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Polymer 40 (1999) 2209–2213

polymer

Decrease in electrical conductivity upon oxygen exposure in polyanilines doped with HCl

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Received 23 January 1998; revised 30 March 1998; accepted 4 June 1998

Abstract

The electrical conductivity of polyanilines doped with HCl was decreased upon exposure to oxygen and was increased reversibly upon evacuation. The line intensity and the line width of the EPR signals were decreased and increased, respectively, upon exposure to oxygen. The former represents the reduction in the concentration of polarons due to the spin–spin interaction of oxygen with paramagnetic polarons, generated by HCl doping process, and the latter the reduction in the mobility of polarons due to the partial localization of delocalized polarons. Therefore, it was concluded that the decrease in conductivity arose from the reduction in both the concentration and the mobility of polarons, the charge carriers for electrical conductivity. However, the decrease in the electrical conductivity was very small whereas the decrease in the polaron concentration was substantial. It was also found that the time scale for the diffusion of oxygen molecules was much longer than that for the spin–spin reaction of oxygen with polarons. Therefore, the small decrease in electrical conductivity may be associated mostly with the reduced mobility of polarons by localizing reaction instead of the reduced polaron concentration. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Electrical conductivity; Oxygen exposure; Polyanilines

1. Introduction

Polyaniline has been paid considerable attention because it is electrically conducting [1,2], thermally stable [3] and soluble in organic solvents such as NMP (N-methyl pyrrolidinone) [1,4,5]. Recently, a remarkable oxygen permselectivity over nitrogen has been observed in the polyaniline membranes when its doping level is controlled with appropriate protonic acids [6–8]. Therefore, polyaniline can be considered as a potential membrane material for gas separation.

The emeraldine base form of polyaniline consists of equal numbers of reduced [–(C_6H_4)–NH–(C_6H_4)–NH–] and oxidized [–(C_6H_4)–N=(C_6H_4)=N–] repeat units. When the emeraldine base form of polyaniline is doped with protonic acid (oxidized state), the bipolarons are initially generated, undergoing a transition to the paramagnetic polarons through an internal redox reaction [9,10] as illustrated in Fig. 1. The two adjacent polarons will be separated owing to their electrostatic repulsion and stabilized. Therefore, the doped polyaniline becomes paramagnetic. Oxygen is also a paramagnetic molecule, having two unpaired electrons in their $2p\pi_g$* molecular orbital. Since both oxygen and doped polyaniline are paramagnetic, there will be a magnetic spin–spin interaction between them.

The doped polyaniline is electrically conductive because the polarons can move through the conjugated π-bonds, termed delocalized polarons. Since the polarons are charge carriers for electrical conductivity, their concentration and mobility determine the electrical conductivity. When doped polyanilines are exposed to an oxygen environment, the concentration and the mobility of polarons depend upon the spin–spin interaction of polarons with oxygen molecules. The spin–spin interaction can be investigated by electron paramagnetic resonance (EPR) and its effect on the electrical conductivity will also be investigated by measuring the changes in both the concentration and the mobility of polarons. Because of the spin–spin interaction, it is expected that the delocalized polarons will be partially localized upon exposure of oxygen molecules and will lose their paramagnetic property, resulting in a decrease in electrical conductivity. EPR has been intensively used to investigate the spin–spin interaction because it enables us to see the spins directly [11–13]. In particular, the width of the

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PII: S0032-3861(98)00441-8

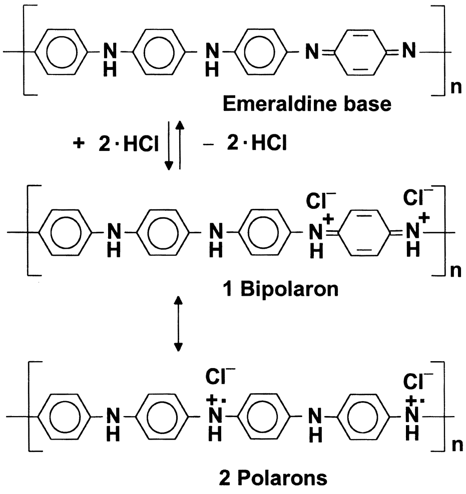

Fig. 1. Schematic doping mechanism of emeraldine base form of polyaniline.

EPR signal is directly connected to the interactions of the spins with their environment and to their motion: the narrowness of the line is a measure of the spin mobility [13]. The line intensity of the EPR signal is known to be proportional to the concentration of spins.

