Magnetic Properties of Conducting Polyanilines Induced by Organic Acids and Solvents

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Characteristic paramagnetism induced by organic acids and solvents was observed for conducting polyanilines. Most of spins in this material are localized below 100 K therfore the Curie spin contribution became large. Above 100 K, however, the polyaniline showed metallic features that is most spins are delocalized. Pauli susceptibility and total density of state at the Fermi level were determined as ~5 × 10⁻⁵ emu/mol and 1-2 state/eV in 2-ring unit, respectively. Curie spin concentration reaches a maximum around 50 K. The effect of solvent on these magnetic properties need to be emphasized for the cases of emeraldine base (EB)-camphosulfonic acid (CSA) and dodecylbenzenesulfonic acid (DBSA)/acetic acid. This solvent can form the localized small spin-domains, in which all the spins align parallel to each other at low temperature. The formation of spin-domains increases the net magnetic dipole and finally enlarges the magnetic susceptibility.

Introduction

Since the first work[1] for application in 1960s, polyaniline has been mostly used in the fields of electrochemistry and secondary battery.[2] For that purpose, the electrical conductivity level of polyaniline had been raised up to ~5 S/cm by adopting the protonic acid like HCl as a dopant.[3] Entering the 1980s, a lot of studies focused on practical applications, such as microelectronics, electrochromic display, electrode material of rechargeable battery, and so on, have been performed: for instance, paramagnetism of polyaniline upon HCl doping.[4] Protonic acid doping induces both changes the electrical and magnetic properties, and these properties are closely related to each other. It has been known[4] that the property changes by the protonic acid doping is due to the formation of half-filled polaron band of the polysemiquinone radical cations having unpaired spins. Even polyanilines doped by pseudo-protonic acids such as CH₃Cl, (CH₃)₂SO₄, etc show the same property changes.

On the other hand, usual polyanilines have a serious problem of limited processibility in the doped form, but it was recently overcome by doping of the functionalized acid,[5] such as camphosulfonic acid (CSA), dodecylbenzenesulfonic acid (DBSA), and this polyanilines are to be prepared in various forms. The system using CSA or DBSA is proved to have paramagnetism.[6,7] The choice of solvent is also important to raise the electrical conductivity of polyaniline doped with functionalized acid; e.g., using m-cresol or o-chlorophenol as a solvent shows 100-400 S/cm. In 1993, MacDiarmid et al.[8,9] defined the increase of electrical conductivity induced by solvent as a secondary doping which is due to the conformational change caused from the interactions between solvent and doped polymer chain. In other words, polymer chain under the secondary doping has rod-like conformation and the conformational change allows both increases in intrachain charge carrier mobility and crys-

tallinity, and these increases bring about the increase of electrical conductivity. The electrical property of polyaniline has been abundantly studied as mentioned above, but the magnetic property is not. In the present study, thus, we report some results of the magnetic properties for the polyanilines doped by various organic acids and solvents.

Experimental Section

Polyaniline was synthesized by oxidative polymerization of aniline at ~0 °C in 1 M HCl. After the deprotonation with 0.1 N NH₄OH, emeraldine base (EB) polyaniline was obtained. The EB was mixed with each functionalized acid of CSA, DBSA, and methanesulfonic acid (MSA) and the mixture was ground in a mortar for 30 min (molar ratio of EB as a tetramer unit to acid is 1 : 2 regarding as a fully doped state). The mixture was added on each solvent of m-cresol, o-chlorophenol, acetic acid, and chloroform to make 1-3% solution. After 30 min of stirring, the solution was sonicated and dried on a hot plate (60-80 °C, 4-6 h) to form the film phase. The magnetic susceptibility of sample was measured by a superconducting quantum interference device (SQUID) magnetometer (Model MPMS-7) with the applied magnetic field of 5000 G and over the temperature range of 5-300 K.

