Effect of Oxygen on Polypyrrole as Studied by Conductivity and ESR Measurements

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The effect of oxygen on polypyrrole (PPy) doped with benzenesulfonate has been investigated by electric conductivity and electron spin resonance (ESR) measurements. There are two regions in the changes of the conductivity, the linewidth and the spin concentration with respect to the pressure of oxygen. When the pressure decreased in the range from ambient pressure to 0.2 Torr (region I), the conductivity increased consistently with the relationship of the Langmuir adsorption, in which we assumed that the amount of adsorption was in proportion to the inverse of conductivity. This effect was reversible with respect to the pressure, indicating physical adsorption in this region I. The oxygen desorption by reducing the pressure caused a rapid decrease of the linewidth as well as the spin concentration. It was concluded that the linewidth variation is due to the reduction of dipole–dipole interactions between the unpaired electrons of the oxygen molecules and radicals of PPy (polarons), while the spin concentration variation is due to the disappearance of the oxygen molecules. Below 0.2 Torr (region II), the conductivity increased, deviating from the Langmuir relationship, while the ESR spectra almost remained constant. These findings were discussed, considering that the interaction positions of the adsorption were radical sites (polarons) in connection with the conductive process and that only a small number of the oxygen molecules adsorbed in this region II.

An understanding of the factors that influence the environmental stability of conducting polymers such as polyacetylenes (PA), polypyrrole (PPy), polythiophene, and polyaniline (PAN) is of paramount importance, especially when their use in practical application is to be realized. In order to evaluate those factors, the environmental stability of conducting polymers has been investigated under several conditions, such as light, heat, and atmosphere, and the conducting polymers with stronger stability have been developed. It has been established that PPy is a more promising candidate among all kinds of conducting polymers for electronic devices from the point of environmental stability.[1] In order to clarify the mechanism of light degradation, we therefore reported the effect of UV irradiation on PPy by electron spin resonance (ESR).[2] Under strong UV irradiation, rearrangement of conducting polymer occurred, and the spin concentration and conductivity therefore decreased. Among the studies relating to the thermal stability of conducting polymer is the effect of dopants on the decay in PPy conductivity under elevated temperature by Samulson et al.[3] They found that the kinetics of degradation followed different processes depending on the kind of dopant in PPy. For example, in the case of PPy doped with *p*-toluenesulfonate, the degradation mechanism can be described by simple first-order kinetics, while in PPy doped with tetrafluoroborate or perchlorate the kinetics follow multiple processes of degradation.

In the case of exposure to air, it is of prime importance to understand the interactions between oxygen molecules and developing materials. An oxygen molecule has two unpaired electrons, forming the triplet state in which the spins are parallel with one another. The oxygen molecule takes an excited state when exposed to light or heat and makes the stronger oxidation product of O_2^- due to the easier acceptance of an electron than at an ordinary state. ESR technique has revealed the interactions between oxygen molecules and developing materials.[4—11] For example, the effect of oxygen on the materials such as active chars, coals, and pyrolized organic materials was ascertained as a drastic broadening of the ESR lines.[4] The ESR linewidth of lithium phthalocyanine (Li-Pc) was also broadened under the introduction of air.[5—7] Using this effect, Li-Pc would be used as a sensitive probe for oxymetry applications.

As for the oxygen effect of PA, the results are comprehensively explained in terms of highly-one-dimensional diffusive spins which can be trapped at impurities, defects, or additionally at the species connected to oxygen contamination.[8—10] In the case of PAN, the oxygen-induced ESR line broadening has been investigated.[12] The oxidation reaction on insulating neutral PPy at room temperature was reported by Pfluger et al.[13] They found that, in the first stage, PPy is changed to an ionic polymer (PPy+anion-), and then chemical reaction with the nitrogen atoms of pyrrole rings takes place.

There is limited information about the microscopic characterization of the effect of oxygen on conducting PPy. In this paper we will discuss the effect of oxygen molecules on PPy at room temperature. We can correlate the ESR parameters with the conductivity changes of PPy.

Experimental

The PPy films employed in this study were provided by BASF. The material is synthesized using a continuously working electrochemical process. These polymer chains contain excess positive charges (about one excess charge unit per three monomer units) which are compensated by appropriate counter ions (in this case benzenesulfonate ions). The thickness and density of PPy are 35 μm and 1.4 $\mathrm{g\,cm^{-3}}$, respectively.

