Low Thermal Conductivities of Undoped and Various Protonic Acid-Doped Polyaniline Films

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Thermal conductivities of undoped and various protonic acid-doped polyaniline films were measured by combination of a laser flash method and a scanning differential calorimeter. The thermal conductivities thus measured are in the range of conventional organic polymers, indicating that the doped polyaniline films have extremely low thermal conductivities among electrically conductive materials.

Electrically conducting aromatic polymers have attracted a great attention because of the electron-transporting property and considerable thermal stability. Among them, polyaniline is well studied due to its feasible background for wide applications to electronic devices.[1] Almost such application of polyaniline has been performed in a processed form, especially in a film.

On the other hand, thermal properties such as thermal diffusivities, specific heat capacities and thermal conductivities, of polyaniline films are crucially important from the viewpoint not only of fundamental aspect for academia but also of various processing and applications of the polymer, especially the thermoelectric application.[2,3] A few researches on polyaniline powders have been reported to elucidate the correlation between thermal conductivity and electric conductivity.[4,5] However, these discussions were carried out without considering thermal diffusivity. To our best knowledge no systematic researches on thermal conductivities of polyaniline films have been reported yet at wide range of temperatures above room temperature. Usually the thermal conductivities of polyaniline films are estimated from engineering plastics.[6]

In this letter, we first present thermal diffusivities, specific heat capacities, and thermal coductivities of undoped and various protonic acid-doped polyaniline films at wide range of temperatures above room temperature.

Undoped polyaniline film (insulative) and various protonic acids, such as 2-naphthalenesulfonic acid-, phosphoric acid-, and (±)-10-camphorsulfonic acid(CSA)-doped polyaniline films (1, 6, and 173 S cm^{-1}, respectively) as well as CSA-doped multilayered polyaniline film (188 S cm^{-1}) were prepared, as previously reported,[2,7,8] for studies on thermal transporting properties.

Thermal diffusivities were measured by a laser flash method.[9] Disk samples (ca. 10 mm in diameter) were set in an electric furnance, and heated to a target temperature under a reduced pressure (4.5×10^{-2} Torr). The front surface of the disk samples was irradiated with laser pulse. Temperature-change at the rear surface was monitored with an infrared detector.

Specific heat capacities were measured with a differential scanning calorimeter (Mac Science DSC-3200S).[10] Four-step temperature program was used: from 203 K to 263 K heated by 5 K min^{-1}, kept at 263 K for 20 min, from 263 K to 453 K by 10 K min^{-1}, and then kept at 453 K for 20 min. As a standard 12.9 mg of α-Al_2O_3 were weighed out and the sample sizes were chosen between 7.1 and 13.4 mg. Weight-difference of sample and reference pans used for the measurements were less than 0.1 mg.

Bulk densities were calculated from weights and diameters of the disk samples. Finally, thermal conductivities (κ) were calculated from thermal diffusivities (α), specific heat capacities (C_p) and densities (ρ) of the films using the following equation:[9]

$$\kappa = \rho \, \alpha \, C_p \qquad (1)$$

The polyaniline films showed considerably different electric conductivities according to the preparation method and a protonic acid (a dopant). However, the bulk densities are not significantly different from each other. All the films have low densities of 1.2 ~ 1.6 g cm^{-3}.

Thermal diffusivities of polyaniline films, reproducibly measured by the laser flash method, are shown in Figure 1. The polyaniline films exhibit extremely low thermal diffusivities at wide range of temperatures regardless of the electric conductivity. It is quite different from the results of polyaniline powders and polypyrrole films doped various dopants, as previously reported by Yoon et al.[4] and Tsutsumi et al.[11] Yoon et al. observed good correlation between electric conductivity and thermal conductivity of polyaniline powders. However, they did not consider thermal conductivity separately into thermal diffusivity and specific heat capacity. In contrast to inorganic materials, organic materials usually exhibit large values of specific heat capacity which has no direct correlation with concentration of electric carriers. Therefore, the specific heat capacity of organic materials should more contribute to thermal conductivity than that of inorganic materials. On the other hand, in the case of polypyrrole films, an increase of thermal diffusivities was observed when increasing in electric conductivites. They postulated an influence of degree of polymerization on both electric conductivity and thermal diffusivities to explain their results.[11] To investigate the influence of the degree of polymerization of polyaniline, thermal diffusivities of polyaniline pellets with two different molecular weights, doped by hydrogen chloride, were measured. Polyaniline pellets with higher (96000 Da, 14 S cm^{-1}) and lower molecular weight (39000 Da, 5 S cm^{-1}) showed the thermal diffusivities 2.4×10^{-3} and 2.3×10^{-3} cm^2 s^{-1}, respectively, indicating no correlations between thermal diffusivity and molecular weight. Highly electrically conducting semiconductor usually shows high thermal diffusivity because of the high order of atoms or a large amout of mobile electric carriers. Thermal diffusivity of semiconductor usually increases with increasing electric conductivity.[12] Therefore, the extremely low thermal diffusivity and no correlation with electric conductivity of polyaniline films in the present results are considered to be originated from their amorphous characters.[13] The thermal diffusivities gradually decreased with increasing in temperature. The temperature-dependences shown in Figure 1 are well consistent with that of phonon lifetime predicted theoretically.[14]