Results and Discussion

The measurement of magnetic properties of conducting polymer is important to know what the charge carrier is and how the electrical conduction occurs. Of these properties, magnetic susceptibility is a significant factor in determining the type of magnetism and the density of states at Fermi level. In general, the observed magnetic susceptibility χ^{obs} can be expressed as follows:[10]

$$\chi^{obs} = \chi^{core} + \chi^{pauli} + \chi^{curie} \qquad (1)$$

where χ^{core} is the diamagnetism of core atoms, χ^{pauli} the Pauli susceptibility by delocalized spin with metallic character, and χ^{curie} the Curie susceptibility by localized spin. The χ^{core} can be calculated from Pascal constant[11] as -112.44×10^{-6} emu/mol 2-ring unit. The χ^{pauli} may be obtained from the intercept in the plot of $\chi^{spin}(-\chi^{pauli} | \chi^{curie})$ versus the inverse of temperature(T) or from the infinitive value in the plot of χ^{spin} versus T. Finally, the χ^{curie} can be given as $\chi^{curie} - \chi^{spin} - \chi^{pauli}$. On the other hand, the total density of states $N(E_F)$ (both signs of spin) at the Fermi level can be determined by

$$\chi^{pauli} = (\mu_B)^2 \cdot N(E_F) \qquad (2)$$

where μ_B denotes Bohr magneton (9.27402×10^{-21} erg/Oe). Curie spin concentration n_s^{curie} can be also obtained by

$$\chi^{curie} = n_s^{curie} \cdot (\mu_B)^2 / k_B T \qquad (3)$$

where k_B indicates Boltzmann constant (1.3066×10^{-23} J/K).

Figure 1 shows the magnetic susceptibility χ^{spin} obtained from the observed one (χ^{obs}) as a function of temperature for the polyaniline samples doped with CSA in various solvents. It is also referred to Figure 2 for the samples doped with DBSA and MSA. All the samples show typical pattern of paramagnetism that the magnetic susceptibility decreases with the temperature increase. The decrease of the susceptibility is thought to be due to the rotations of parallel spins to
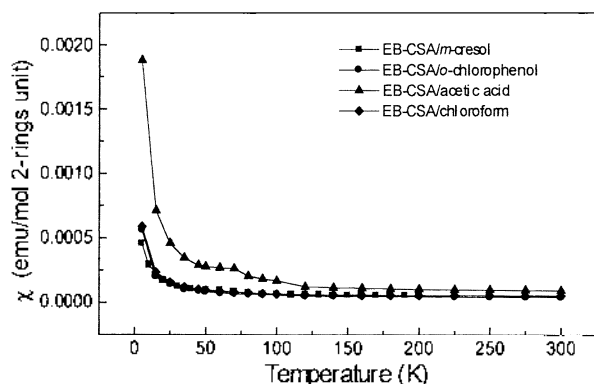

Figure 1. Magnetic susceptibility versus temperature for the polyaniline doped with CSA in organic solvents.
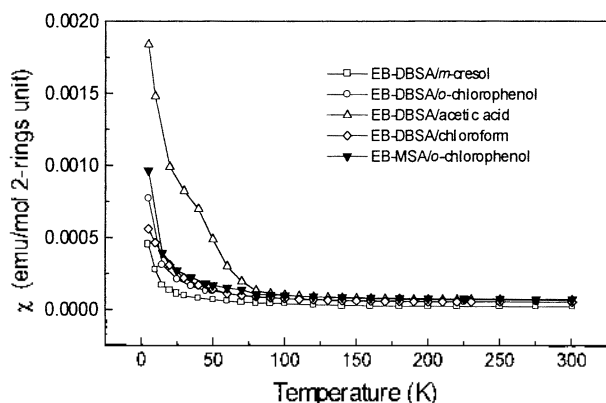

Figure 2. Magnetic susceptibility versus temperature for the polyaniline doped with DBSA and MSA in organic solvents.

anti-parallel direction by thermal energy. Particularly, the temperature dependence is enhanced at the temperature below 100 K where the concentration of temperature-sensitive Curie spins becomes higher. One may expect here that in the region below 100 K, most spins are localized and thus have a large portion of the Curie susceptibility with non-metallic character. In the region above 100 K, however, the magnetic susceptibility does not depend on temperature, which implies the delocalization of spins to have metallic character.

At the same temperature, magnetic susceptibility for polyaniline induced by organic acids is all of similar values. These dopants do not have any effect on magnetic susceptibility. However, magnetic susceptibility for polyaniline induced by solvents is very much dependent on these solvents. Particularly, the system of EB-CSA/acetic acid is distinguished in that the decreasing rate of magnetic susceptibility is highest in low temperature range. This is due to, we think, the formation of localized small spin-domains where the parallel spins are aligned with each other at low temperature. The formation of spin-domains increases net magnetic dipole and thus enlarges the magnetic susceptibility. As the temperature is raised, the localized spin-domains fade away rapidly giving the low values of magnetic susceptibility.