2. Experimental

2.1. Polymerization of aniline

Polyaniline was prepared by oxidative polymerization of aniline in aqueous acidic media (1 M HCl) with ammonium persulfate as an oxidant. The molar ratio of monomer/oxidant used was 4/1. The reaction was carried out at 0°C for 3 h, and the precipitate was formed during the reaction. The precipitate was subsequently filtered and washed with deionized water until the filtrate was colorless. The as-synthesized polyaniline in its protonated form was treated with 1 M NH_4OH for 15 h to yield emeraldine base powder, followed by drying under vacuum for over 48 h at room temperature.

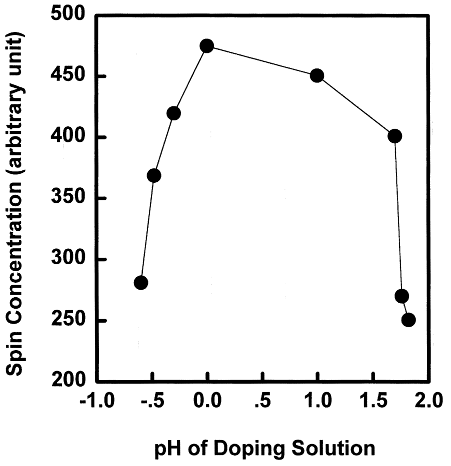

Fig. 2. Spin concentration as a function of dopant HCl concentration at ambient environment.

2.2. Doping and dedoping of polyaniline

Following the method used by Mattes et al. [7,8] the emeraldine base powder was dissolved in NMP (8 wt%). The emeraldine base solution in NMP was cast on to a glass plate and the solvent was removed under 120°C for 3 h. The as-cast membrane was then immersed into a 4 M HCl solution for 24 h to give a fully doped membrane. The fully doped membrane was completely dedoped by immersion into 1 M NH_4OH solution for 48 h. The dedoped membrane was subsequently redoped with 0.0150, 0.0175 and 0.0200 ($\pm$ 0.0002) M HCl solution. Each membrane was dried under vacuum for 48 h at room temperature.

2.3. EPR Experiment

Narrow strips of polyaniline membrane (1 mm $\times$ 5 mm) were put into an EPR cell. In order to study the interaction of oxygen molecules with polarons, the cell was connected to a large volume (1 L) of oxygen reservoir so that the applied pressure was maintained constant during the experiment. The EPR spectra were obtained in either ambient or vacuum environment. For vacuum environment, each sample was evacuated for at least 3 days prior to experiment. The EPR line intensity was monitored with oxygen contact time from a Bruker EPR spectrometer (ER 200E-SRC). The spectrum obtained was doubly integrated to obtain the spin concentration.

2.4. Electrical conductivity

The van der Pauw method was employed to measure the electrical conductivity at 25.6°C [14]. The electrical conductivity, σ, is

$$\sigma = \frac{\ln 2}{\pi d}\frac{i}{V} \qquad (1)$$

where i is the electric current applied to the sample, d the sample thickness, and V the voltage difference between two adjacent probes.

3. Results and discussion

3.1. Spin concentration

The total spin concentration of doped polyanilines including the Pauli and the Curie susceptibilities were calculated from the EPR intensity [15], and plotted against the pH of the doping solutions as shown in Fig. 2. It is well known that the polarons can be generated by the reaction between protonic acid dopants and imine nitrogens of the emeraldine base form of polyaniline [16]. The EPR experiment was

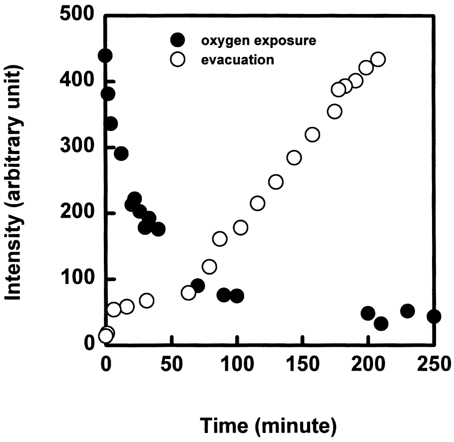

Fig. 3. The change in spin concentration in polyaniline doped with 1 M HCl with oxygen exposure time and evacuation time: (●) oxygen exposure at 137.9 kPa; (○) evacuation time.

conducted in ambient environment. It is seen from Fig. 2 that the spin concentration initially increases with decreasing pH (i.e. increasing dopant concentration), reaches a maximum near pH = 0, and then decreases. This is consistent with the result that the level of protonation is nearly completed when the emeraldine base polyanilines were treated with aqueous HCl of pH = 0 [9]. The initial increase in the spin concentration is expected because of the increased possibility of reaction between the dopant HCl and imine nitrogens of polyaniline.

