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Pressure-Induced Enhancement of the Ferromagnetic Intermolecular Interaction of an α-Nitronyl Nitroxide Organic Radical

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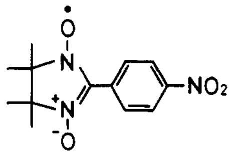
The effect of high pressure on the ferromagnetic properties of a crystalline sample of an organic radical, 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide (I), has been studied with the use of a combination of a Faraday susceptometer and a Be–Cu high-pressure clamp cell. The magnetic susceptibility of I increases markedly with increasing pressure at low temperatures, and furthermore its increment increases monotonically with decreasing temperature down to about 5 K. The Weiss constant under a pressure of 9 kbar corresponds to a 40% increase in the ferromagnetic intermolecular interaction, and the magnetization at 9 kbar also comes to saturation more rapidly compared with the behavior under an ambient pressure. A simple calculation of the intermolecular overlap integrals between the frontier orbitals can semiquantitatively interpret the pressure-induced enhancement of the ferromagnetic coupling.

Introduction

The magnetic properties of organic/molecular solids have been extensively studied, and the search for ferromagnetism in them is of current interest.[1,2] Recently, we have discovered weak ferromagnetic (FM) coupling in an α-nitronyl nitroxide, 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide (I). This



I

radical possesses an FM intermolecular interaction in a crystalline state comparable to a thermal energy of 1 K, although it does not exhibit a phase transition to a 3-D FM ordered state down to 2 K.[3,4] We have also determined the crystal structure[5] of I and examined the magnetic properties of some derivatives of I[4,6] to study the magnetochemical and the magnetostructural correlations for FM coupling. The crystal of nitroxide I has a 2-D network structure linked mainly by the Coulomb attraction force between N$^{\delta+}\cdots$O$^{\delta-}$.[5] The molecular orbital (MO) calculation[5] suggests that the intermolecular overlaps between SOMO–NHOMO and between SOMO–NLUMO are much larger than that between SOMO–SOMO,[7] at the N$\cdots$O contact point in the 2-D network. This feature in the intermolecular conformation is considered to result in FM coupling, as previously discussed.[4,8] More recently, Wudl et al. have reported the presence of another polymorph of I that has a 1-D stacking structure and weak FM coupling.[9]

Physical measurements under high pressure have been useful and important for the study of organic/molecular solids. For example, the discovery[10] of superconductivity in (TMTSF)$_2$PF$_6$ under high pressure is one of the prime examples using this technique. It has been demonstrated theoretically[8,11,12] and experimentally[13,14] that the FM intermolecular interaction depends greatly on the intermolecular conformation as well as on the intramolecular electronic state. High pressure could, therefore, bring about a large change in the FM behavior in a molecular solid, and the pressure dependence could give us important information about the FM interaction and, in some cases, about the magnetic ordering. The FM coupling in organic crystals is generally known to be rather weak,[15-18] and high pressure may prompt a phase transition into a 3-D FM ordered state in such FM organic systems. For these reasons, we have initiated a study of the effect of high pressure on organic/molecular ferromagnetism.

In this paper, we describe the observed magnetic properties of the FM nitroxide I under high pressure up to 9 kbar. The pressure dependence of the FM properties is semiquantitatively interpreted in terms of the pressure dependence of the intermolecular orbital overlap.

Experimental Section

The radical I was prepared by the literature procedure,[19] and its recrystallization from benzene produced blue-green columnar crystals. These crystals correspond to the β-phase identified by Wudl et al.[9]

A quasi-hydrostatic pressure was maintained on about 30 mg of the nitroxide I with the pressure fluid, Daphne 7373 oil (Idemitsu Co. Ltd., Tokyo), in a miniature Be–Cu pressure clamp cell of 52-g mass shown in Figure 1. The pressure was calibrated with a Manganin gauge at room temperature in a separate ex-

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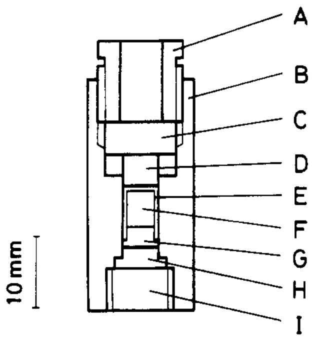

Figure 1. Be–Cu pressure clamp cell suitable for high-pressure static magnetic susceptibility studies of up to 10 kbar: A, locking screw; B, clamp cylinder; C, piston cap; D, piston; E, teflon sample cell; F, sample and pressure fluid; G, sample cell cap; H, piston; I, retaining screw.