Two pieces of the same PPy film were mounted into two different pieces of glass apparatus: The first was equipped for four-probe conductivity measurements (ADVANTEST R6551); the second was an ESR sample tube. Both parts were attached to the same vacuum system and pumped to a given pressure. In this paper, the value of the pressure means the partial pressure of oxygen. When the pressure decreased, the conductivity and the ESR signal changed gradually. After reaching equilibrium, the conductivity and the ESR signal were recorded. All of the ESR measurements were performed with a JEOL JES-FE1XG ESR or PX-1050 spectrometer at X band (9.4 GHz) at room temperature. The microwave power was fixed well below (about 1% of) the value which caused signal saturation. The width of magnetic filed modulation (100 kHz) was kept at 10% of the peak-to-peak linewidth (ΔHpp) of each sample. A $\mathrm{Mn^{2+}}$–MgO solid solution was used as a reference for the *g*-value and magnetic field calibration.

Results

Conductivity Measurements. Figure 1 shows the relationship between the conductivity of PPy and the pressure. The initial value of the conductivity is approximately 100.0 $\mathrm{S\,cm^{-1}}$. As the pressure decreases, the conductivity of PPy increases. When the pressure is under 0.2 Torr (1 Torr = 133.322 Pa), the conductivity increases rapidly. When air was leaked into the system, the conductivity returned to the initial value, 100.0 $\mathrm{S\,cm^{-1}}$. This reversible effect suggests that the change in the conductivity is caused by adsorbed oxygen molecules.

When an undoped conducting polymer is doped with oxygen, its conductivity usually increases.[13] This is because the acceptance of electrons from the conducting polymer leads to the increase of positive carriers. But our heavily doped PPy seems to show different behavior from the above-mentioned doping effect. Therefore, it is important in our observation that the conductivity decreased when oxygen molecules were introduced around the conducting polymer. This result means that the oxygen has no effect on the number of charge carriers but influences the decreasing of the mobility of the charge carriers. In other words, the result may imply that the adsorbed oxygen restricts the motion of spin polarons in the conducting polymers.

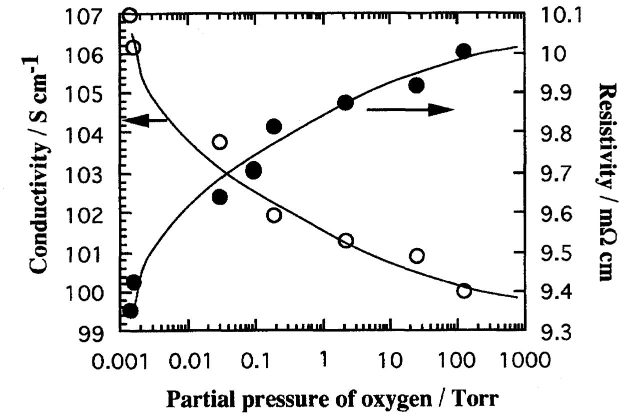

Fig. 1. Conductivity or resistivity of polypyrrole vs. partial pressure of oxygen.

ESR Studies. The ESR spectra of all the pristine samples consist of a single narrow line with no hyperfine splitting. The lineshape can be characterized by several parameters defined in Fig. 2. It is well known that highly conductive polymers sometimes exhibit asymmetrical lineshape (A≠B) which is called Dysonian.[14] But in our sample almost symmetrical lineshapes were observed ($A/B = 1.1$), as was reported in the previous paper, because the thickness of PPy film is sufficiently thinner than the skin depth.[2]

As shown in Fig. 3, after the system was evacuated, in the range from ambient pressure to 0.2 Torr the peak-to-peak linewidth ΔHpp decreased from 0.14 mT to 0.02 mT rapidly. Under 0.2 Torr, however, it only decreased gradually. Figure 4 indicates the decrease of the spin concentration when the pressure decreased. This behavior is similar to that of the peak-to-peak linewidth. As we will discuss later in detail, these results would imply that the change of both

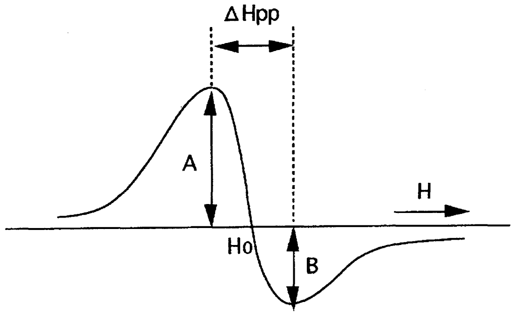

Fig. 2. Illustrative definition of ΔHpp (peak-to-peak linewidth), A (left height of the differential peak) and B (right height of the differential peak) of an ESR spectrum.

