CHEMISTRY LETTERS, pp. 2331-2334, 1987.

Preparation and Properties of Magnetically-interacting Polymer with Cupper(II) and Vanadyl(II) Poporphyrins

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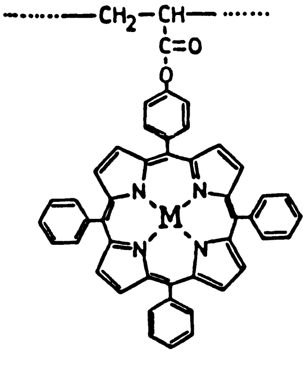
Polyacrylate having tetraphenylporphinatocupper(II) and tetraphenylporphinatovanadyl(II) in its side chains (Cu : V = 1 : 1.2) has been prepared by the radical copolymerization of the corresponding acrylates. The temperature dependence of its magnetic susceptibility indicates the existence of ferromagnetic interaction.



PolyAOTPPM
M: Metal ion

Recently, we prepared polyacrylate having tetraphenylporphin(TPP) by the radical polymerization of 5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphin (AOTPP),1,2) and then obtained polyacrylates containing paramagnetic metalloporphins (TPPM) by the polymer reactions with the metal salts.3-5) In the course of study on magnetic behavior of the polymers, we found that polyacrylate having tetraphenylporphinatosilver(II) in the side chains indicated the occurrence of antiferromagnetic interaction between TPPAg(II) moieties in the side chains. Since TPPAg(II) and 5-(4-propyloyloxyphenyl)-10,15,20-triphenylporphinatosilver(II) (POTPPAg(II)) showed only a small antiferromagnetic interaction, polymer chains seem to play an important role in the occurrence of the magnetic interaction. Accordingly, polymers having paramagnetic metalloporphyrins are expected to provide a new class of magnetic properties owing to the magnetically long-range ordering of unpaired electrons through spin-spin interactions. We have expanded this study to polymers having other paramagnetic ions. Ferromagnetic behavior was found in the polymers obtained by the radical copolymerization of AOTPPCu(II) and AOTPPVO(II).

Poly[AOTPPCu(II)-co-AOTPPVO(II)] was prepared as follows: AOTPPCu(II)1) (0.5 g), AOTPPVO(II)6) (0.5 g) and AIBN (3 mg) were put into an ampoule, and then dissolved in benzonitrile(3 ml). The solution was degassed under high vacuum, and the copolymerization was carried out at 60 °C for 50 h. The copolymer was isolated and purified by three dissolution-precipitation-separation steps from chloroform-methanol and then three dissolution-precipitation-separation steps from chloroform-hexane (yield 67%). The molecular weight of the copolymer was estimated to be 8000-40000 by the GPC measurement calibrated by standard polystyrenes. According to the elemental analysis, the content of Cu(II) and VO(II) ions in the copolymer was 3.1% and 3.1%, respectively. The content of both metal ions was a little smaller than that calculated on the assumption that all porphyrin moieties have Cu(II) or VO(II) ions. This fact suggests that Cu(II) ions and VO(II) ions partly were lost during the copolymerization. The elemental analysis is consistent with the copolymer whose component are AOTPP, AOTPPCu(II), and AOTPPVO(II).

Found: C, 75.57%; H, 4.70%; N, 7.79%; Cu, 3.1%; V, 3.1%. Calcd. for $(\mathrm{AOTPP})_{0.18}$: $(\mathrm{AOTPPCu(II)})_{0.38}$: $(\mathrm{AOTPPVO(II)})_{0.44}$: C, 76.08%, H, 4.38%; N, 7.58%; Cu, 3.1%; V, 3.1%

Magnetic susceptibility (X_A) at room temperature was determined by the Gouy method. The temperature dependence of X_A was determined by the Faraday method, using a Cahn 1000 electric balance in the temperature range from 4 to 300 K.

The IR spectra of the copolymer and the monomers are shown in Fig. 1. The C=C absorption bands of AOTPPCu(II) and AOTPPVO(II) at 1630 cm^{-1} disappeared in the copolymer, and the C=O bands at 1745 cm^{-1} due to unsaturated ester group of both monomers shifted to 1755 cm^{-1} assinable to the C=O bond of the saturated ester in the copolymer. The absorption bands due to porphyrin ring did not change before and after the copolymerization. These results show that the copolymerization takes place through the C=C bond of the monomers.

