Polymerization of $N$-isopropylacrylamide under magnetic levitation

Y Fujiwara$^1$, Y Katsumoto$^1$, Y Ohishi$^2$, M Koyama$^1$, K Ohno$^1$, M Akita$^1$, K Inoue$^1$, and Y Tanimoto$^1$

$^1$Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8526, Japan

$^2$Faculty of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8526, Japan

fuji0710@sci.hiroshima-u.ac.jp

Abstract. A study of an effect of the magnetic levitation on polymerization of $N$-isopropylacrylamide at room temperature was carried out. The magnetic levitation environment, which is created by strong and upward magnetic force counterbalanced with the downward gravitational force, is multiple environment consisting of both the microgravity and the strong magnetic field which is lacking in a space vehicle orbiting around the earth. In this work, the effect was evaluated from the viewpoint of the number-average molecular weight ($M_n$) and the polydispersity (the index of the molecular weight distribution) of the synthesized polymer. A small extent (~10 %) of the effect was observed on both the parameters. When the polymer was synthesized under the magnetic levitation environment, $M_n$ increased while the polydispersity decreased as compared with those of the polymer synthesized under the gravity.

1. Introduction
Recently superconducting magnets affording strong magnetic fields more than 10 T are attractive for use in the fields of material processing. Especially the strong magnetic force created by the strong magnetic field gradient invokes a new field of the study on chemical syntheses under the magnetic levitation environment which is produced by counterbalance of the strong magnetic force with the gravitational force. The magnetic levitation environment is characterized by not merely the microgravity but also the strong magnetic field, in which the latter is lacking in a space vehicle orbiting around the earth. Although the diffusion and convection in solution are known to alter under the microgravity, the strong magnetic field also actually causes significant influence such as the magnetic orientation of polymers, biological materials, crystals, and so forth [1, 2].

Therefore, if the microgravity and strong magnetic field work simultaneously, effects unobtainable in space might be expected. The aim of this work is presenting an effect of the magnetic levitation environment on the chemical synthesis of a polymer, poly($N$-isopropylacrylamide), since polymers are usually prepared by intermolecular reactions to be governed by the diffusion and convection, and are sometimes arranged by the strong magnetic field. As for characteristics and behaviors of poly($N$-isopropylacrylamide) [3-9], Ozeki et al. focused their attention on the magnetic field effect in the strong magnetic fields (~30 T) under the usual gravity (1 G) on the earth [3-7]. They showed the effects that the volume at a swelling state of the polymer gels greatly increased together with the
applied magnetic field intensity and that the anisotropy of the polymer appeared. In this work, we attempted to estimate the effect of the magnetic levitation environment characterized by both the microgravity and strong magnetic field by means of the number-average molecular weight ($M_n$) and its distribution (polydispersity) of the polymer prepared.

2. Experiments

2.1. Samples and Reaction Scheme
Poly(N-isopropylacrylamide) (polyNIPA) was synthesized by radical polymerization of a 0.59 mol/kg monomer (N-isopropylacrylamide, Wako, >98%) (NIPA) dissolved in water at room temperature. The reaction was controlled by a 0.047 mol/kg initiator (ammonium peroxodisulfate, Wako, >98%) (APS) and a 0.092 mol/kg promoter ($N,N,N',N'$-tetramethylethylenediamine, Wako, >98%) (TMEDA). All the reagents were used without further purification. These concentrations were adjusted by the way that the polymerization ceased throughout one day at room temperature. The reaction scheme is shown in figure 1. Isotropic magnetic susceptibilities were obtained to be $-5.297 \times 10^{-5}$, $-9.605 \times 10^{-5}$, and $-6.451 \times 10^{-5}$ cm$^3$/mol for NIPA, APS, and TMEDA, respectively, by using a Quantum Design MPMS-5S SQUID at 300 K. The value ($-1.296 \times 10^{-5}$ cm$^3$/mol at 293 K) of water was cited from the literature.

2.2. Superconducting Magnet and Experimental Setup

![Figure 1. Reaction scheme of polymerization of NIPA.](image1)

![Figure 2. A photograph of a superconducting magnet affording the magnetic levitation environment (~0 G, 10.7 T) located above the magnet centre (1 G, 15 T). White arrows show locations for the effective gravities and magnetic fields together with the location for 1 G at 0 T obtained outside the magnet.](image2)
downward gravitational force. Figure 2 shows a photograph of the superconducting magnet and indicates respective locations of the reaction solutions set under the magnetic levitation environment (−0 G, 10.7 T) inside the magnet and under the usual gravity (1 G, 0 T) at the geomagnetic field (abbreviated to 0 T) outside it. The reaction solution was levitated without a container under the magnetic levitation environment immediately after mixing TMEDA with the reaction solution dissolving NIPA and APS in advance. The reaction solution for 0 T was left alone after TMEDA was mixed in a container outside the magnet.

2.3. Determination of the number-average molecular weight and the polydispersity
The number-average molecular weight ($M_n$) and the polydispersity (the index of the molecular weight distribution) were evaluated by size exclusion chromatography (SEC) (Jasco, PU-2080Plus, DG-2080-53, CO-2065Plus, RI-2031-Plus, 807-IT) with polystyrene standard in degassed N,N-dimethylforamide at 313 K on a polystyrene gel column (Shodex, KF-805L). The refractive index was used as an index in SEC.