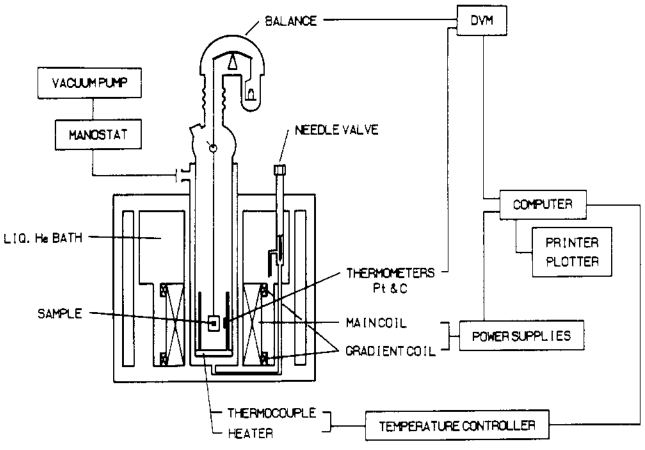

Figure 2. Construction of the Faraday magnetosusceptometer system.

periment. The pressure retained at low temperatures was determined by measuring the superconducting transition temperature of Pb.[20] The decay of pressure at 7 K was about 3% of its initial pressure clamped at room temperature. The magnetic data of this clamp were experimentally determined as follows: the diamagnetic susceptibility $\chi_d = -7.2 \times 10^{-8}$ emu g^{-1} and the Curie constant $C = 3.0 \times 10^{-6}$ emu K g^{-1}.

Static magnetic susceptibility and magnetization under high pressure were measured with a standard Faraday susceptometer similar to those employed by the others.[21,22] The construction of the susceptometer system is schematically illustrated in Figure 2. A homogeneous field of up to 50 kOe and a field gradient of up to 1 kOe cm^{-1} are produced by separate superconducting magnets set in a cryostat (Oxford Instruments Ltd.). The relation between the loading current and the generated field is calibrated with a Copal TC-8101A Hall generator. The magnetic force is detected by a Cahn 1000 electric microbalance whose maximum loading capacity is 100 g. Sample temperatures below 20 K are measured with a carbon resistor and from 20 to 300 K with a Pt resistor. These thermometers are calibrated by measuring the magnetic susceptibility of a paramagnetic compound and then by the superconducting transition temperatures of Pb, Sn, and In. Temperatures above about 6 K are controlled with an Oxford ITC4 temperature controller. Temperature control below about 6 K is carried out by regulating a manostat and a needle valve. Through an HP 3457A multimeter, the outputs from the electric balance and the thermometers are processed by an NEC PC9801vm microcomputer, which is also used to control the temperature controller and the power supplies for the superconducting magnets. The temperature dependence of the magnetic susceptibility above 6 K can be measured automatically.

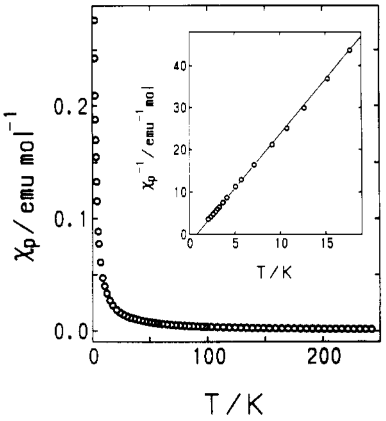

Figure 3. Temperature dependence of the paramagnetic susceptibility of I at ambient pressure. The inset shows the reciprocal susceptibility below 20 K. The straight line in the inset is calculated by the Curie–Weiss law. The experimental error bar is within the size of each plotted circles (from ref 3) .

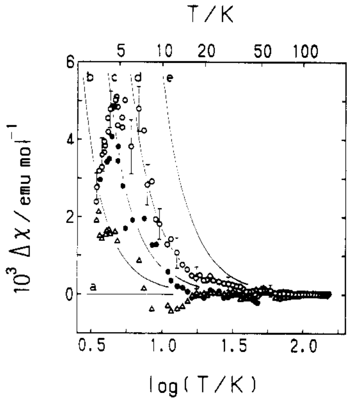

Figure 4. Temperature dependence of the magnetic susceptibility of I at three different high pressures: 9 (○), 6 (●) and 3 kbar (△). The difference in magnetic susceptibility between ambient pressure is plotted as a function of common logarithm of temperature. The solid curves, a–e, are the theoretical ones of eq 1 for $\theta(P)$ = 0.90 (a), 0.95 (b), 1.05 (c), 1.25 (d), and 2.00 K (e), respectively.

