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MAGNETIC PROPERTIES OF POLYMER LB FILMS CONTAINING FERROCENE DERIVATIVES

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Abstract Langmuir-Blodgett (LB) films of copolymer with ferrocenyl-methyl-acrylate(FcMA) and *N*-dodecyl-acrylamide(DDA) were fabricated. The FcMA moiety is supposed to enter into the alkyl chains of DDA and be arranged two-dimensionally form the X-ray diffraction analysis. The magnetization curve showed a steep rise up to several kOe and a gentle increase with the magnetic field up to 55 kOe. This behavior seems to be ferromagnetic. Even more than room temperature, the half of the magnetic moment at 4.5K remained, and the magnetization curve showed ferromagnetic. Furthermore, this LB film had a magnetic anisotropy depending on the dipping direction. On the other hand, the magnetization curves for the powder and the cast film of the copolymer were paramagnetic. The magnetic moment of the LB film is about 30 times larger than those of the powder and the cast film. These results indicate that a configurational interaction is important to explain the enhancement of magnetic moment of this copolymer.

INTRODUCTION

Many ferromagnetic molecular materials have been investigated in the recent years.[1,2] Especially, some polymer materials and polymeric inorganic materials exhibiting relatively high magnetic ordering temperature are interesting.[3-5] These magnetic polymers should be expected to present a certain degree of structural disorder and/or non-crystalline.[6] On the other hand, Langmuir-Blodgett (LB) films of polymer materials can have an excellent molecular orientation highly controlled and a pseudo-crystalline structure.[7] In this paper, we report the magnetism of polymer LB films containing ferrocene derivatives. The ferrocene is known to be a diamagnetic organic material though it has an iron atom.[8] However, it has a strong donor characteristic so that its charge transfer complex can have an unpaired spin. It is interesting to investigate the magnetism of the polymer LB film with the degree of the structural disorder. We also fabricated the LB film of the mixture with the polymer and a stearic acid in order to give

the LB film a structural disorder. The X-ray diffraction and magnetic properties were measured for these LB films and the powder. The results will be discussed by the charge transfer mechanism.

EXPERIMENTAL DETAILS

N-dodecylacrylamide (DDA) and ferrocenylmethylacrylate (FcMA) monomers were synthesized by the reaction of acryloyl chloride with dodecylamine and ferrocenemethanol, respectively, in the presence of triethylamine in dichloromethane at room temperature. The crude products were recrystallized from chloroform-hexane mixed solvent. DDA copolymer with FcMA was prepared by free radical polymerization in benzene at 60 °C with 2,2'-azobis(isobutyronitrile) as shown in Fig.1. The copolymer was purified twice by precipitation in a large excess of acetonitrile from chloroform solution and dried under vacuum at the room temperature. The mole fraction of ferrocene moiety in the copolymer, which was determined by the maximum absorbance of ferrocene moiety using UV spectroscopy, was 0.14.

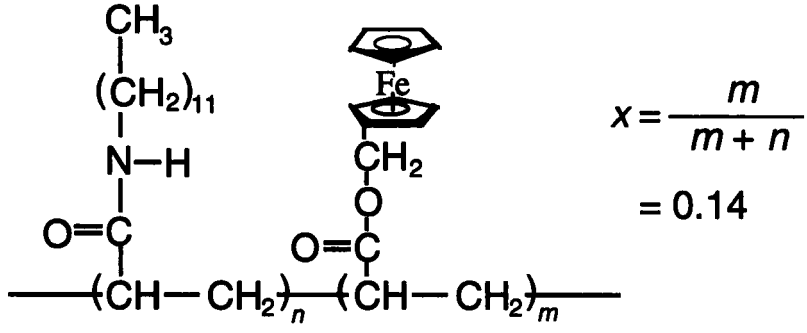

FIGURE 1 The chemical structure of the copolymer of DDA and FcMA.

The copolymer was spread from chloroform (1.0×10^{-3} M) onto an aqueous subphase. The films were dipped up by the standard technique using an automatic feedback Langmuir trough. The substrates were polyethylene terephthalate (PET) of 100 μm thick. PET substrates were only supersonically cleaned in chloroform and benzene. These substrates were dipped and lifted across the floating monolayer at a constant velocity of 10 mm/min. We obtained 80 layered samples. All the fabrications were performed under a constant subphase temperature of 20 °C. The low angle X-ray diffraction pattern of the LB Films was recorded with automated X-ray diffractometer system using Cu K_α line with Ni-filter. The tube voltage and the current were 40 kV and 20 mA, respectively. The magnetization was measured by SQUID magnetometer in magnetic fields up to 55 kOe at the temperature from 4.5 K to 400 K.

