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Articles

Hydrogen Bonding between Thioacetamide and Some N,N-dimethylalkylamides in Chloroform

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The near-IR spectra of thioacetamide were recorded for the investigation of hydrogen bonding between thioacetamide (TA) and N,N-dimethylalkylamides (DMF, DMA, DMP) in chloroform over the range of 5 °C to 55 °C. The $\nu_a +$ amide II combination band has been resolved into contributions from monomeric TA, 1:1 hydrogen bonded complex and 1:2 complex by the parameterized matrix modeling method. The association constants (K_a) of the complex have been obtained at various temperatures and used to determine the thermodynamic parameters for the hydrogen bonding by the usual Van't Hoff method. It was found that N,N-dimethylalkylamide forms less stable hydrogen bonded complex with TA in chloroform than in carbon tetrachloride.

Introduction

An understanding of the macromolecular conformation of protein or polypeptides in biological systems requires an examination of the various kinds of bonds that might be expected to form in a native protein. One interaction which undoubtedly contributes to the secondary structure of the protein is the amide-amide hydrogen bonding¹. Recently, the thermodynamics of hydrogen bond formation in model compounds containing carbonyl and amide groups has been studied in connection with the stability of protein structure²⁻⁸.

Amide to amide hydrogen bonding has been investigated by means of infrared spectroscopy and pure base calorimetric method⁹⁻¹¹. Relative strengths of the interaction for amide-amide and amide-water systems have been studied by near-IR and Raman spectroscopies^{12,15}.

Thioamide as a proton donor can be used for the study of the hydrogen bonding because no self-association is to be expected in the dilute solution. Thioacetamide and N,N-dimethylalkylamides (DMAA) system has been found very suitable for the study of amide-amide hydrogen bonding in carbon tetrachloride solution¹⁴. There have also been many studies of the solvent effects on the thermodynamics of hydrogen bond formation¹⁶⁻²⁰. The study of hydrogen bonding between amides in chloroform solution is of interest in assessing the role of hydrogen bonds in the secondary structure of proteins under conditions where amide-amide hydrogen bonds can compete with amide-solvent hydrogen bonds.

It has been demonstrated that the near-IR spectroscopic method is more suitable for systems of the type studied here (*i.e.*, systems with low equilibrium constants and small enthalpy changes) than other methods.

Experimental

Materials. Thioacetamide (TA), by Aldrich 99%, was dried at room temperature under reduced pressure for 24 hours and stored over P_2O_5 in a glove box. N,N-dimethylalkylamides (N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), N,N-dimethylpropionamide (DMP)), by TCI, were purified by distillation under reduced pressure, and stored over 3Å molecular sieves. Chloroform ($CHCl_3$), by Merk G. R., was purified by distillation, after refluxing with calcium chloride and P_2O_5 for about 1 to 2 days and stored over 4Å molecular sieves.

Near-IR measurements. All measurements were carried out with a Cary 17DX spectrophotometer. The $\nu_a +$ amide II combination band of TA was used for the determination of equilibrium constants. Special quartz cells (by Varian) of 5 and 0.5 cm path length were used for TA-DMAA- $CHCl_3$ and TA-DMAA solutions, respectively. The bands due to the DMAA and $CHCl_3$ were eliminated by placing a matched cell containing equal amounts of DMAA and $CHCl_3$ in the reference beam. Temperature was controlled with a constant temperature bath Polytemp, by Polyscience.

The concentration ranges of the proton acceptor (DMAA) and proton donor (TA) were 1-0.1 M and 0.1-0.01 M, respectively. The concentration ratio of proton donor/proton acceptor was sustained in such a way as to reduce the possibility of the self-association of proton donors. The molarity of the solutions was corrected at various temperatures from the change in density with the temperature of solutions.

Computer Resolution of Spectrum. It is indispensable to separate overlapped bands for the spectroscopic determination of equilibrium constants and molar absorptivities of the 1:1 and 1:2 complexes. Though it was known that over-

lapped bands of TA and TA-DMAA in CCl_4 could be resolved into each components by using band shape functions¹⁴, we used the parameterized matrix modeling method. It was recognized that the asymmetry of the bands, caused by the interaction between TA and CHCl_3 , made it difficult to use band shape function.

