihilation lifetime measurements at room temperature were performed for PAA doped with CB, Cr_2O, and cupferron as a function of their concentrations at 0.25, 0.5, 0.75, and 1 wt %. In the absence of dopant, the short-lived components (τ_1 constraint, I_1 = 35.6 ± 0.4%) are attributed to positron annihilation from the bulk. The second components (τ_2 = 0.354 ± 0.002 ns, I_2 = 57.03 ± 0.3%) are attributed to positron annihilation from a trapped state, and the long-lived components (τ_3 = 1.95 ± 0.03 ns, I_3 = 7.36 ± 0.1%) are attributed to the o-Ps annihilation in the polymer. Figure 9 shows the variation of I_1

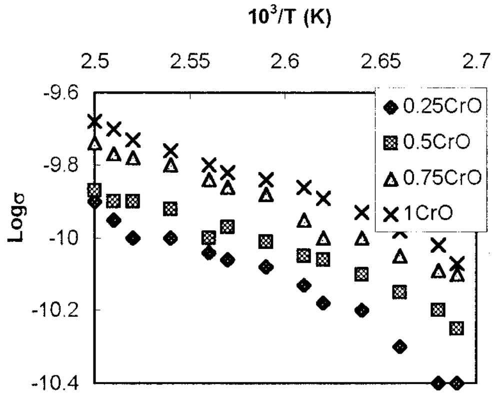

Figure 4 Plot of log σ versus $10^3/T$ for PAA doped with Cr_2O.

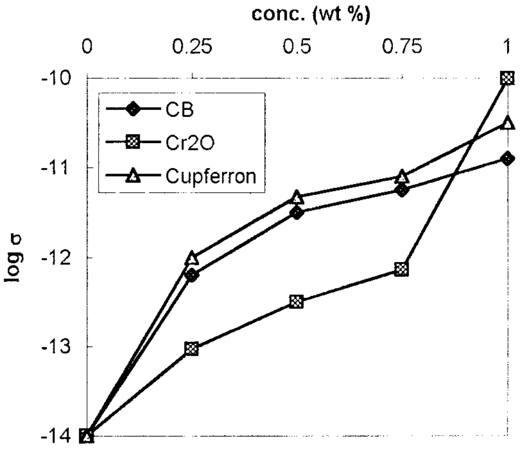

Figure 6 Plot of log σ versus concentration of dopants.

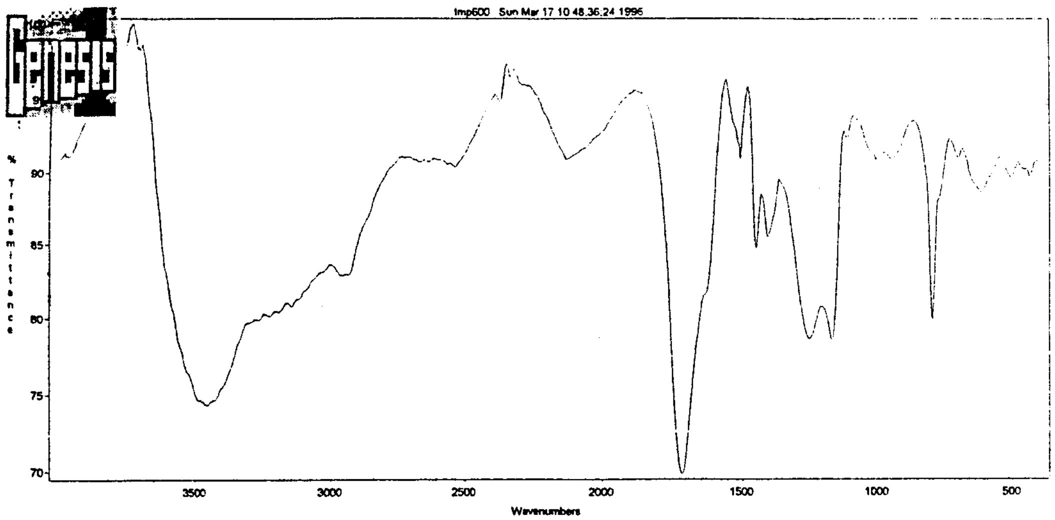

Figure 7 IR spectrum of plain PAA.

with the concentrations of different dopants. I_1 is decreased with increasing the concentrations of electron density in the bulk of materials when the concentration of dopants is increased. On the other hand, I_1 first decreased at low concentrations of CB, then increased at higher concentrations (>0.5 wt % CB).

The variation of the intermediate component (I_2) with respect to the doping is related to the conductivity of the material, as shown in Figure 10. A comparison of Figure 6 and Figure 10 shows that I_2 has almost the same trend as σ for PAA doped with Cr_2O_3, cupferron, and at low concentrations of CB. I_2 was decreased for higher concentrations of CB (>0.5 wt %). This intermediate intensity is just an indicator of metallic regions, according to the conducting island model.[23] The increase of dopants in PAA leads to phase separation between the metallic and insulating regions. The metallic regions reduce the potential barrier and increase the conductivity. This was obvious for Cr_2O_3 and cupferron as well as at low concentrations of CB. However, the decrease in I_2 at high concentrations of CB most probably was the result of the trapping of positrons from the local negatively charged regions, which were cre-