3. Results and Discussion
Table 1 summarizes the results of SEC for polyNIPA synthesized under the gravity outside the magnet (1 G, 0 T) and under the magnetic levitation environment (−0 G, 10.7 T).

| $M_n$ (x10^5) | Polydispersity |
|---------------|---------------|
| outside | magnetic | outside | magnetic |
| (1 G, 0 T) | levitation | (−0 G, 10.7 T) | levitation |
| (2.26±0.05) | 1.10±0.03 | (2.48±0.05) | 2.58±0.03 |
| Ratio | | ratio | | 2.37±0.03 | 0.92±0.02 |

The $M_n$ and polydispersity were approximately 2.5 x 10^5 and 2.5, respectively, which can be both regarded as average values of polyNIPA prepared by the radical reaction. The polydispersity should be unity when there is no distribution in the molecular weight. When the value becomes larger than two, it means that not only the monomer but also the polymers of small size formed in the radical reaction process participate in the polymer generation reaction. These parameters in the presence and absence of the magnetic levitation environment represented a small extent (~10 %) of the effects in the respective values. That is to say, the $M_n$ increased and the polydispersity decreased, as seen in the respective ratios, when polyNIPA was synthesized under the magnetic levitation environment. The effect in the polydispersity means that the distribution in the polymer molecular weight became narrower. In spite of the small extent of the effects, these effects are notable since they frequently become favorable features for polymers synthesized, namely, the larger molecular weight and its narrower distribution. Individually different magnetic susceptibilities measured by SQUID mean that each reagent preserves no balance with the gravitational force under the magnetic levitation environment for water. However, since the reaction solution formed a homogeneous solution where all the reagents completely dissolved unlike inhomogeneous suspension such as solids floating inside water, individually different magnetic forces working on the reagents seem to be no more significant in this experiment. It is because the reaction solution should behave as one diamagnetic liquid that shows an apparent magnetic susceptibility obtained from the susceptibilities for all the reagents and water and their concentrations. Therefore, it seems difficult to conclude that the observed effects result from individually different magnetic forces of the reagents and therefore induced convection. As one of other mechanisms, on the other hand, there exists convectional inhibition caused by the strong magnetic field intensity itself without a magnetic field gradient [10]. However, it appears that this mechanism conflicts with the result of larger $M_n$ obtained under the magnetic levitation environment.
At the moment, hence, we guess that the polymer levitating under the microgravity is left exposed to successive attack of the monomers and the intermediate polymers of small size from all directions more effectively and more spatially homogeneously, compared with the polymer synthesized outside the magnet. Whereas the polymer in the reaction solution tends to sink along with a degree of the growing outside the magnet, the sinking is considered to be inhibited under the microgravity because of a large number of water molecules participating in hydration of the polymer. Detailed investigation is necessary for more reasonable interpretation which includes the influence of the strong magnetic field which is the other feature of the magnetic levitation environment.

4. Conclusion
The number-averaged molecular weight (\(M_n\)) and the polydispersity of polyNIPA were compared in terms of the employed reaction environments of the magnetic levitation with ~0 G and 10.7 T and the usual gravity outside the magnet with 1 G and 0 T. A small extent (~10 %) of the effect of the magnetic levitation was observed in the parameters. Under the magnetic levitation environment, it was found that the polymer showed a favourable tendency to become larger in the molecular weight and narrower in its distribution, indicating the potential use of the magnetic levitation for polymer syntheses. To the best of our knowledge, these effects seem to be the first observation in chemical synthesis using the magnetic levitation. We want to argue greater advantages of convenience, availability, and cost performance in use of the magnetic levitation on the earth in future although there remains necessity to differentiate between effects obtained in the magnetic levitation environment on the earth and in space which both provide the microgravity.

Acknowledgements
This work was partly supported by Grants-in-Aid for Scientific Research both of Area 767 No. 15085208 (Priority Area “Innovative utilization of strong magnetic fields”) and of No. 16205003 from MEXT of Japan. We thank Natural Science Center for Basic Research and Development (Cryogenic Center) in Hiroshima University for supplying cryogen. We are also obliged to Workshop for Advanced Techniques in Hiroshima University for making experimental instruments.

References
[1] For example: Yamaguchi M and Tanimoto Y (eds.) 2006 Magneto-Science (Tokyo: Kodansha), in press
[2] For example: Fujiwara Y, Tomishige M, Itoh Y, Fujiwara M, Shibata N, Kosaka T, Hosoya H and Tanimoto Y 2006 Mol. Phys. 104 1659-66
[3] Otsuka I, Kawasaki H, Maeda H and Ozeki S 2001 Symposium on New Magneto-Science 2001, Proceedings of the 5th Meeting (Tsukuba, Japan, 7-9 November 2001) pp 13-15
[4] Otsuka I, Takahashi T, Yaguchi Y, Abe H and Ozeki S 2005 Materials Processing in Magnetic Fields, Proceedings of the International Workshop on Materials Analysis and Processing in Magnetic Fields (Tallahassee, FL, U.S.A., 17-19 March 2004) pp 330-336
[5] Otsuka I and Ozeki S 2005 International Symposium on Magneto-Science 2005, Program and Abstracts (Yokohama, Japan, 14-17 November 2005) p 132
[6] Otsuka I and Ozeki S 2005 International Chemical Congress of Pacific Basin Societies, Abstracts (Honolulu, U.S.A., 15-20 December 2005) No. 618
[7] Otsuka I, Abe H and Ozeki S 2006 Sci. Tech. Adv. Mater. 7 327-331
[8] Katsumoto Y, Tanaka T, Sato H and Ozaki Y 2002 J. Phys. Chem. A 106 3429-35
[9] Katsumoto Y, Tanaka T and Ozaki Y 2004 Macromol. Symp. 205, 209-223
[10] Sazaki G, Durbin S D, Miyashita S, Ujihara T, Nakajima K and Motokawa M 1999 Jpn. J. Appl. Phys. 38 L842-L844