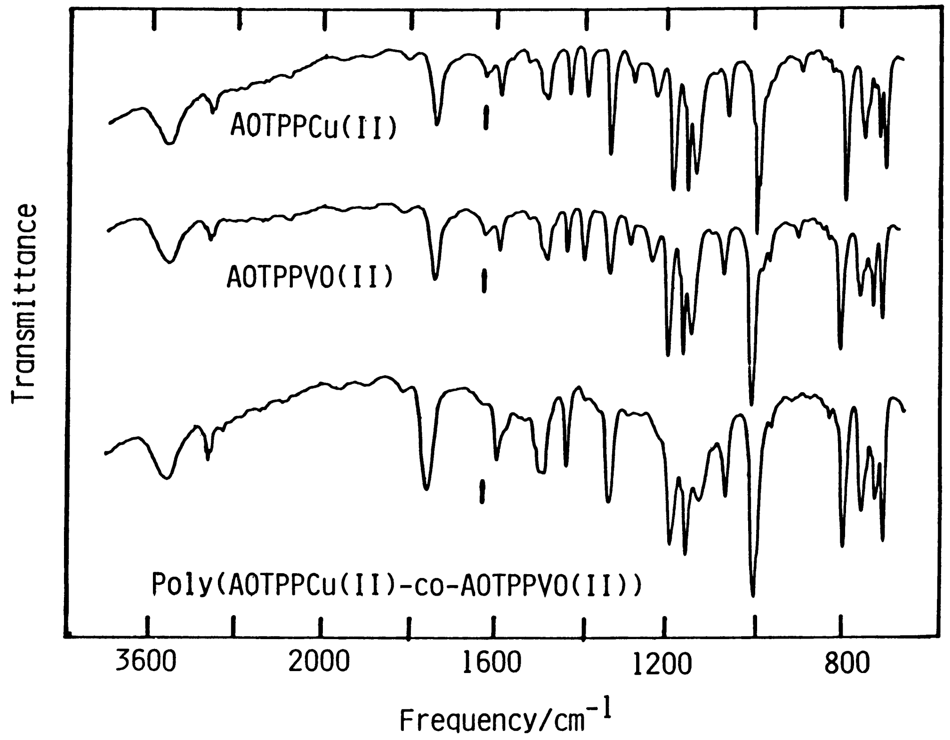


Fig. 1. IR spectra of poly(AOTPPCu(II)-co-AOTPPVO(II)) and monomers.

The visible spectra of the copolymer, AOTPPCu(II), AOTPPVO(II), and a 1:1 mixture of AOTPPCu(II) and AOTPPVO(II) are shown in Fig. 2. The Soret band of the copolymer is much weaker and broader than those of monomers and their mixture. Since the molecular extinction coefficient (ε) of the Soret band of AOTPP (4.0 x10^{5})2) is about the same as those of AOTPPCu(II) and AOTPPVO(II), the value of ε for the Soret band of the copolymer is considered to be almost the same as that of the mixture of the monomers, even if the copolymer contains a considerable amount of AOTPP unit. This consideration is not the case. Accordingly, the decrease in the value of ε of the Soret band of the copolymer is ascribable to the hypochromism which is caused by electronic interaction between the porphyrin moieties. Similar hypochromism at 540 nm and new absorption band at 630 nm were observed in the copolymer. The change in the absorption bands might be correlated with an electronic interaction between porphyrin moieties, because these bulky moieties bound to a polymer chain are probably forced to make some electronic interactions due to their close approach.

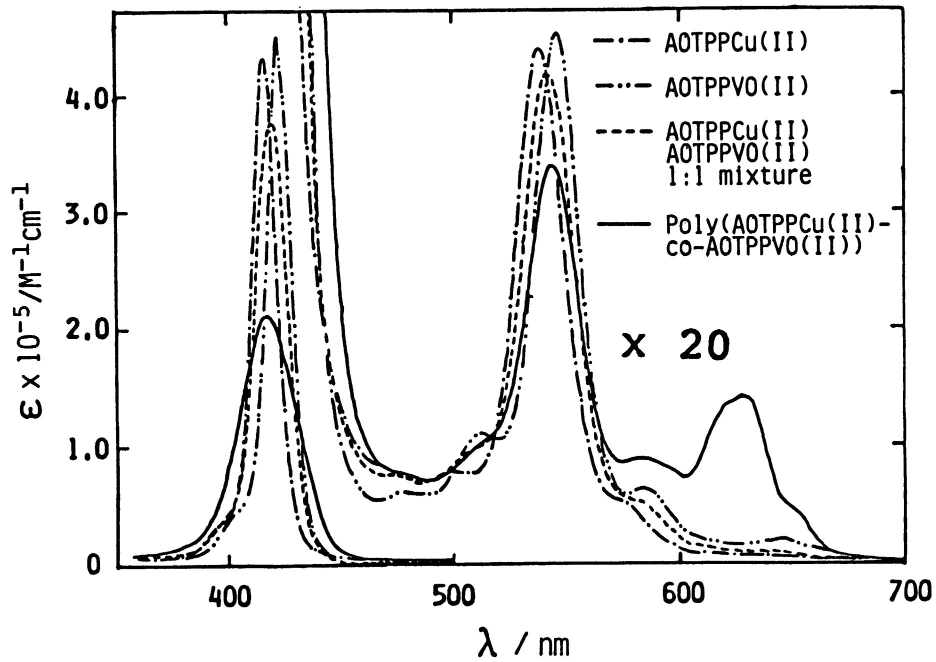


Fig. 2. Visible spectra of poly(AOTPPCu(II)-co-AOTPPVO(II)), monomers, and a 1:1 mixture of the monomers.

