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# Organic Ferromagnetism and Antiferromagnetism of 4-Methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl and 4-Acryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl

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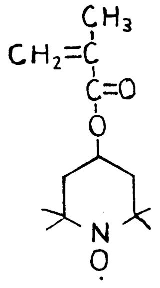
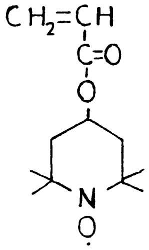
The temperature dependence of the magnetic susceptibilities for 4-methacryloyloxy- and 4-acryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl(MOTMP and AOTMP, respectively) was measured. Intermolecular magnetic coupling in these radicals was changed from antiferromagnetic to ferromagnetic by substituting hydrogen at $\alpha$-position with a methyl group. A magnetic phase transition for MOTMP was observed at 0.14 K in the measurement of the temperature dependence of heat capacity. The circumstantial evidences support that the ordered state is of ferromagnet.

Recently, there has been an increasing interest in organic/molecular ferromagnetism.[1-4)] When we became interested in magnetic behavior of polymers having pendant free radicals in 1978, only a few studies had been reported on the ferromagnetism of organic compounds.[5-9)] In our ealier work on the magnetic behavior of polymers with pendant nitroxyl radicals, a weak antiferromagnetic interaction between the nitroxyls was indicated by a negative Weiss constant of $\theta$=-2 - -3 K in the Curie-Weiss law.[10,11)] A ferromagnetic interaction was vaguely noticed below 4.2 K for 4-methacryloyoxy-2,2,6,6-tetramethylpiperidin -1-oxyl(MOTMP) when the magnetic behavior was compared between the polymers and the corresponding monomers. However, we paid no attention to the magnetic behavior of MOTMP, because the magnetic interaction was much weaker than that of the MOTMP polymer:10) the magnetic susceptibility had to be measured below 4.2 K for the ferromagnetic interaction to be detected. Recently, the existence of ferromagnetic ordering of electron spins in organic free radical crystals has been confirmed by several groups.4,12) Therefore, we reinvestigated the magnetic behavior of MOTMP and 4-acryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl(AOTMP), and found that intermolecular magnetic coupling in these coupling in these radicals was changed from antiferromagnetic to ferromagnetic by substituting hydrogen at $\alpha$-position with a methyl group. In addition, a magnetic phase transition for MOTMP was observed at 0.14 K in the measurement of the temperature dependence of heat capacity. The present paper reports the magnetic behavior of MOTMP and AOTMP.


1 MOTMP


2 AOTMP

The compounds were synthesized by the Schotten-Baumann reaction of acryloyl chloride or methacryloyl chloride with tempol which was kindly provided by Asahi Denka.10) They were purified by repeated recrystallizations from cyclohexane solutions. Gram magnetic susceptibility($\chi_g$) was determined by the Gouy method at room temperature. Distilled water($\chi_g$ = -0.72x10$^{-6}$ cgsemu) was used as the standard. The temperature dependence of $\chi_g$ was determined by the Faraday method, using a Cahn 1000 electric balance in the temperature range from 2.5 to 300 K. Heat capacity measurements were carried out for MOTMP in the temperature range from 0.07 to 25 K by use of an adiabatic calorimeter working with a $^3$He/$^4$He dilution refrigerator.13) A 0.9 g sample was used for the measurement.

The temperature dependence of the molar paramagnetic susceptibility $\chi_p$ for MOTMP and AOTMP was measured in the range from 2.5 to 250 K. The $\chi_p$ values of them were found to follow the Curie-Weiss law over the temperature range employed. The Weiss constants of MOTMP and AOTMP are 0.2 K and -1.2 K, respectively. The results are shown in Fig. 1 in terms of $\chi_p$T as a function of temperature. The values of $\chi_p$T of MOTMP are fairly constant at temperature above about ca. 50 K, while they gradually increase with lowering the temperature, indicating the presence of a weak ferromagnetic interaction. The temperature dependence of $\chi_p$ of AOTMP is quite different from that of MOTMP. The values of $\chi_pT$ of AOTMP decrease monotonously with lowering the temperature, indicating that there is an antiferromagnetic intermolecular interaction between the nitroxyl radicals. Since the magnetic susceptibility of MOTMP suggested the possibility of a ferromagnetic ordering below 1 K, the heat capacity of MOTMP was measured.