EXPERIMENTAL RESULTS AND DISCUSSION

Fig.2 shows the diffraction patterns for the LB films. The appearance of Bragg's peaks indicates that the LB films have a layer structure. The average periodicity of the LB films was calculated from the diffraction peak at the lowest angle. The value of the periodicity is 34.2 Å for the film of PDDA and 32.8 Å for the film of $DDA_{0.86}FcMA_{0.14}$ copolymer. The space-filling molecular model of PDDA indicated that the maximum length of a dodecyl alkyl chain was estimated to be 18 Å (thus the periodicity of the LB film becomes 36 Å). Therefore, the alkyl chains in the LB film of $DDA_{0.86}FcMA_{0.14}$ are proposed to have an tilt angle of 24.3° to the film normal. On the other hand,the LB film of the 1:1 mixture of $DDA_{0.86}FcMA_{0.14}$ with stearic acid (SA) indicates weak peaks corresponding to two types of the crystal structure (hexagonal and orthorhombic) of SA molecule.[9] Namely, small crystallines of SA should be formed and interfere with the formation of the periodic layer structure of the $DDA_{0.86}FcMA_{0.14}$. The peaks due to SA disappeared after annealing up to 400 K.

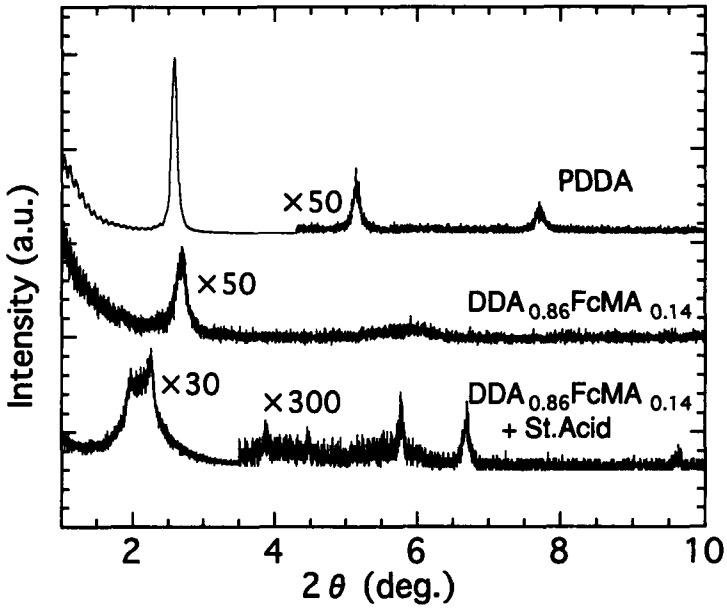

FIGURE 2 The diffraction patterns for the LB films of PDDA, $DDA_{0.86}FcMA_{0.14}$ and the 1:1 mixture of $DDA_{0.86}FcMA_{0.14}$ with SA.

Fig.3 shows the magnetization curves for the LB film of $DDA_{0.86}FcMA_{0.14}$ at 4.5 K. The magnetic field was applied parallel (●) and vertical (▲) to the dipping direction. The magnetic moment is the value per mol in the ferrocene moiety. The curves of the film show a steep rise with the low magnetic field and a gentle increase with increasing the magnetic field up to 55 kOe. This behavior seems to be ferromagnetic. Furthermore, this LB film has a magnetic anisotropy depending on the dipping direction.

On the other hand, the magnetization curves for the powder of $DDA_{0.86}FcMA_{0.14}$ (indicated by ■ in the figure) and the cast film of the copolymer showed paramagnetic. The magnetic moment of the LB film became about 30 times larger than those of the powder and the cast film.

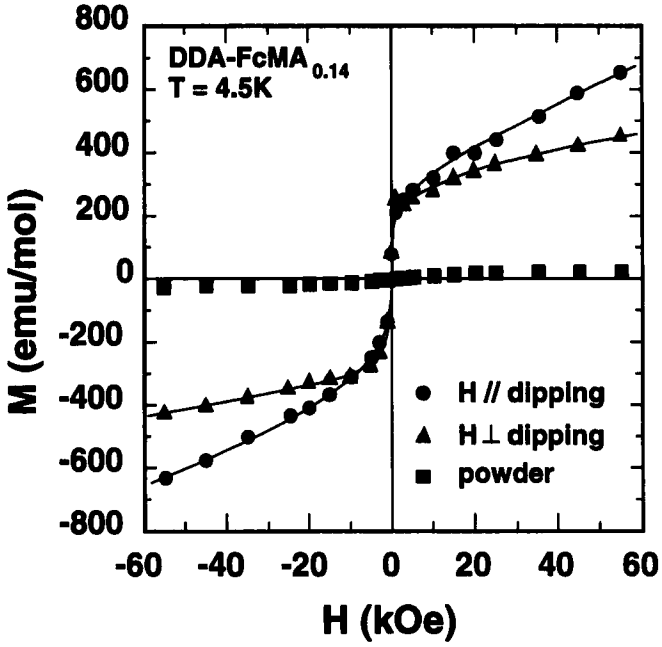

FIGURE 3 The magnetization curves for the LB film and the powder of $DDA_{0.86}FcMA_{0.14}$ at 4.5 K.

