Ion Conductive and Flexible DNA Films

Hiroyuki Ohno* and Naomi Takizawa
Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588

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Ion conductive film was prepared from flexible poly(ethylene oxide) (PEO) and double stranded DNA chains from salmon milt. The ionic conductivity of this DNA/PEO film was greatly improved by the addition of $NaClO_4$. The highest ionic conductivity of 4.2×10^{-4} S cm^{-1} was observed at 25 °C.

PEO is expected to have polar characteristics similar to water because of structural similarity of ethylene oxide unit to water molecule. PEO has large dipole moment and low glass transition temperature (Tg) which are quite suitable for ion conductive polymers. PEO/salts mixture has been studied as a typical component to design ion conductive matrix.[1] However, there are some drawbacks such as limited salt solubility in PEO, elevation of Tg by the salt addition, poor film property, and so on. In our previous study, considerable amount of ions were homogeneously dispersed in PEO matrix without elevating Tg by introducing salt unit on the PEO chain, so-called PEO/salt hybrid.[2-6] In spite of excellent ionic conductivity, these hybrids were viscous liquid or wax-like solid. On the other hand, DNA is known as a rigid polymer complex through inter-chain hydrogen bonding between complementary base pairs. DNA is also reported to be interesting material to provide flexible films.[7-9] Since DNA has many phosphate residues, it was expected to disperse and retain ions in the domain. Recently, lots of gel-type polymer electrolytes are reported.[10-12] This kind of ion-conductive material is generally composed of polar and rigid frame structure and highly ion conductive fluid. DNA is comprehended as a rigid polymer complex having a lot of charged sites. Ordinary polyelectrolytes cannot provide these characteristics. In the present study, DNA was used to prepare ion conductive films and the effect of some additives on the ionic conductivity was analyzed.

Purified DNA sodium salt from salmon milt (Nippon Chemical Feed Co.) was used. The aqueous solutions of DNA and PEO were mixed, and the solution was poured on the Teflon plate. The solvent was evaporated slowly at room temperature, followed by the vacuum drying. Equimolar amount of PEO_{1000} (average molecular weight of 1000) to phosphate anion was mixed with DNA, and $NaClO_4$ was further added. Molar ratio of Na^+ to ether oxygen unit was varied from 15 to 45 mol%. The sample solution was cast on the Teflon plate and evaporated at room temperature, and then dried *in vacuo* for 24 h. The water content of these films was checked by the Karl-Fischer moisture titration (Kyoto Denshi Kogyo Co.). The ionic conductivity was measured by the complex-impedance gain-phase analyzer (Solartron model 1260; Schlumberger). The glass transition temperature (Tg) of these samples was determined by DSC (DSC-120, SEIKO). After cooling samples to -155 °C, they were heated from -150 °C to 170 °C with the scanning rate of 10 or 3 °C min^{-1}.

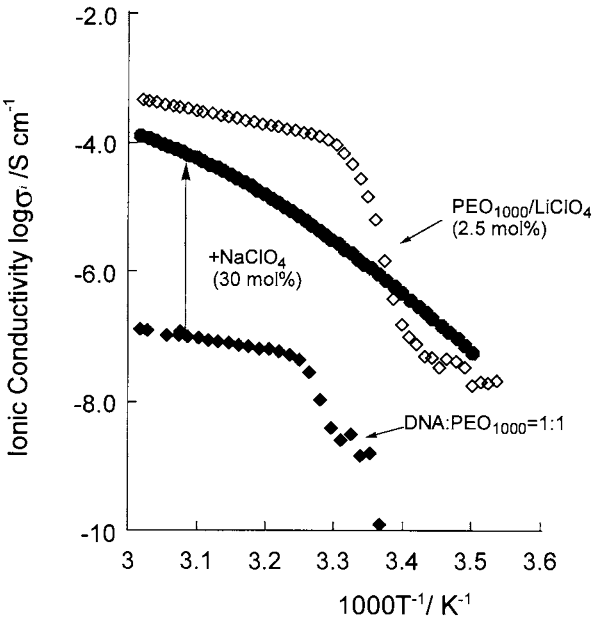

Figure 1. Temperature dependence of the ionic conductivity of DNA/PEO_{1000} mixture with (●) and without (◆) $NaClO_4$. That of PEO_{1000}/$LiClO_4$ mixture (◇) was also depicted as reference.