When pH of the dopant solution is lower than zero, the spin concentration decreases with increasing dopant concentration. The maximum spin concentration was also reported in electrochemically polymerized polyanilines [15,17]. The maximum behavior can be explained by the formation of bipolarons at high doping levels, which has been observed in polypyrrole [18,19]. It has been known that the polaron and the bipolaron are in equilibrium, and the pairing of polarons at the high doping levels can occur to form bipolarons [15].

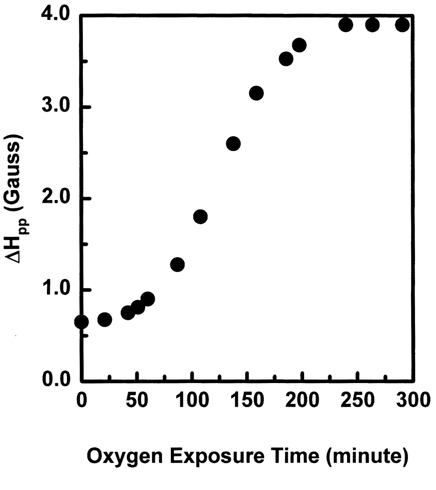

Fig. 4. The line width broadening of polyaniline doped with 1 M HCl at 137.9 kPa oxygen with time.

3.2. Change in the spin concentration upon oxygen exposure

In order to verify the interaction between polarons and oxygen molecules, the polyaniline doped with 1 M HCl was exposed to oxygen at 137.9 kPa and the calculated spin concentration was plotted against the oxygen exposure time as shown in Fig. 3. It is clearly seen that the spin concentration decreased when the sample was exposed to oxygen. This manifests that the polaron reacts with molecular oxygen and loses its paramagnetic property. Consequently, its concentration diminishes with oxygen exposure time. The spin concentration was also measured while evacuating, and plotted in Fig. 3. The initial spin concentration was completely recovered after evacuation, which demonstrates a reversible spin–spin interaction. Therefore, it was found that the polarons in doped polyaniline reversibly react with molecular oxygen resulting in the reduction in the polaron concentration.

3.3. Change in the polaron mobility upon oxygen exposure

The line width of EPR signals is influenced not only by the interaction between the spin and the external magnetic field applied, but also by the interaction of the spin with its environment [20]. In particular, the width is directly connected to the interactions of the spins with their environments and to their motion and the line-broadening is inversely proportional to the polaron mobility [13]. It has been found that EPR line width, characterized here by the peak-to-peak line width ΔH_{pp}, increased under an oxygen environment as shown in Fig. 4. It was 0.65 G in the initial vacuum state and increased to 3.90 G when exposed to oxygen. This result is analogous to that of Nechtschein and Genoud [21] and demonstrates that the mobility of polarons is partially reduced by the spin–spin interaction. This is because the polarons react with molecular oxygen to be localized momentarily by oxygen molecules and to lose their paramagnetic property.

In summary, when the delocalized polarons meet oxygen molecules, they react with oxygen molecules to form an oxygen–polaron complex owing to their relatively strong magnetic spin–spin interaction. The complex formation results in the reduction in both the effective concentration and the mobility of the polarons as evidenced by the EPR line intensity and line-broadening, respectively.

3.4. Change in the electrical conductivity upon oxygen exposure

The electrical conductivity of doped polyanilines depends on the presence of water and the pH of dopant solutions in an oxygen-free environment. It has been known that the electrical conductivity increases with the amount of water present in the sample [22,23]. In order to avoid the effect of water and oxygen molecules on the electrical conductivity, the doped polyanilines were evacuated to remove the water

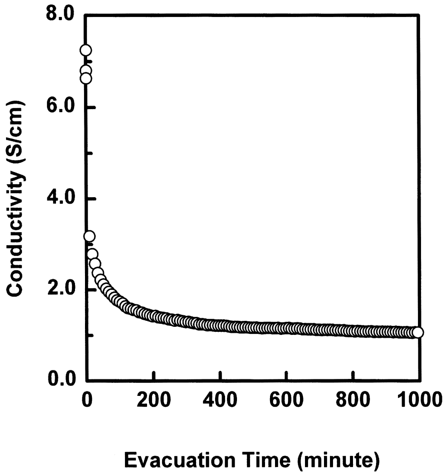

Fig. 5. The decrease in electron conductivity as a function of evacuation time in polyaniline doped with 4 M HCl.