Fig.4 shows the temperature dependence of the magnetic moment at 55 kOe for the LB film. The magnetic field was applied vertical to the dipping direction. Those for the LB film of $DDA_{0.86}FcMA_{0.14}$ shows a gentle decrease with increasing temperature. Surprisingly, even more than room temperature, the half of the magnetic moment at 4.5 K remained, and the magnetization curve showed ferromagnetic. The temperature dependence of the magnetic moment for the LB film of the 1:1 mixture of $DDA_{0.86}FcMA_{0.14}$ with SA are also shown in the figure. That shows, on the contrary, a gradual increase with increasing temperature after a gentle decrease up to about 300 K. The melting point of the monolayer of SA is reported to be 317K,[10] which value corresponds to the turning point in the temperature dependence of the magnetic moment. The X-ray diffraction pattern after the annealing actually showed no Bragg's peak by SA. Namely, the melting of SA should cause to relax the structure of the 1:1 mixture LB film.

Fig.5 shows the magnetization curves for the mixture film at 4.5K before and after the annealing. The magnetic field was applied vertical to the dipping direction. The magnetization at 4.5 K after the annealing at 400 K becomes larger than that before the annealing. The inset shows the detail of the magnetization curve after the annealing in the low magnetic field region. The magnetization curve shows a small magnetic

hysteresis. Further annealing for this LB film of 1:1 mixture was carried out and the magnetization curves at 4.5 K were measured. After annealing up to 550 K the PET substrate was melted and the magnetization decreased to the value corresponding to that of the copolymer powder. These results indicate that the molecular orientation is important to explain the enhancement of the magnetization in the LB films.

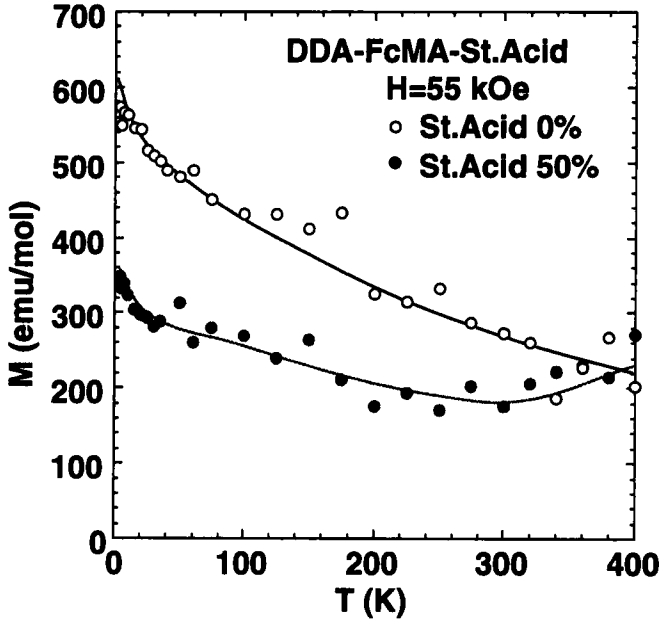

FIGURE 4 The temperature dependence of the magnetic moment at 55 kOe.

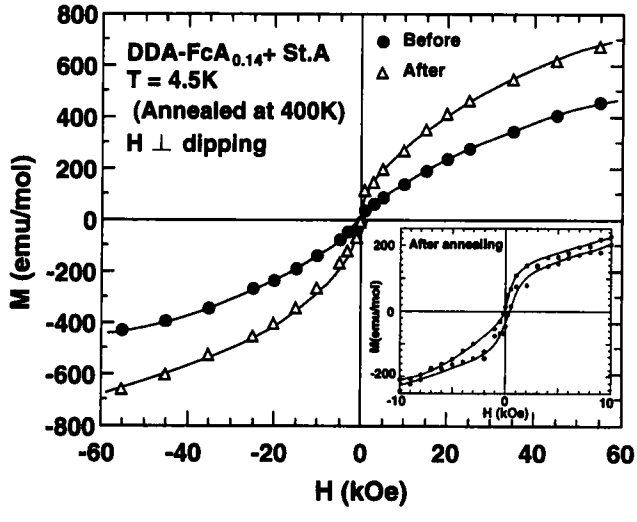

FIGURE 5 The magnetization curves for the mixture film at 4.5K before and after the annealing.

As described above, ferrocene is known to be a diamagnetic organic materials and the electronic structure has been the subject of numerous theoretical and experimental papers.[8] The characteristics of ferrocene are highly symmetric molecule with parallel cycropentadiene rings and the closed-shell molecule with formal d^6 configurations. Therefore, the derivatives cause to break the symmetry so that a slight change of the electronic structure can occur. Actually, the powders of FcMA and the copolymer with DDA showed paramagnetism. This indicates that the weak polarization occur in the molecular. This can be due to the intramolecular charge transfer from the ferrocene moiety to the another. However, some magnetic interaction between the polarized moieties is needed for the explanation of the enhancement of the magnetic moment in the LB film.

CONCLUSIONS

The magnetic properties of copolymer LB films of $DDA_{0.86}FcMA_{0.14}$ were investigated. The magnetization curves of LB films showed ferromagnetic while those of the powder and cast film showed paramagnetic. These indicate that a configurational interaction is important. The origin of the ferromagnetic interaction is not clear at present. The fabrication of the copolymer with the different fraction of ferrocene moiety is in progress. Further investigation for the LB films will be reported in the near future.

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