The film prepared by casting an aqueous solution of only DNA was clear but brittle. However, a flexible film was prepared when DNA was mixed with PEO_{1000} before casting. Water content of all of DNA/PEO film was less than 0.02 wt%.

Temperature dependence of the ionic conductivity of DNA films is shown in Figure 1. PEO_{1000} chain was added to DNA equimolarly to phosphate anions on the DNA. Since the average molecular weight of DNA base pair unit is 650, about 75 wt% of PEO was added in the mixture. Even this considerable amount of PEO, DNA/PEO mixture was obtained as a flexible film. Since mobile carrier ion in this DNA/PEO simple mixture film was only sodium cation, counter ion of the phosphate anion, the observed ionic conductivity was very poor (Figure 1, ◆). When 30 mol% $NaClO_4$ was added to the mixture before casting, the ionic conductivity of the film was improved about 1000 times (Figure 1, ●). DNA/PEO_{1000}/$NaClO_4$ was obtained as a film when $NaClO_4$ was added up to 45 mol% to OE unit. The Arrhenius plot of the ionic conductivity for PEO_{1000} containing 2.5 mol% $LiClO_4$ is also shown as reference. This mixture shows excellent ionic conductivity as seen in Figure 1 (◇), but it showed transition attributable to the melting point of the PEO chains at around 33 °C. Against this model, DNA/PEO/$NaClO_4$ mixed system showed no transition. Crystallization of PEO chains was suppressed in the DNA matrix due to the effect of ion-dipole interaction, steric hindrance, and so on.

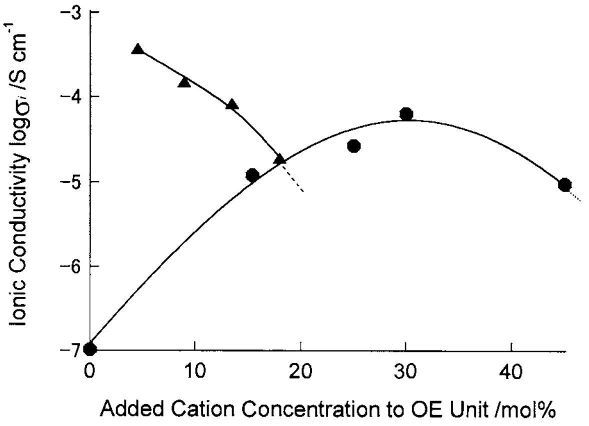

Figure 2. Effect of cation concentration on the ionic conductivity for $PEO_{1000}/LiClO_4$ (▲) and $DNA/PEO_{1000}/NaClO_4$ (●).

PEO content of the $DNA/PEO/NaClO_4$ mixture was concluded to be sufficient to prepare successive pathway for ion conduction. One of approaches to improve the ionic conductivity is to determine the optimum amount of the added $NaClO_4$. Figure 2 shows the effect of cation concentration on the ionic conductivity for $DNA/PEO_{1000}/NaClO_4$ (●) and $PEO_{1000}/LiClO_4$ (▲) as reference. The ionic conductivity of DNA/PEO_{1000} mixture without $NaClO_4$ was 1.03×10^{-7} S cm^{-1} at 50 °C. When $NaClO_4$ was added to the mixture, the ionic conductivity increased. The highest ionic conductivity, 6.43×10^{-5} S cm^{-1} was found at 50 °C when 30 mol% $NaClO_4$ was added to the DNA/PEO mixture. Further addition of salt made the ionic conductivity low. This tendency was similar to that for simple mixture of PEO and salt. The $DNA/PEO/NaClO_4$ mixture showed high ionic conductivity comparable to that of PEO/salt simple model. However, most suitable salt concentration which provided the highest ionic conductivity shifted considerably to higher concentration side as seen in Figure 2. Following points are now considered as possible reasons, i.e., suppression of chain crystallization in the DNA/PEO mixture, contribution of polar environment of DNA, influence of micro phase separation, and so on. Higher ionic conductivity should be observed as long as ion motion was supported by the PEO matrix. From these results, DNA/PEO mixture was concluded to be suitable matrix to solubilize and to stabilize ions without suppressing their motion.