Results and Discussion

Temperature Dependence of the Magnetic Susceptibility. Figure 3 shows the temperature dependence of the paramagnetic susceptibility, χ_p, of the radical I at an ambient pressure, which was reported previously.[3,4] The inset shows the reciprocal χ_p below 20 K. χ_p follows the Curie–Weiss law with $C = 0.375$ emu K mol^{-1} and a positive Weiss constant of $\theta = +0.9$ K, indicating a weak FM intermolecular interaction in I.

The temperature dependence of the magnetic susceptibility, χ, of the radical I in the high-pressure cell was measured at 30 kOe at atmospheric pressure and 3, 6, and 9 kbar between 3 and 150 K. The differences, $\Delta\chi = \chi(P) - \chi(0)$, are plotted as a function of the common logarithm of the temperature in Figure 4, where the saturation effect of the magnetization at low temperatures is not corrected.[23] Compensation for the pressure dependence of χ of both the pressure cell and the pressure fluid are not carried out, but it has been confirmed in a separate experiment that

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(23) In this paper, the magnetic susceptibility is defined as M/H, which could have a deviation from the original definition, $\lim_{H\to 0}(M/H)$ in the low-temperature range with the magnetization saturation. Unfortunately, it is difficult to correct this effect, because the magnetization curve of I depends on temperature.

these extrinsic contributions are negligibly smaller than the observed $\Delta\chi$ shown in Figure 4. The dependence of the diamagnetic susceptibility, χ_d, of I on pressure is also likely to be negligible because χ_d itself is of the order of 10^{-4} emu mol^{-1}.[3] Therefore, $\Delta\chi$ in Figure 4 is considered to result from the intrinsic change in the paramagnetic susceptibility of I.

The open circles in Figure 4 show $\Delta\chi$ measured at 9 kbar. $\Delta\chi$ is almost zero in the high-temperature range. A separate measurement showed that there is little effect of pressure up to 250 K. Below 20 K, $\Delta\chi$ suddenly increased with decreasing temperature and reached a maximum of about 5×10^{-3} emu mol^{-1} near 5 K. However, $\Delta\chi$ decreased abruptly after passing through the maximum: it was still positive at about 3 K, the lowest temperature attainable in our apparatus. The closed circles and the triangles in Figure 4 show the results at 6 and 3 kbar, respectively. They show a temperature dependence of $\Delta\chi$ similar to that observed in the 9-kbar experiment, but the maximum $\Delta\chi$ clearly decreases in magnitude with decreasing pressure. Furthermore, the temperature at the maximum $\Delta\chi$ seemed to decrease slightly with decreasing pressure. The study of the temperature dependence of the magnetic susceptibility under high pressure confirmed that χ of I increases in magnitude with increasing pressure and that the increment in susceptibility, namely $\Delta\chi$, increases with decreasing temperature below 20 K and has a maximum at around 5 K.

The increase in χ indicates enhancement of the paramagnetism and could be due to the enhancement of the FM intermolecular coupling in I as the pressure increases. Assuming that the Weiss constant, which expresses the magnitude of magnetic coupling, depends on pressure, $\theta(P)$, we can write $\Delta\chi$ as

$$\Delta\chi = C/(T - \theta(P)) - C/(T - 0.9) \qquad (1)$$

The solid curves, a–e, in Figure 4 are the theoretical ones for some different $\theta(P)$ values. The theoretical curves are found to reproduce the sudden increases in $\Delta\chi$ below 20 K very welll, while they cannot explain the decreases below 5 K.

There may be two possibilities for the divergence of the theoretical curves below 5 K. One is the saturation effect of the magnetization; the $\Delta\chi$ measurements were done under a field of 30 kOe and the saturation appearing at low temperatures may result in a decrease in $\Delta\chi$. The other is the presence of an antiferromagnetic (AFM) interaction, strictly speaking, a metamagnetic behavior. This compound has a 2-D network structure and an MO calculation suggests that an FM interaction occurs in this network.[5] However, it is still possible that the internetwork interaction is AFM, which may also decrease $\Delta\chi$ in the low-temperature range.