Beer's law for three-component system takes the form

$$A(\lambda) = E_a(\lambda) C_a + E_1(\lambda) C_1 + E_2(\lambda) C_2 \quad (1)$$

where E_a , E_1 , E_2 are the wave lengths dependent molar absorptivities of the acceptor, the 1:1 complex and 1:2 complex, and C_a , C_1 , C_2 are the corresponding molar concentrations. When the spectra over a range of concentrations are known, the generalized form of Lambert-Beer's law can be represented by the matrix equation.

$$A = EC \quad (2)$$

where A is the n (number of wavelength) \times m (number of sample) absorbance matrix, E is the $n \times 3$ matrix of molar absorptivities and C is the $3 \times m$ matrix containing the equilibrium concentrations. In Eqn.(2) the elements of matrix C and two rows of the E matrix are initially unknown. Assuming K_1 and K_2 are used as adjustable parameters, the concentrations C_1 and C_2 can be expressed in terms of C_a° , C_a° , K_1 , K_2 and each other,

$$C_1 = \frac{R \pm (R^2 - 4K_1^2(C_a^\circ C_a^\circ - 2C_a^\circ C_2 - C_a^\circ C_2 + 2C_2^2))}{2K_1} \quad (3)$$

$$C_2 = \frac{K_2(C_a^\circ C_1 - C_1^2)}{2K_2 C_1 + 1} \quad (4)$$

and

$$C_a = C_a^\circ - C_1 - C_2 \quad (5)$$

where $R = K_1 C_a^\circ + K_1 C_a^\circ - 3K_1 C_2 + 1$

After the matrix C has been obtained by successive iteration, it is used to solve the unknown elements in the matrix E'

$$E' = AC^T(CC^T)^{-1} \quad (6)$$

where E' is a complete matrix containing the values of E_1 , E_2 and E_a . A new absorbance matrix can be generated from Eqn. (2)

$$A' = E' C \quad (7)$$

The elements of A' may or may not differ from the elements of A . The values of K_1 and K_2 can be determined by varying the K_1 and K_2 in some systematic way and minimizing the chi-squared error between the calculated and measured data. The method of the simplex search was used to minimize the chi-squared error²¹.

Results and Discussion

The near-IR spectra of 5×10^{-3} M TA in CHCl_3 is shown in Figure 1 in the range of 1930–2200 nm. This shows the combination bands of $\nu_a +$ amide II, $\nu_s +$ amide II, $\nu_a +$ amide III and $\nu_s +$ amide III which are in good agreement with the spectrum of primary amides observed by Krikorian and Mahpour²². It has been demonstrated that all of the absorption bands of TA in the near-IR region can be attributed to

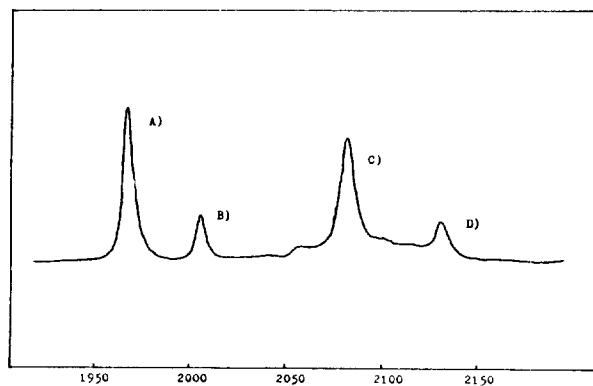


Figure 1. Near-IR spectrum of 5×10^{-3} M TA at 25 °C in CHCl_3 .^a Band: A) $\nu_a +$ Amide II; B) $\nu_s +$ Amide II; C) $\nu_a +$ Amide III; D) $\nu_s +$ Amide III.