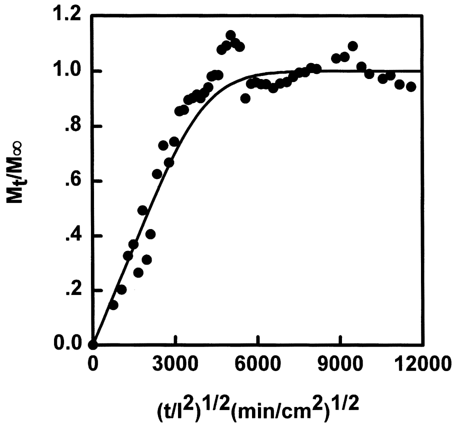

Fig. 7. Reduced sorption curve of oxygen in polyaniline with 1 M HCl at 137.9 kPa oxygen pressure. The solid line is from theoretical predictions by Fick's law with diffusion coefficient of $1.88\text{x}10^{-10}$ cm^2/s [22]. M_t and M_∞ are the amount of oxygen sorbed at time t and at equilibrium, respectively. l is the film thickness.

and oxygen molecules. The electrical conductivity of the polyaniline membranes doped with 4 M HCl was measured with evacuation time. Its conductivity decreased sharply from 7.0 to 1.0 S/cm (Fig. 5) primarily due to the water desorption.

The electrical conductivity of dried, doped polyanilines was also measured as function of oxygen exposure time at an oxygen pressure of 137.9 kPa as shown in Fig. 6. It is clearly seen that the electrical conductivity decreased from 1.02 to 0.94 S/cm with the oxygen exposure time. However, the conductivity increased again with the evacuation time and recovered to its original value. The conductivity also shows the reversible behavior as shown in the spin–spin interaction between polarons and oxygen molecules.

It is well known that the polarons are delocalized through the conjugated π-bonds, resulting in an electrical conductivity. Therefore, the electrical conductivity depends upon the concentration and mobility of charge carriers. As mentioned previously, polarons react with oxygen molecules and lose their paramagnetic property, evidenced from the EPR intensity measurement. This gives that the concentration of polarons, charge carriers, is reduced upon the reaction with oxygen molecules. It was also found that the mobility of spin was reduced upon oxygen exposure. That is, oxygen molecules induce the reduction in both the concentration and the mobility of the charge carriers. Therefore, the reduced conductivity can arise from the reduction in both the concentration and the mobility of the charge carriers. The effect of each term on the decrease in conductivity will be examined as follows.

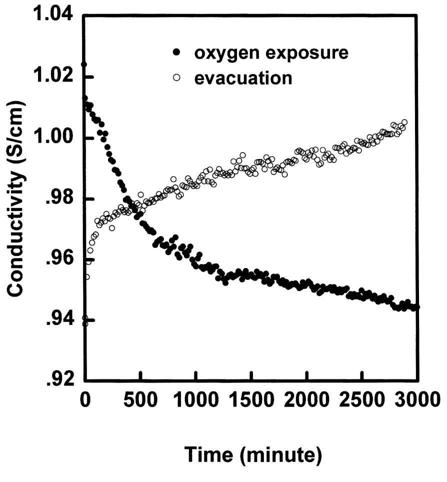

Fig. 6. The change in electron conductivity as a function of oxygen exposure time and re-evacuation time in polyaniline doped with 4 M HCl: (●) oxygen exposure at 137.9 kPa; (○) re-evacuation time.

It was found that the extent of the conductivity decrease upon oxygen exposure was small. According to Fig. 6, it decreased only from 1.02 to 0.94 S/cm. However, almost 90% of the polarons reacted with oxygen molecules and lost their paramagnetic property, as shown in Fig. 3. This means that the major factor to determine the electrical conductivity is not the concentration but the mobility of charge carriers. The effect of the mobility reduction by oxygen exposure on the small decrease in the electrical conductivity will be explained as follows.

The spin–spin interaction of oxygen molecules with polarons can be expressed by a simple reversible chemical reaction, for convenience:

$$O_2 + P \Leftrightarrow [O_2 - P] \tag{2}$$

where P is the polaron, and $[O_2–P]$ is the oxygen–polaron complex. Thus, the forward reaction is equivalent to the localization reaction of polaron by oxygen. There will be two transport modes of oxygen in doped polyanilines: one is the diffusion of oxygen molecules through the matrix and the other is the chemical reaction, i.e. the spin–spin interaction of oxygen molecules with the polarons. It was found that the chemical reaction of Eq. (2) was very fast compared with the oxygen diffusion rate [24]. In other words, the time scale ratio of the reaction to the diffusion is very small, and the oxygen transport is Fickian with a constant diffusion coefficient of $1.88 \times 10^{-10}\,\mathrm{cm}^2/\mathrm{sec}$ [24] as shown in Fig. 7. If the time scale ratio is close to or bigger than unity, the oxygen transport does not follow Fick's law, but non-Fickian behavior.