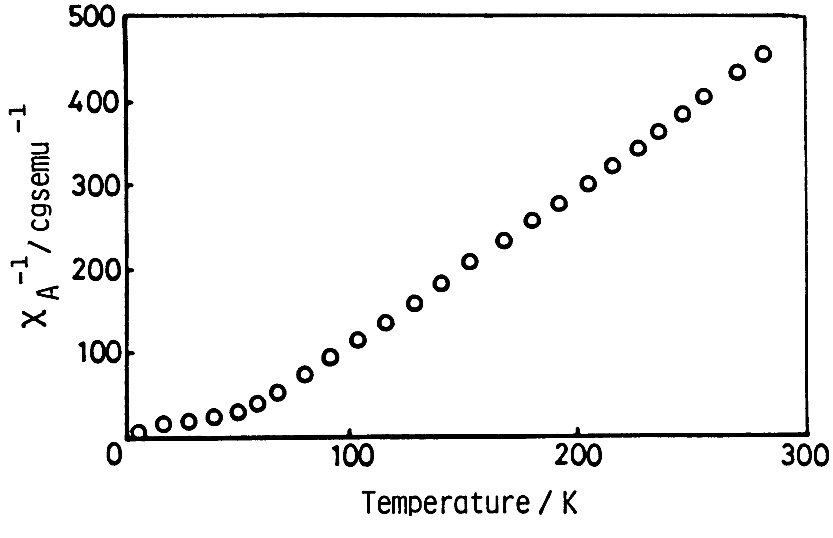


Fig. 3. Temperature dependence of magnetic susceptibility of poly(AOTPPCu(II)-co-AOTPPVO(II)).

The temperature dependence of X_A of the copolymer is shown in Fig. 3. The value of X_A obeys the Curie-Weiss law ($X_A = c/(T-\theta)$) with θ =50 k, which indicates the existence of a ferromagnetic interaction between paramagnetic metal ions in the copolymer. The field dependence of magnetization is given in Fig. 4. The saturation magnetization observed shows that there are ferromagnetically ordered sites in the copolymer. Since no ferromagnetic interaction occurs in AOTPPCu(II), AOTPPVO(II), and their homopolymers, the apparent ferromagnetic interaction in the copolymer is probably ascribed to an ferromagnetic interaction between the TPPCu(II) and TPPVO(II) moieties. Recently, Kahn[7)] demonstrated the occurrence of ferromagnetic intraction between the Cu(II) and VO(II) ions in the binuclear complex. A ferromagnetic interaction between the TPPVO(II) and TPPCu(II) moieties is possible, if TPPCu(II) and TPPVO(II) moieties are located in the position suitable for the occurrence of ferromagnetic interaction. The ESR spectrum(not shown) of the copolymer suggests that the TPPCu(II) and TPPVO(II) moieties are mostly paramagnetic and that ferromagnetically-interacting moieties are not predominant. The X ray diffraction shows amorphous patterns due to the copolymer, and no inorganic moiety could be detected by the X-ray analysis. Since the TPPCu(II) and TPPVO(II) moieties are not always regularly bound to the side chains of the copolymer, the ferromagnetic interaction in the copolymer is probably ascribable to the result of an exchange interaction between the TPPCu(II) and TPPVO(II) moieties located casually in the position suitable for the occurrence of ferromagnetic interaction.

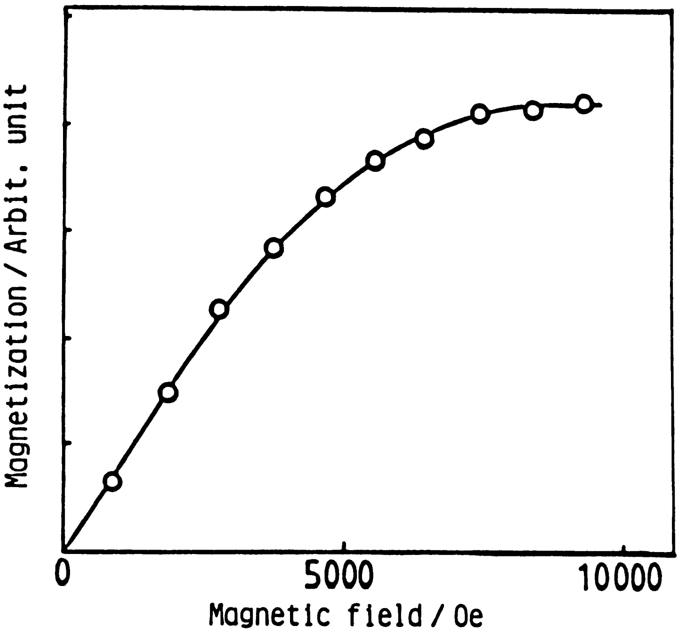


Fig. 4. Field dependence of magnetic susceptibility of poly(AOTPPCu(II)-co-AOTPPVO(II)) at room temperature.

The authors would like to express their sincere appreciation to Professor Shun-ichi Nozakura, Osaka University, for his helpful discussion and encouragement. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Area "Macromolecule-Complexes(No 62612001)" from the Ministry of Education, Science, and Culture, Japan.

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(Received September 10, 1987)