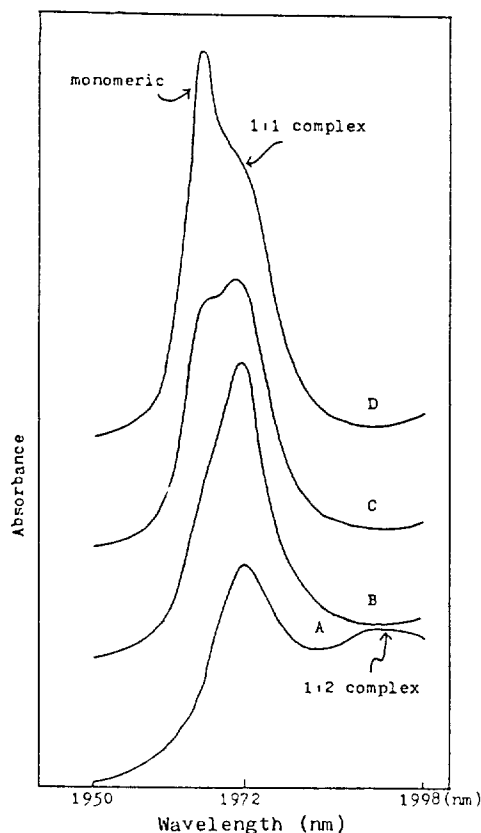


Figure 2. Spectra of $\nu_a +$ amide II combination band of TA in TA-DMF- CHCl_3 solutions at 25 °C. A; volume fraction of CHCl_3 ; 0.6, B; 0.9, C; 0.95, D; 0.98.

characteristic hydrogenic vibrations of the amide group²². In order to investigate the hydrogen bonding of TA and DMAA in CHCl_3 , it is necessary to choose the most suitable bands of TA. It was reported that $\nu_a +$ amide II combination band is the most promising one to investigate the hydrogen bond for this system rather than other combination or overtone bands¹⁴.

Figure 2 presents a spectrum of TA-DMF solution and spectra of dilutions of TA-DMF solutions in CHCl_3 , which shows three overlapped bands due to monomeric TA, 1:1 complex and 1:2 complex. Figure 3 represents the temperature dependence of the spectra of TA-DMP solutions in

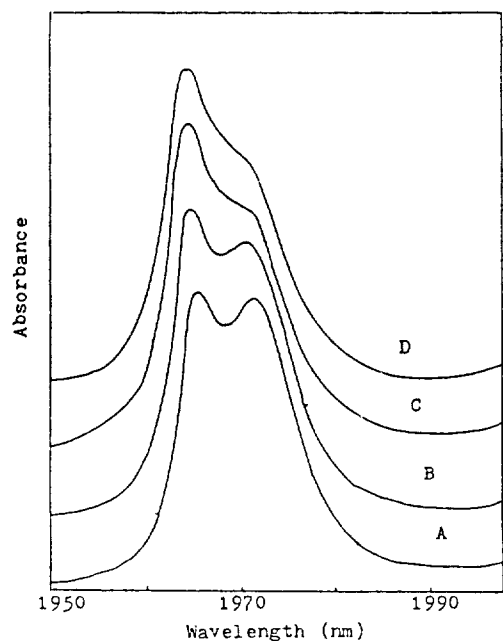


Figure 3. Temperature dependence of the spectra. The ratio of TA to DMP remains constant at 9 to 1, and the volume fraction of CHCl_3 is 0.97. A) 5°C, B) 15°C, C) 45°C, D) 55°C.