DSC measurement for $DNA/PEO_{1000}/NaClO_4$ film was carried out to analyze the glass transition temperature. It is known that DNA shows no peak from -50 to +25 °C at this cooling rate.[13] The observed Tg was attributable to the PEO_{1000}. The Tg was originally -80 °C for PEO/DNA mixture, and it was jumped to -30 °C after addition of $NaClO_4$. Figure 3 shows Vogel-Tamman-Fulcher(VTF) plot of the ionic conductivity for a series of samples. The concentration of $NaClO_4$ is 15 (◆), 25 (●), 30 (■) and 45 mol% (▲) to OE unit, respectively. Since all of these are depicted as almost straight lines when Tg/1.05 was used as To in the VTF equation, observed Tg was confirmed to be due to $PEO/NaClO_4$ mixture. Little elevation of Tg in spite of increase of salt content might be due to the effect of DNA moiety, but detailed discussion is in progress.

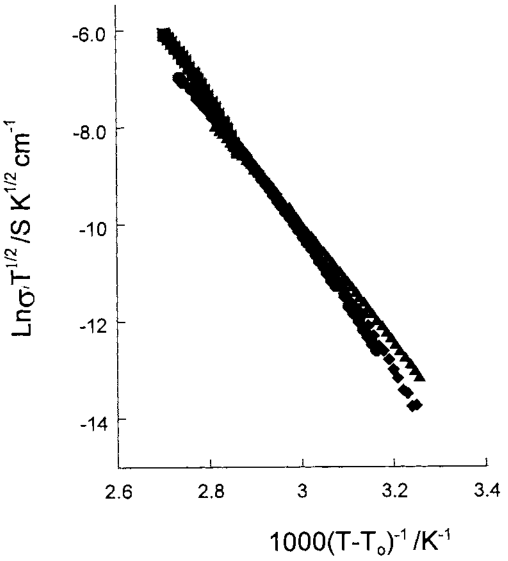

Figure 3. VTF plots for $DNA/PEO_{1000}/NaClO_4$. Amount of $NaClO_4$ was 15(◆), 25(●), 30(■) and 45mol% (▲) to OE unit , respectively.

Flexible films were obtained from DNA after mixing with PEO. The ionic conductivity was greatly improved when $NaClO_4$ was added to the film. The $DNA/PEO_{1000}/NaClO_4$ mixture was revealed to have similar ion conduction ability to PEO/salt mixture. It was suggested that $DNA/PEO_{1000}/NaClO_4$ could improve the number of carrier ion because of high solubilization ability of salt.

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References

1 D. Baril, C. Michot, and M. Armand, *Solid State Ionics,* **94,** 35 (1997).
2 K. Ito, N. Nishina, Y. Tominaga, and H.Ohno, *Solid State Ionics,* **86-88,** 325 (1996).
3 H. Ohno and K. Ito, *Polymer,* **36,** 891 (1995).
4 Y. Tominaga, K. Ito, and H. Ohno, *Polymer,* **38,** 1949 (1997).
5 K. Ito, N Nishina, and H. Ohno, *J. Mater. Chem.,* **7**, 1357 (1997).
6 Y. Tominaga and H. Ohno, *Chem. Lett.,* **1998**, 955.
7 K. Tanaka and Y. Okahata, *J. Am. Chem. Soc.,* **118,** 10679 (1996).
8 G. B. Sukhorukov, H. Möhwald, G. Decher, and Y. M. Lvov, *Thin Solid Films,* **284-285,** (1996).
9 N. Takizawa and H. Ohno, Proceedings of the 196th Annual Meeting of The Electrochemical Society, Hawaii, October 1999, Abstr., No. 49.
10 T. Osaka, X. Liu, and M. Nojima, *J. Power Sources,* **74**, 122 (1998).
11 K. M. Abraham and M. Alamgir, *J. Electrochem. Soc.,* **137,** 1657 (1990).
12 E. Tsuchida, H. Ohno, and K. Tsunemi, *Electrochim. Acta,* **28,** 833 (1983).
13 S. Rüdisser, A. Hallbrucker, and E. Mayer, *J. Phys. Chem.* **100**, 458, (1996).