Field Dependence of the Magnetization. The magnetization curves of I at ambient pressure were reexamined at 3.5 and 4.8 K up to a field of 50 kOe, to compare with the following data at high pressure. The open circles and triangles in Figure 5, where M is plotted as a function of H/T, show the results at 3.5 and 4.8 K, respectively. The results here agree well with those reported previously.[3,4] Magnetization of the paramagnetic spin entities is given theoretically as[24]

$$M = M_s B_J(x) \qquad (2)$$

with

$$x = Jg\mu_B H/k_B T$$

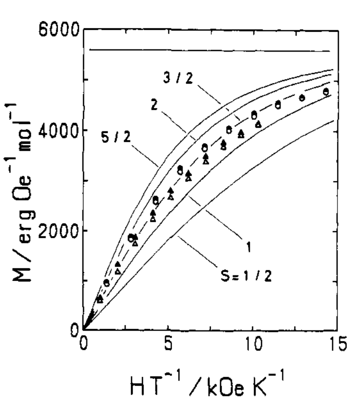

Figure 5. Pressure and temperature dependence of the magnetization curve of I. The open cirvles (3.5 K) and triangles (4.8 K) show the magnetization at ambient pressure, and the closed circles (3.5 K) and triangles (4.8 K) at 9 kbar. The experimental error bar is within the size of each plotted circles or triangles.

where M_s is the saturation magnetization, J is the quantum number of the total angular momentum, g is the Lande g factor, μ_B is the Bohr magneton, $B_J(x)$ is the Brillouin function for J, and k_B is the Boltzmann constant. The g factor of the nitroxide radical is known to be about 2.006[19] and, therefore, $J = S$ (spin quantum number) is a good approximation in our case. The solid curves in Figure 5 are the theoretical ones for $J = S = n/2$ ($n = 1, 2, \cdots, 5$; $L = 0$) paramagnetic spin entities. They are drawn so as to reach $M_s = 5.60 \times 10^3$ erg Oe^{-1} mol^{-1}, which corresponds to the observed Curie constant of I.[3,4] The magnetization curve of I indicates a higher spin multiplicity with decreasing temperature, which is due to the fact that the FM coupling in I is comparable to the thermal energy of this measurement temperature.

The effect of the 9-kbar pressure on the field dependence of the magnetization of I was examined in the same temperature region and under the same conditions as the ambient pressure measurements, to confirm the pressure-induced enhancement of the FM coupling and to understand the reason for the abrupt decrease in $\Delta\chi$ below 5 K. The closed circles and triangles in Figure 5 show the 9-kbar magnetization at 3.5 and 4.8 K, respectively. The magnetization curves at 9 kbar exhibit more rapid saturation compared with the corresponding curves at ambient pressure, which firmly supports the pressure-induced enhancement of the FM coupling in I. It is an important observation that at a constant temperature, the magnetization at 9 kbar is larger than that at ambient pressure in the whole field range of up to 50 kOe; moreover, spin-flop behavior was not observed. This fact suggests that the contribution of AFM interaction to the decrease in $\Delta\chi$ below 5 K is negligible. The decrease in $\Delta\chi$ shown in Figure 4 can be ascribed to a saturation of the magnetization. Both the increase below 20 K and the decrease below 5 K in $\Delta\chi$ are induced by the enhancement of the FM interaction.

The high-pressure magnetization also indicates that the pressure increases the FM coupling in I. The results of these measurements are quite consistent with the magnetic susceptibility measurements described earlier. However, a hysteresis loop of magnetization was not observed at 9 kbar and 3.5 K. The nitroxide I would still be in a paramagnetic state under these conditions.

Enhancement of the FM Interaction. Equation 1 is valid in the temperature range without the saturation effect, namely above about 5 K in our case. Therefore, we have to use $\Delta\chi$ above 5 K for the fit with eq 1. The observed $\Delta\chi$ at 3, 6, and 9 kbar correspond approximately

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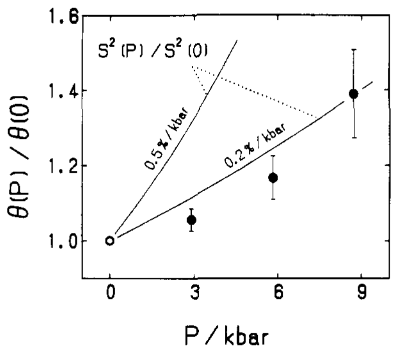

Figure 6. Pressure dependence of the Weiss constant of I. The two solid curves show the pressure dependence of S^2, calculated by assuming constant compressibilities of 0.2 and 0.5% kbar^{-1}. See the text.