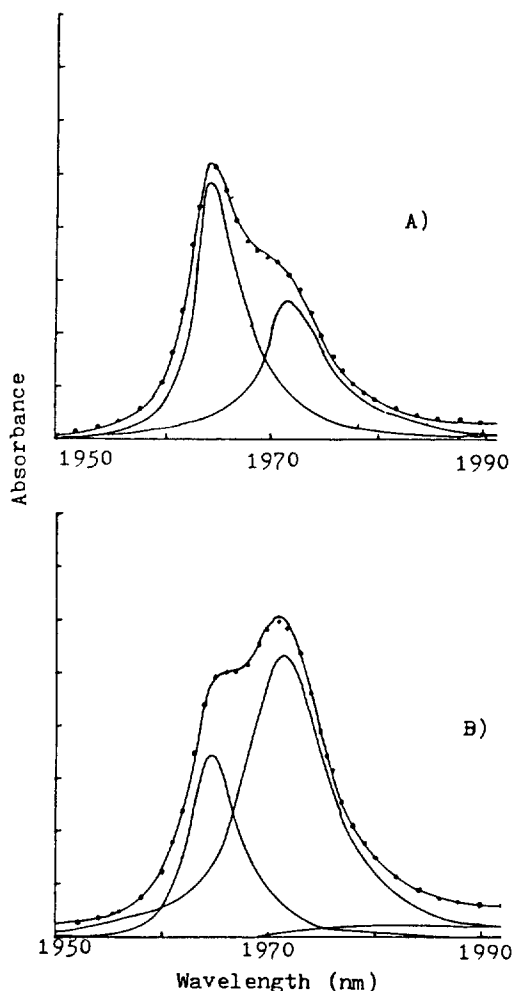


Figure 4. Concentration dependence of the ν_{NH}^+ amide II band of TA at 25°C. A) 0.00985M TA, B) 0.0567M TA.

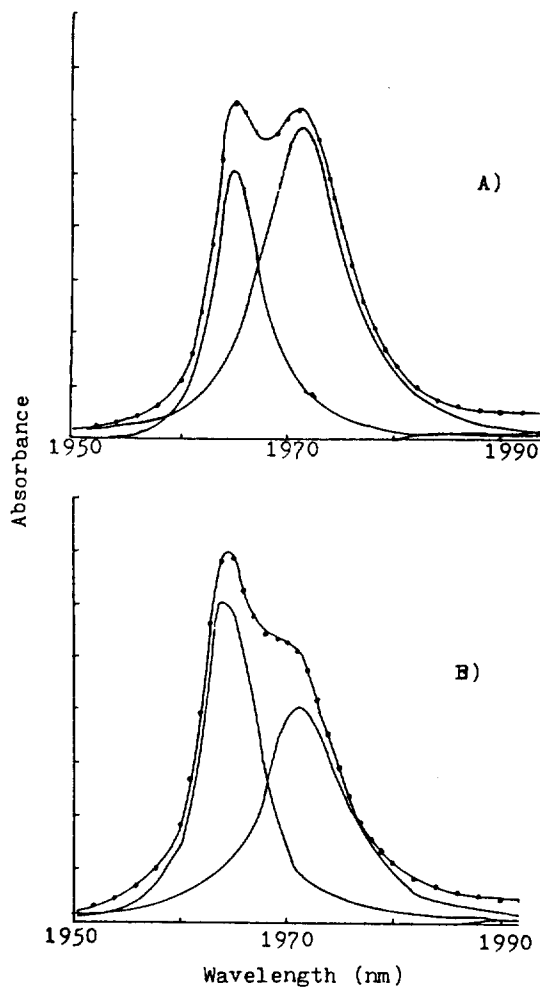


Figure 5. Computer resolution of spectra of 3% TA-DMP in CHCl_3 . A) 5°C, B) 45°C.

CHCl_3 .

The hydrogen bonding between TA and DMAA forms a two step equilibria. The parameterized matrix modeling method makes it possible to determine association constants for the 1:2 complex as well as that for the 1:1 complex. It was found that the association constant of the 1:2 complex evaluated by this method did not have the anticipated outcome and the formation of the 1:2 complex did not occur to any detectable extent except at very high concentrations. Experiments were carried out in very dilute solutions to eliminate the influence of activity terms. However, even in this condition, contribution of the 1:2 complex has been considered to obtain more accurate results for the 1:1 complex. It was also assumed that the activity coefficients of species are values of unity. Figure 4 shows the results of the computer resolution of the spectra of TA-DMP solutions at various concentrations. At low concentration the observed spectrum is resolved into only the components of the monomeric TA and the 1:1 complex. While, there appears to be little contribution from the 1:2 complex with increasing concentration. This suggests that the contribution of the 1:2 complex has to be considered in this system.