Since the time scale ratio of the reaction to the diffusion is very small, the interaction reaction occurs very rapidly and the polarons are localized only momentarily. Therefore, the reduction in the polaron mobility will be small. This is consistent with the small decrease in the electrical conductivity. Since the contribution of charge mobility (μ) is much larger than the charge concentration (n) in electrical conductivity ($\sigma = n\mu$), the electrical conductivity σ decreases only to a small extent even after the considerable decrease in n. This is because the decrease in μ remains small after the exposure of oxygen.

4. Conclusions

The decrease in the electrical conductivity in polyanilines doped with aqueous HCl solution was small upon oxygen exposure, although the concentration of polarons, the charge carriers for the electrical conductivity, was decreased to a great extent. The decrease in conductivity in an oxygen environment was interpreted in terms of the reduction in both the concentration and the mobility of the polarons, observed from the line intensity and line-broadening of EPR signals, respectively. Further, both the small decrease in the electrical conductivity and the transport phenomena of oxygen confirmed that the contribution of charge mobility was much larger than the charge concentration in electrical conductivity.

References

[1] Chiang JC, MacDiarmid AG. Synth Met 1986;13:193.
[2] Ginder JM, Richter AF, MacDiarmid AG, Epstein AJ. Solid State Comm 1987;63:97.
[3] Hagiwara T, Yamaura M, Iwata K. Synth Met 1988;25:243.
[4] Oh EJ, Min Y, Wiesinger TM, Manohar SK, Scherrer EM, Prest PJ, MacDiarmid AG, Epstein AJ. Synth Met (Vol. 55–57) 1993:977.
[5] MacDiarmid AG, Epstein AJ. Synth Met 1994;65:103–116.
[6] Rebattet L, Escoubes M, Genies E, Pineri M. J Appl Polym Sci 1995;58:923.
[7] Mattes BR, Anderson MR, Conklin JA, Reiss H, Kaner RB. Synth Met (Vol. 55–57) 1993:3655.
[8] Anderson MR, Mattes BR, Conklin JA, Reiss H, Kaner RB. Science 1991;252:1412.
[9] Epstein AJ, Ginder JM, Zuo F, Bigelow RW, Woo H-S, Tanner DB, Richter AF, Huang W-S, MacDiarmid AG. Synth Met 1987;18:303.
[10] MacDiarmid AG, Chiang JC, Richter AF, Epstein AJ. Synth Met 1987;18:285.
[11] Mizoguchi K, Kume K. Solid State Comm 1994;89:971.
[12] Javadi HHS, Laversanne R, Epstein AJ, Kohli RK, Scherr EM, MacDiarmid AG. Synth Met 1989;29:E439.
[13] Houze E, Nechtschein M. Phys Rev B 1996;53:14309.
[14] Skotheim TA, editor. Handbook of conducting polymers. New York: Marcel Dekker, 1986:224.
[15] Genoud F, Nechtschein M, Santer C. Synth Met (Vol. 55–57) 1993:642.
[16] Ray A, Richter AF, MacDiarmid AG. Synth Met 1994;29:E151.
[17] Genoud F, Kruszka J, Nechtschein M, Santier C, Davied S, Nicolau N. Synth Met 1991;41:2887.
[18] Scott JC, Pfluger P, Krounbi MT, Street GB. Phys Rev B 1983;28:2140.
[19] Bredas JL, Scott JC, Yakushi K, Street GB. Phys Rev B 1984;30:1023.
[20] Ranby B, Rabek JP. EPR spectroscopy in polymer research. Berlin: Springer, 1977:19.
[21] Nechtschein M, Genoud F. Solid State Comm 1994;91:471.
[22] Nechtschein M, Santier C, Travers JP, Chroboczek J, Alix A, Ripert N. Synth Met 1987;18:311.
[23] Travers JP, Nechtschein M. Synth Met 1987;21:135.
[24] Kang YS, Lee HJ, Namgoong J, Ko HC, Lee H, Jung B, Kim UY. In: Tant MR, Hill AJ, editors. Glassy polymers. ACS Symposium Series. Washington, DC: American Chemical Society, 1998.