A differential scanning calorimeter (DSC) is a well-recognized tool for determination of specific heat capacities. The

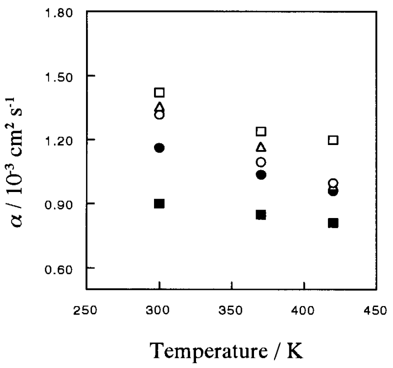

Figure 1. Thermal diffusivities (α) of undoped (○), 2-naphthalenesulfonic acid- (●), phosphoric acid-(△), (±)-10-camphorsulfonic acid- (□) doped polyaniline films, and (±)-10-camphorsulfonic acid- (■) doped multilayered polyaniline film at various temperatures.

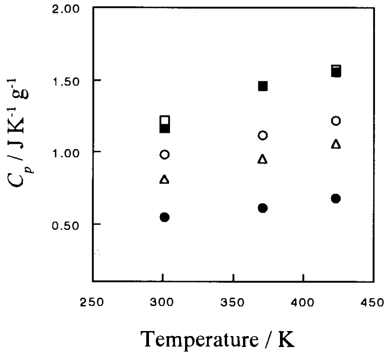

Figure 2. Specific heat capacities (C_p) of undoped (○), 2-naphthalenesulfonic acid- (●), phosphoric acid-(△), (±)-10-camphorsulfonic acid- (□) doped polyaniline films, and (±)-10-camphorsulfonic acid- (■) doped multilayered polyaniline film at various temperatures.

measurement under our conditions provided reasonable values of specific heat capacities and temperature-dependence for poly(4-bromostyrene) which is well studied.[10] The specific heat capacities of polyaniline films, shown in Figure 2, are higher than those of inorganic materials and still keep themselves in the range of those of organic polymers.[15] The CSA-doped polyaniline film has slightly higher specific heat capacities than others probably because of the low frequency-vibration modes due to the bulky alkyl group of the dopant.[10] The temperature-dependence of the specific heat capacity is postive for all the polyaniline films investigated here, which is the same with that of poly(4-bromostyrene) and those of most organic polymers.[10,15]

The thermal conductivities of polyaniline films, calculated according to eq. 1, are shown in Figure 3. All polyaniline films exhibit lower thermal conductivities at least in two order of magnitude than conventional inorganic semiconductors regardless of the doping ratio and electric conductivity. As previously mentioned, the polyaniline films are completely or dominantly amorphous. Thus, strong phonon scattering in amorphous materials usually results in low thermal conductivity.[16] These extremely low thermal conductivities of the polyaniline films, especially of the multilayered film, are of significant profit for thermoelectric figure of merits ($ZT = (S^2\ \sigma/\kappa)\ T$) when it is used as organic thermoelectric materials.[2]

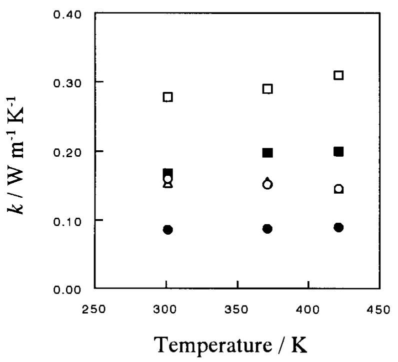

Figure 3. Thermal conductivities (κ) of undoped (○), 2-naphthalenesulfonic acid- (●), phosphoric acid-(△), (±)-10-camphorsulfonic acid- (□) doped polyaniline films, and (±)-10-camphorsulfonic acid- (■) doped multilayered polyaniline film at various temperatures.

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