The temperature dependence of the observed molar heat capacity($C_p$) is shown in Fig. 2 on a semi-logarithmic scale. A transition peak due to the magnetic ordering was found at about 0.14 K. This temperature is reasonable, because it is almost consistent with that expected from the Curie-Weiss temperature observed by the magnetic susceptibility. After subtraction of the lattice heat capacity, the transition entropy was determined to be 5.8 J $K^{-1}$ $mol^{-1}$. This value agrees well with Rln 2 (= 5.76 J $K^{-1}$ $mol^{-1}$), where R is the gas constant. This fact guarantees the radical purity, each nitroxyl group being characterized by a spin-1/2. A remarkable feature of the present magnetic heatcapacity anomaly is that the transition peak at 0.14 K is followed by a broad heat-capacity hump centered around 0.4 K. This hump is well interpreted in terms of the Heisenberg model for a ferromagnetic linear chain.13) Although the crystal structure has not been resolved yet, the excellent agreement supports the existence of a low-dimensional structure. A paramagnetic crystal characterized by a positive Weiss constant generally exhibits a ferromagnetic phase transition, but this rule cannot be directly applied to the present crystal because of the existence of dimensional crossover.13) However, the spin-wave analysis below 0.1 K suggested that the weak interchain interaction might be ferromagnetic, leading to a bulk ferromagnetism below 0.14 K. Definitive evidence for the ferromagnetic ordering will be obtained by exam-

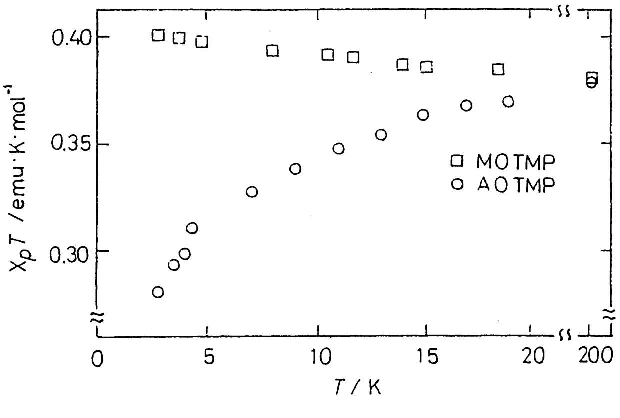


Fig. 1. Temperature dependence of the values of $\chi_pT$ of **1** and **2**.

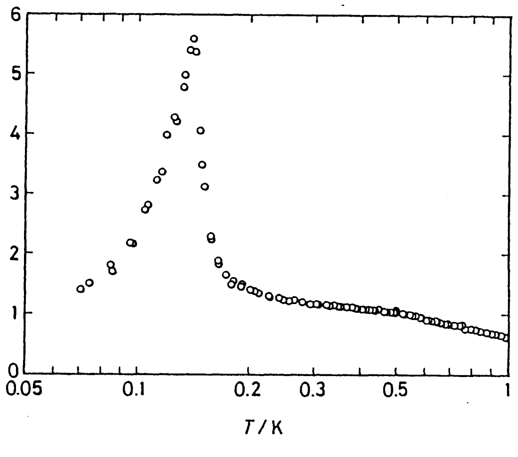


Fig. 2. Temperature dependence of the molar heat capacity of MOTMP.

ining a spontaneous magnetization. Such an experiment is now planned.

Although an origin of the magnetic behavior is an intermolecular exchange interaction between nitroxyl radicals in both compounds, the magnetic interaction of AOTMP was remarkably different from that of MOTMP. AOTMP having no methyl group at the $\alpha$-position showed an antiferromagnetic interaction. Yamaguchi et al.15) theoretically showed that an intermolecular exchange interaction of organic radicals changed from antiferromagnetic to ferromagnetic one by changing relative molecular orientation. Accordingly, the present result may be ascribed to a difference in relative orientation of the nitroxyl radicals in the crystalline states of both monomers. The crystal structures of both compounds and further discussion on the heat capacites will be reported in a forthcoming paper. Ovchinnikov et al.16) obtained ferromagnetic polymers by the polymerization of diacetylene containing 2,2,6,6-tetramethylpiperidin-1-oxyl. However, the origins of their ferromagnetism are not clear. Our study probably provides a clue to elucidation of organic ferromagnetism of the polymer obtained by Ovchinnikov et al.

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