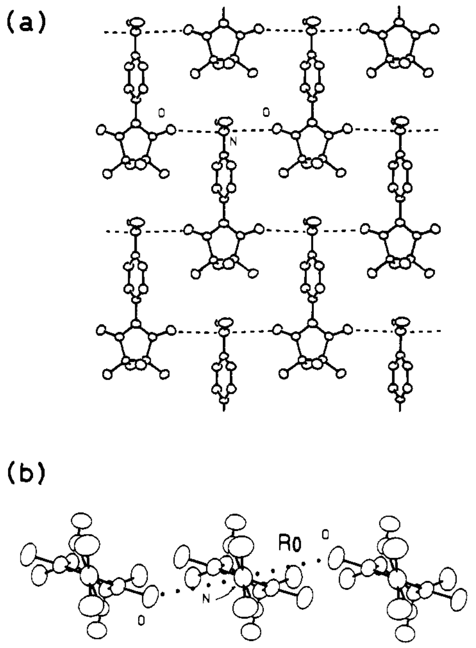

Figure 7. (a) Projection of the structure of I along the *b* axis. (b) Molecular arrangement of I in the 2-D network projected on the *ab* plane. The N···O distance is R_0 = 3.359 (8) Å (from ref 5).

to the theoretical curves for $\theta(P)$ = 0.95 (b), 1.05 (c), and 1.25 K (d), respectively. It is not realistic to discuss these numerical values of $\theta(P)$ directly, because $\theta(0)$ = +0.9 K itself includes rather a large error of ±0.5 K. However the enhancement factor $\theta(P)/\theta(0)$ may be more reliable, because it should not depend on $\theta(0)$. Thus, $\theta(P)/\theta(0)$ is plotted as a function of pressure in Figure 6. The FM coupling is increased by about 40% by applying 9-kbar pressure.

The pressure-induced enhancement of the FM coupling can be interpreted by taking into account the pressure dependence of the intermolecular orbital overlap. Figure 7a shows the 2-D network of the nitroxide I (β-phase).[5] This 2-D network is linked mainly by the Coulomb attraction force between the $N^{\delta+}$ in the NO_2 group and the $O^{\delta-}$ in the NO group.[5] Figure 7b shows the intermolecular conformation in this network, which is projected along the 2-D plane. The N atom is located at the midpoint between the O atoms in the neighboring radicals, with the N···O distance of R_0 = 3.359 (8) Å. The nitrophenyl plane is almost perpendicular to the O···N···O vector.

An MO calculation[5] indicated that the unpaired electron occupying the SOMO is localized on the side of the nitronyl nitroxide and has little population in the nitrophenyl ring, whereas NHOMO and NLUMO are distributed in the nitrophenyl ring. The FM interaction of I is considered to originate mainly in the SOMO–NHOMO and/or SOMO/NLUMO intermolecular overlaps at the contact points in the 2-D network.[5] These overlaps bring about the resonance with the triplet charge-transfer (CT) excited state.[8] The admixture of the triplet CT state results in the FM intermolecular interaction. This idea was originally proposed by McConnell.[25] The stabilization energy of the triplet state, namely the magnitude of FM coupling, is given to be proportional to the square of the overlap integral between the CT interacting orbitals, according to perturbation theory.[26]

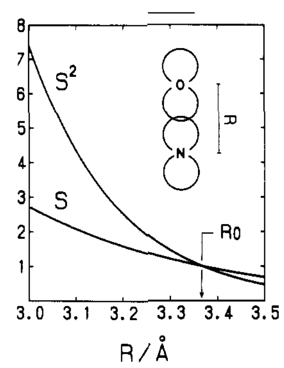

Figure 8. Distance dependence of the 2pσ-2pσ overlap integral S and S^2 between oxygen and nitrogen. S and S^2 are normalized by those at the observed N···O distance, R_0 (see Figure 7); $S(R_0)$ = 3.74 × 10^{-3} and $S^2(R_0)$ = 1.40 × 10^{-5}.