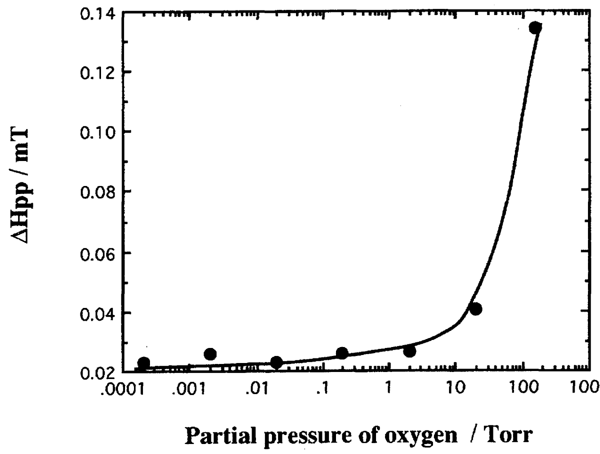

Fig. 3. The peak-to-peak linewidth ΔHpp vs. partial pressure of oxygen.

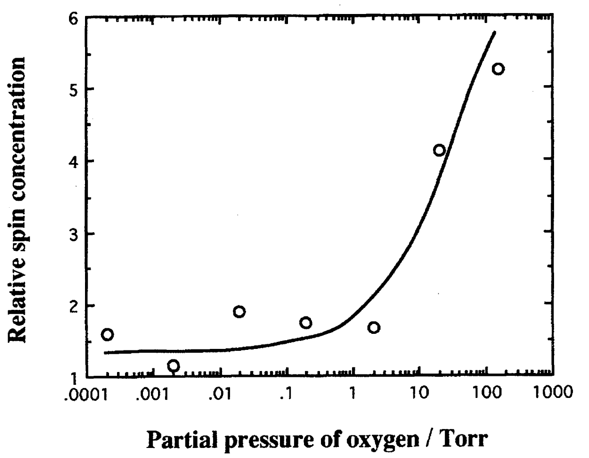

Fig. 4. Relative spin concentration vs. partial pressure of oxygen.

spin concentration and ΔHpp comprises two regions, as the change in conductivity does.

The asymmetrical parameter A/B and the *g*-value (which is equal to $h\nu/\mu_B H_0$ in Fig. 2, where h and μ_B are the Planck constant and the Bohr magneton, respectively) did not change by pumping over the sample, and these samples have the *g*-value in the range 2.00235—2.00236, comparable with those of a free electron (2.0023).

Discussion

Analysis of Conductivity. As mentioned above, the adsorbed oxygen molecule seemed to affect the change in the conductivity. Therefore, we will analyze this data on the basis of the relationship of the Langmuir adsorption. In the case of Langmuir's adsorption, the relationship between the adsorption amount and the pressure is expressed by the following relation:

$$v = abP/(1+aP) \tag{1}$$

where v is the adsorption amount, P is the pressure, and a and b are constants.[15] This equation can be changed to the next expression.

$$P/v = 1/ab + \mathrm{P}/b \tag{2}$$

The data being plotted as P/v vs. P, the graph becomes a straight line. Here we assume that the amount of adsorbed oxygen molecule v is in proportion to the resistivity ρ (inverse of conductivity). Figure 5 shows the relationship between P/ρ and P; the consistency of our data with the theoretical line proves our assumption to be valid. The trapping effect of the charge carrier by the adsorbed oxygen molecules leads to the decrease of the mobility. As a result, the amount of the adsorbed oxygen molecules appears to be proportional to the resistivity.

In order to analyze the values of a lower pressure in detail, the scale of both the vertical and horizontal axes was converted into a logarithm-plot. As shown in Fig. 6, in the range less than 0.2 Torr, the data deviated from the theoretical line. There exist both physically and chemically adsorbed oxygen molecules on PPy before pumping. It seems that as the pressure decreases the physically adsorbed oxygen molecules, which are adsorbed more weakly than chemically adsorbed one, are desorbed and after decreasing the pressure furthermore, the chemically adsorbed oxygen molecules are desorbed. Thus, one can conclude that there exist two regions in the pressure effect; one is the range from ambient pressure to 0.2 Torr (region I), and the other is the range less than 0.2 Torr (region II). Therefore, the change of the conductivity from ambient pressure to 0.2 Torr would be caused by physical adsorption of oxygen molecules on PPy, and the deviation from the Langmuir plot in the range less than 0.2 Torr would result from the chemical adsorption of oxygen molecules which were adsorbed more strongly than in the case of physical adsorption. By the desorption of the chemically adsorbed oxygen molecule as well as the physically adsorbed one, the conductivity increased.

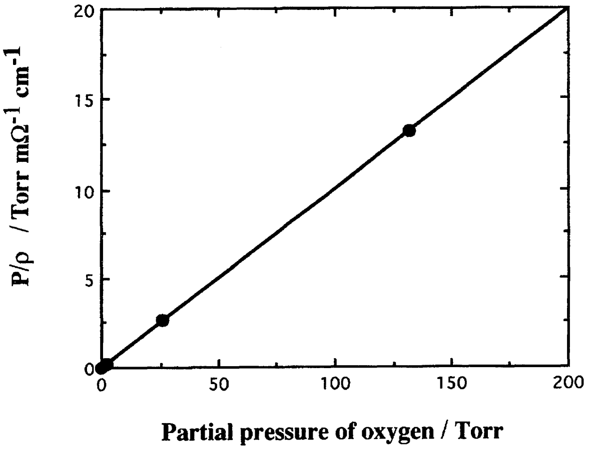

Fig. 5. Partial pressure of oxygen divided by resistivity. P/ρ vs. partial pressure of oxygen.