The area ratio of the monomeric TA to 1:1 TA-DMP complex gradually increases with successive dilutions. This means that the hydrogen bonding between TA and DMP is

Table 1. Spectroscopic Thermodynamic Parameters for the Hydrogen Bonding of TA with DMAA in CHCl₃

Temperature (°C)	ΔG° (KJ mol ⁻¹)		
	DMF	DMA	DMP
5	-4.33	-4.16	-3.99
15	-4.23	-3.96	-3.74
25	-4.06	-3.78	-3.59
35	-3.98	-3.67	-3.41
45	-3.78	-3.45	-3.25
55	-3.61	-3.29	-2.99

Table 2. Spectroscopic Thermodynamic Parameters for the Hydrogen Bonding at 25 °C

	in CHCl ₃			in CCl ₄		
	DMF	DMA	DMP	DMF ^a	DMA ^b	DMP ^c
K	5.06	4.06	4.26	58.3	51.3	50.0
ΔG°	-4.06	-3.78	-3.59	-10.1	-9.9	-9.8
ΔH°	-8.49	-8.89	-9.29	-13.4	-14.4	-14.6
ΔS°	-14.8	-17.1	-19.1	-10.6	-15.5	-16.2

Units: ΔG° (KJ.mol⁻¹), ΔH° (KJ.mol⁻¹), ΔS° (J.mol⁻¹.deg⁻¹).

^aFrom ref. 14. ^bFrom ref. 23. ^cFrom ref. 15.

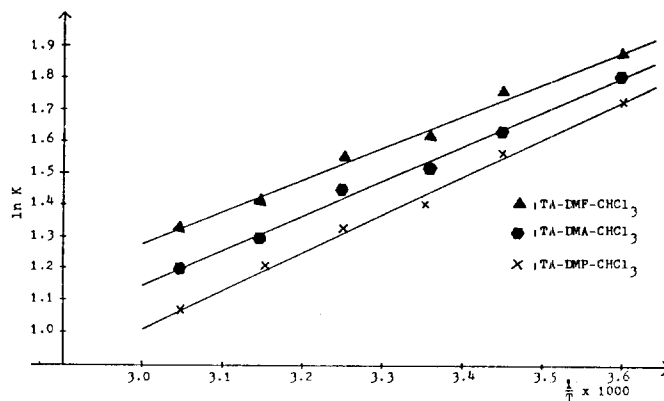
breaking upon dilutions with CHCl₃.

A series of temperature dependent spectra of TA-DMP solutions in a given concentration are presented in Figure 5. As expected, the peak of the monomeric TA increases and that of the 1:1 complex decreases in intensity with increasing temperature. It indicates that equilibrium constants for the hydrogen bond decrease with temperature and the interaction is exothermic. Values of K_1 and ΔG° for the hydrogen bonding between TA and DMAA at various temperatures are obtained and listed in Table 1. Other thermodynamic functions for the hydrogen bonding can be calculated from the Van't Hoff equation.

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^\circ}{R} \quad (8)$$

If $\ln K$ is plotted against $1/T$, ΔH° can be obtained from the slope. Figure 5 shows the plots of $\ln K$ vs. $1/T$ for TA-DMF, TA-DMA and TA-DMP systems in CHCl₃. The slope is almost constant in the range of 5 °C to 55 °C. This means that the enthalpy change is practically constant in this range. The evaluated ΔH° and ΔS° are also listed in Table 1.

Thermodynamic parameters taken from previously reported spectroscopic studies on TA-DMAA system in CCl₄ are given in Table 2 with the data for the TA-DMAA complex in CHCl₃ studied here^{14,15,23}. The enthalpy changes for the hydrogen bonded complexes of TA with DMF, DMA and DMP are -8.49, -8.89 and -9.29 KJ/mol, respectively, which indicates that the DMP C=O is about a 0.4 KJ/mol better proton acceptor than the DMA C=O and about 0.8 KJ/mol better proton acceptor than DMF C=O. The methyl group is more polarizable than hydrogen and stabilizes the amide resonance form $\text{O}=\text{C}=\text{N}^+$ to a great extent than hydrogen does. Thus the carbonyl group of DMP should be more basic than those of DMA and DMF. Del Bene's ab initio-SCF cal-

**Figure 6.** Temperature dependence of $\ln K$ for the DMF, DMA and DMP with TA.

culations of the effects of methyl substituents on amide hydrogen bonding predicted that the carbonyl of NMA should be a better proton acceptor than the carbonyl of NMF⁶. The results of this study are in good agreement with the predicted increase in carbonyl basicity due to methyl substitution. The entropy changes also show a clear trend with methyl substitution. The unfavorable trend of entropy change would be attributed to the increased molecular rigidity from methyl substituents.