Table 1 lists the Pauli susceptibility χ^{pauli} and the total density of state $N(E_F)$ at Fermi level obtained from the value of χ^{spin} as $T \rightarrow \infty$ in the figures and from the Eq. (2), respectively. The Pauli susceptibilities of most samples are in the range of $\sim 5 \times 10^{-5}$ emu/mol in 2-ring unit, which coincides with the result of Cao and Heeger.[6] The total density of states falls on 1-2 state/eV in 2-ring unit.

Curie susceptibility which means χ^{spin} excluding Pauli susceptibility contribution is mostly observed below 100 K. The Curie spin concentration n_s^{curie} was obtained from the χ^{spin} and showed shown in Figure 3. The value of n_s^{curie} implies that when giving the 100 units (2-ring basis) of doped polyaniline, the corresponding number of 2-ring units is in the localized Curie spin states and the rest in the delocalized Pauli spin sites or undoped units. Curie spin concentration of polyaniline doped by organic acids which rarely depend on temperature is in the range of ~ 0.005 in 2-ring unit. The

Table 1. Values of χ^{pauli} and $N(E_F)$ obtained for the polyaniline samples

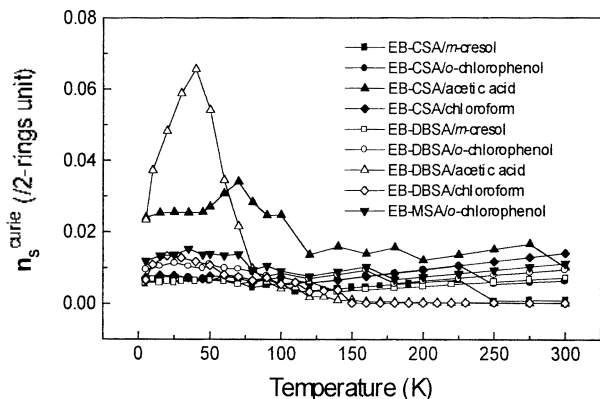| Sample	χ^{pauli} (emu/mol 2-ring unit)	$N(E_F)$ (state/eV 2-ring unit)
EB-CSA/m-cresol	4.882×10^{-5}	1.51
EB-CSA/o-chlorophenol	3.197×10^{-5}	0.989
EB-CSA/acetic acid	7.721×10^{-5}	2.39
EB-CSA/chloroform	4.229×10^{-5}	1.31
EB-DBSA/m-cresol	2.096×10^{-5}	0.648
EB-DBSA/o-chlorophenol	4.807×10^{-5}	1.49
EB-DBSA/acetic acid	8.423×10^{-5}	2.61
EB-DBSA/chloroform	5.957×10^{-5}	1.84
EB-MSA/o-chlorophenol	6.594×10^{-5}	2.04

Figure 3. Curie spin concentration versus temperature for the polyaniline induced by organic acid and solvent.

most solvents do not also show the temperature dependence except acetic acid. However, the systems acetic acid exhibit high Curie spin concentration up to 0.07/2-ring unit below 100 K. As mentioned above, this is due to the formation of localized small spin-domains of parallel spin alignment.

Furthermore, Curie spin concentration has the maximum point around 50 K. Curie spin concentration gradually increased with increasing temperature in the region under 50 K This is due to transition of spinless bipolarons into localized polarons by thermal energy. At higher temperature region from 50 K to 100 K, since localized polarons may become the delocalized polarons by residual thermal energy,[4] Curie spin concentration decreased. On the other hand, Pauli spin contribution is increased and finally Curie spin concentration is almost zero.

In conclusion, conducting polyaniline doped by organic acids and solvents shows paramagnetic behavior. In the region below 100 K, most spins are localized and thus have a large portion of the Curie susceptibility with non-metallic

character. However, at the region above 100 K, the magnetic susceptibility does not depend on temperature, which implies the delocalization of spins with metallic character. The Pauli susceptibility and the total density of states (both signs of spin) at the Fermi level ($N(E_F)$) of the sample are ~5 × 10^{5} emu/mol 2-rings unit and 1-2 state/eV 2-rings unit, respectively. Curie spin concentration shows a maximum point pattern around 50 K. Especially the effect of solvents is large in the case of EB-CSA and DBSA/acetic acid below 100 K. This solvent forms localized small spin-domains where spins are parallel to each other in polymer at low temperature region. These domains increase the net magnetic dipole, which enlarges the magnetic susceptibility. This phenomenon results from the solvent effects on the magnetic properties.

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