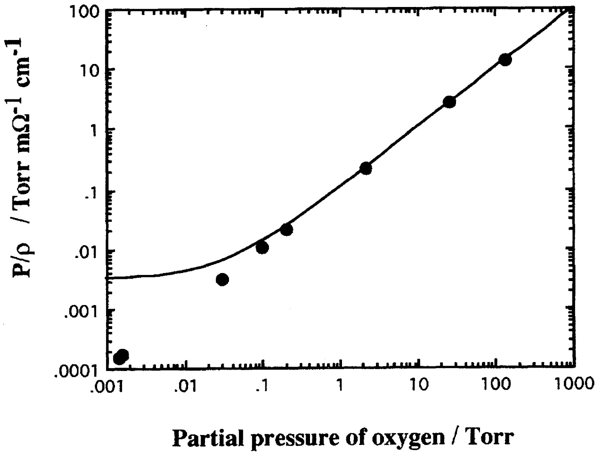

Fig. 6. Partial pressure of oxygen divided by resistivity, P/ρ vs. partial pressure of oxygen in logarithmic scale. The solid line is the theoretical expression (2) normalized at high pressure region.

As for the change in the ESR spectra, there were also two regions at the boundary of 0.2 Torr in the same way as the result of conductivity; we will also discuss this regional division in the following section.

Analysis of ESR Spectra. It has been proved by the

ESR technique that the transport properties of PPy are related to polarons and bipolarons, which are the kinks in the polymer structure.[16—20] A polaron is a radical ion with a carrying spin of $S=1/2$, while a bipolaron ($S=0$) is formed by the reunification of two polarons. Bipolarons have been considered to be the fundamental charge-carrying species in the conduction process. Using these ideas, we will discuss each region of the pressure as follows.

In region I, the change in the linewidth may be due to dipole–dipole interactions between unpaired electrons of oxygen molecules and radicals of PPy (polarons), and the spin concentration consists of the superposition of the spin concentration from both polarons of PPy and unpaired electrons of oxygen molecule. Therefore, the desorption of the oxygen molecules leads to the rapid decrease of the linewidth, caused by the reduction of the dipole–dipole interactions, and also leads to the decrease of the spin concentration because of the disappearance of the oxygen molecule's spins.

In region II, there were only slight decreases in both the linewidth and spin concentration. When the pressure was reduced to 0.2 Torr, almost all the physically adsorbed oxygen molecules were desorbed due to the easiness of the desorption. Moreover, below 0.2 Torr, the chemically adsorbed oxygen molecules are much fewer than the physically adsorbed oxygen molecules and would result in a minor effect to the ESR spectra. As a result both the linewidth and spin concentration remained almost constant in region II.

Effect of Oxygen Molecule. There were two regions in the change of both the conductivity and ESR spectra with respect to the pressure of oxygen. This change with two regions reflected the differences of the adsorption types, that is, the physical and chemical adsorptions. The physically adsorbed oxygen molecules on PPy in region I did not act as dopants, but trapped the conductive carriers (polarons). By this trapping effect, the decrease of the carrier mobility resulted in the broadening of the linewidth, as well as the decrease of the conductivity. When the pressure was reduced below 0.2 Torr, there were only chemically adsorbed oxygen molecules. Regardless of the small amount of adsorbed oxygen molecules, the desorption increased the conductivity, in spite of slight change of the ESR spectra, due to the small number of adsorbed oxygen molecules. For this reason, the interaction positions of the oxygen molecules would be radical sites (polarons) in connection with the conductivity of PPy, the desorption of the oxygen molecules leading to a larger increase of the carrier mobility.

Conclusion

We investigated the effect of oxygen on PPy doped with benzenesulfonate using conductivity and ESR measurements. The partial pressure of oxygen around PPy was changed with a vacuum system. We found that there are two regions of the change in the conductivity and ESR parameters such as the linewidth and spin concentration with respect to the pressure. In the range of the high pressure, the physically adsorbed oxygen molecules decreased the carrier mobility, due to trapping the conductive carriers (polarons). As a result the conductivity decreased, while both the linewidth and spin concentration increased. In the range of the low pressure, the chemically adsorbed oxygen molecules affected the conductivity only. It should be considered that the interaction positions of the adsorption were radical sites (polarons) in connection with the conductive process. This interaction caused the change in the conductivity, while no appreciable change of the ESR spectra resulted because of the small number of oxygen molecules.

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