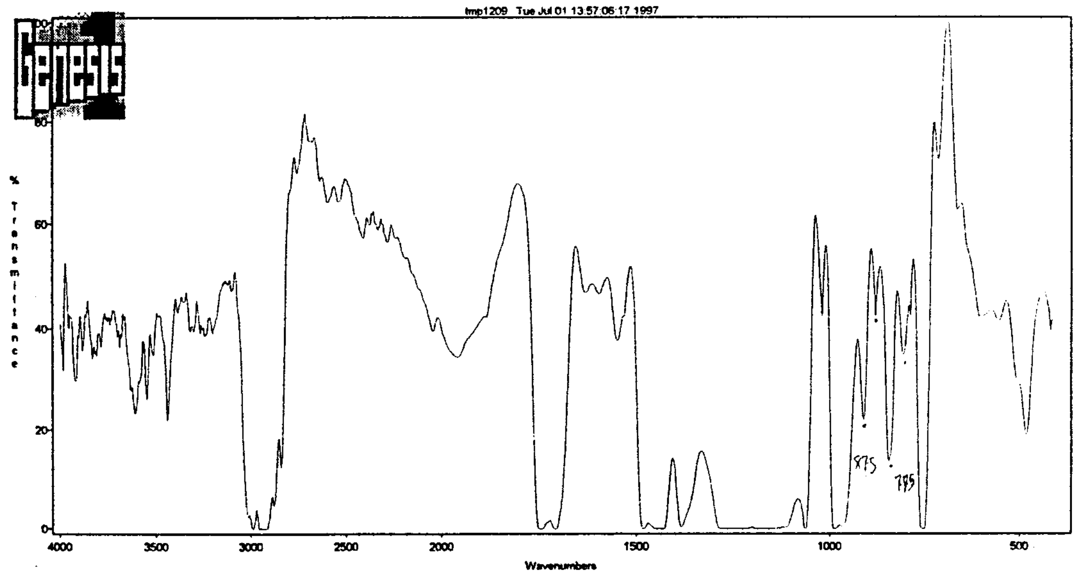

Figure 8 IR spectrum of PAA doped with 0.5 wt % CB.

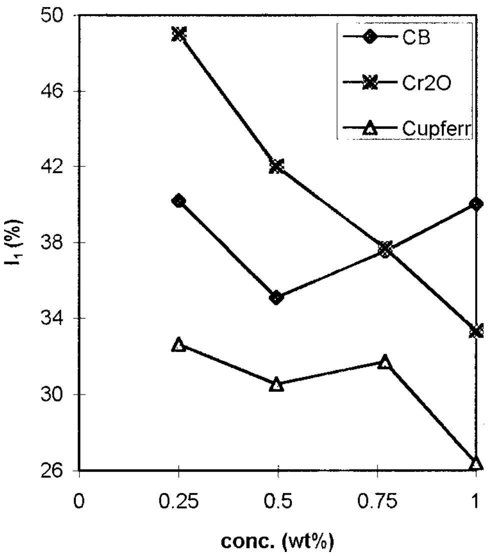

Figure 9 Plot of I_1 versus concentration of dopants.

ated by the localized dopant, thus perturbing the intermolecular force at the vicinity. A correlation between σ and I_2 was made at room temperature. Figure 11 shows a positively correlation between I_2 and log σ. The larger the I_2 value, the greater the conductivity for PAA doped with Cr_2O_3, cupferron, and low concentrations of CB.

CONCLUSIONS

The specific electric conductivity was measured for PAA of molecular weight 720 and that of PAA doped with CB, Cr_2O_3, and cupferron with different concentrations (from 0.25 to 1 wt %). The effect of dopant concentration on the electrical conductivity of PAA was investigated. It was found that σ of PAA doped with different dopants is near that of semiconductors. Also, the relation between log σ and 1/*T* is linear, and σ ranges between 2.2×10^{-14} and 1.4×10^{-9} Ω^{-1} cm^{-1}. IR spectra showed that when PAA was doped with 0.5 wt % CB, a C—O—C band appeared at 755–875 cm^{-1}, because CB was present inside the polymer in the form of granules at the interface between the polymer and CB. The PAL results, which showed that I_2 is related to σ, were discussed in terms of the conductivity island model. There was a distinct positive relation between σ and I_2, linking the PAL parameters with σ, when PAA was doped with Cr_2O_3, cupferron, and at low concentrations of CB.

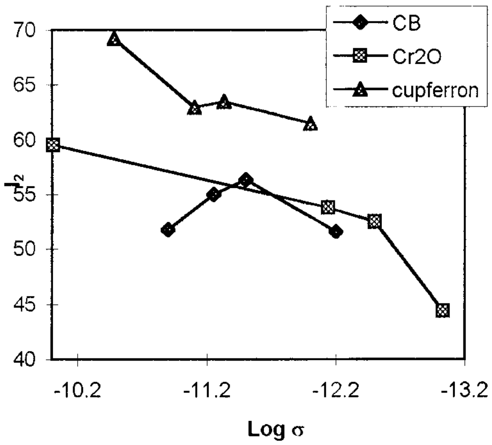

Figure 11 Plot of I_2 versus log σ.

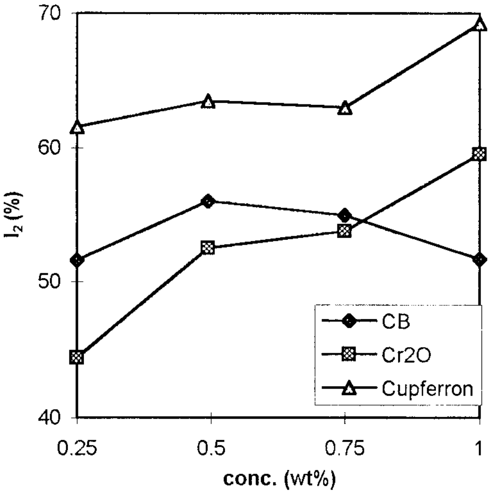

Figure 10 Plot of I_2 versus concentration of dopants.

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