The data given in Table 2 show that the enthalpy change for the formation of the TA-DMAA adduct in CCl₄ is about 5 KJ/mol more exothermic than for the corresponding adduct formation in CHCl₃. While it has been suggested that for a given donor-acceptor pair the intrinsic enthalpy of hydrogen bond formation should be nearly the same regardless of solvent. Thus it can be concluded that the differences in enthalpy change are largely due to the solvation effect. The value of K_1 reported here is about 1/10 times the value given by Kim, Huh and Lee^{14,15,23} for TA-DMAA dimerization in carbon tetrachloride solution, reflecting the strong competition between dimerization and solvent interaction in the studied system. When the complex is formed in CHCl₃, the hydrogen bonding interaction between DMAA C=O and chloroform hydrogen should be considered. William Klemperer, *et al.*² estimated that the magnitude of the energy of interaction of chloroform with an amide is about 8 KJ/mol. When the interaction of amide carbonyl with CCl₄ is considered, their results are in good agreement with our prediction. The obtained results do indicate that even a relatively weak proton donor, such as chloroform, reduces considerably the overall enthalpy change accompanying amide to amide hydrogen bond formation because a weak bond of amide to solvent has to be broken in the process.

Conclusions

The association constants for the hydrogen bond formation between TA and DMAA have been obtained from the near-IR spectra by means of the parameterized matrix modeling method. Thermodynamic data show that the strength of hydrogen bonding between amides increases with methyl substitution and the inter-amide hydrogen bonded complex is more stable in CCl₄ than in CHCl₃.

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Conduction Mechanism for PAP and Comparison of Physical Properties of PAP with other Polyaniline-based Conducting Polymers

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Polyaniline perchlorate (PAP) was synthesized by the chemical oxidation of aniline using ferric perchlorate as a strong oxidant. The electrical conductivity of PAP was measured at temperatures from -170 to 25 °C. It is suggested from the conductivity measurements that the conduction mechanism for PAP is a polaron hopping conduction. From the dependence of resistivity on the reciprocal temperature, the activation energy was computed to be 0.072 eV. From the comparison of the ESR parameters and conductivity at 25 °C for the polyaniline-based conducting polymers, the conductivities of PAP, PATFB and PATS increase with increasing ΔH_{pp} , decreasing A/B ratio and decreasing g-value, respectively. It is shown by TGA results for PAP, PATFB and PATS that the maximum weight loss rates (Pr) are 0.185 (at 269 °C), 0.366 (at 324 °C) and 0.23 mg/min (at 338 °C), respectively.

Introduction

As shown by previous studies¹⁻⁵, many conjugated polymers have been produced in efforts to obtain conducting polymers with higher conductivity. In particular, conducting polymers doped with a variety of chemical species have been synthesized extensively to obtain systems having semiconducting or metallic properties. These materials are obtained by the electrochemical or chemical doping technique using electron acceptors or donors. Conducting polymers are important from a basic scientific point of view and for various technological applications. They are useful materials for batteries, microelectronic devices and electrochromic displays. They are also being applied in the new fascinating areas of condensed matter physics. Hitherto, many studies on anion- or cation-doped polymers produced by chemical or electrochemical doping methods have been reported. Examples of such polymers include polyacetylene, poly-p-phenylene and polypyrrole-based conducting polymers. Satisfying re-

sults have been obtained from these materials.

Chiang *et al.*² have reported that the electrical conductivity of halogen-doped polyacetylene can be increased by more than eight orders of magnitude. The associated thermal activation energy decreases from initial values of about 0.3 eV to 0.01 eV, and the maximum room temperature conductivity with iodine as dopant exceeds 500 (ohm-cm)⁻¹. Mermilliod *et al.*³ reported that polypyrrole could be obtained by a very simple one-step chemical oxidation of monomer using a strong oxidant in various solvents. Studies on conducting polymers doped with the perchlorate anion can also be found in reports by Pfluger¹ and Mermilliod³. These researchers synthesized the polypyrrole perchlorate by chemical oxidation of pyrrole using a strong oxidant, ferric perchlorates. The oxidized polypyrrole is stable and can even be handled in air without changes in its electrochemical properties. Also, study of this chemically synthesized polypyrrole perchlorate has shown satisfying results in such applications as electrode materials for secondary batteries. Shirakawa *et al.*⁶ reported