Intermolecular orbital overlap in the 2-D network of I would approximate to the 2pσ–2pσ type overlap between an oxygen and a nitrogen, as shown in the inset of Figure 8. The distance dependence of the 2pσ–2pσ overlap integral, S, between Slater-type orbitals was calculated by using eq 31 in ref 27 as reported by Mulliken et al. The calculated S and S^2 are plotted as a function of distance in Figure 8, where S and S^2 are normalized by those at the observed N···O distance, R_0 (see Figure 7). Since neither the crystal structure under high pressure nor the compressibility data have been reported for I, we assume a linear relation between the applied pressure and the compressive axial strain, with the compressibility reported[28-32] for typical aromatic organic crystals 0.2–0.5% kbar^{-1}. The two solid curves in Figure 6 show the calculated dependence of normalized S^2 on pressure, by assuming constant compressibilities of 0.2 and 0.5% kbar^{-1}. The pressure dependence of the Weiss constants of I in Figure 6 deviate slightly from the region between the two curves with small differences. The normalized S^2, based on the above simple model and calculation, gives a pressure dependence of the same degree as does the enhancement factor of the Weiss constant. The discrepancy between the observed $\theta(P)/\theta(0)$ and the calculated S^2 may be due to the neglect of the AFM interaction, which also originates in the intermolecular orbital overlap.

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The effect of high pressure on the FM properties of I is essentially explained by the pressure dependence of the intermolecular overlap integrals between SOMO–NHOMO and/or between SOMO–NLUMO. This fact further confirms that the FM intermolecular interaction results from the intermolecular orbital overlaps, i.e., CT interaction.

Summary

The effect of hydrostatic high-pressure on the temperature dependence of the static magnetic susceptibility and the field dependence of the magnetization of the FM organic radical I indicates a pressure-induced enhancement of the FM intermolecular interaction. The FM coupling is increased by 40% at a pressure of 9 kbar. This rather large change suggests the possibility that the high-pressure prompts a phase transition into a 3-D FM ordered state in the FM organic solid. The pressure dependence of the FM interaction in I is approximately interpreted in terms of an increase in the intermolecular overlap integrals between SOMO/NHOMO and/or between SOMO/NLUMO by the application of pressure.

This work indicates that high-pressure experiments are useful and interesting in the study of organic/molecular ferromagnetism. Studies of the high-pressure effects on other FM systems are now in progress.

Acknowledgment. We thank Dr. K. Imaeda of the Institute for Molecular Science (IMS) for his helpful discussions and the pressure calibration of the Be–Cu clamp cell. We thank Mr. S. Bandow of IMS for his kind help in the setup of the Faraday susceptometer system. We are grateful to Dr. T. Inabe and Mr. T. Ida of IMS for their helpful discussions.

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Influence of Cryptands and Crown Ethers on Ion Transport and Vibrational Spectra of Polymer–Salt Complexes

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Complex impedance data demonstrate that addition of 2.2.2-cryptand increases the conductivity of $NaSO_3CH_3$ in amorphous poly(ethylene oxide) (aPEO) but decreases that of $NaSO_3CF_3$ in aPEO. Vibrational spectroscopic and X-ray diffraction measurements indicate that the influence of 2.2.2-cryptand is to dissolve crystallites of $NaSO_3CH_3$ into the polymer phase. The decrease in conductivity for $NaSO_3CF_3$–aPEO upon addition of 2.2.2-cryptand correlates with the precipitation of a crystalline phase, presumably [Na:2.2.2][SO_3CF_3].

Introduction

Solvent-free polymer electrolytes exhibiting high ionic conductivities are amorphous materials and are therefore difficult to characterize structurally.[1,2] Information about the mechanism of ion conduction in solvent-free polymer electrolytes has been obtained by physical measurements on chemically modified series of electrolytes. Chemical modifications include the synthesis of amorphous host polymers with low glass transition temperatures, T_g's,[3,4] the addition of plasticizers to reduce the T_g of polymer–salt complexes,[5,6] and the preparation of amorphous forms of PEO.[7-9]

Polymer electrolytes can be regarded as concentrated salt solutions in a medium with local solvent mobility but negligible long-range solvent motion. The dielectric constant of the host polymer is low and is implicated as a factor that reduces conductivity.[10] Spectroscopic studies indicate that there is considerable cation–anion interaction in polymer–salt complexes.[11-13] One chemical modification aimed specifically at reducing ion pairing is the addition of cation complexing agents, such as crown ethers or cryptands to polymer–salt complexes[14] or polyelectrolytes.[15,16] These complexing agents have been observed to enhance the conductivity 10–1000-fold. The nature of the conductivity enhancement has not been well elucidated. It is commonly supposed that the main influence of the complexing agent is to decrease ion pairing by in-

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