Electroconductive Organogel. 6. Thermal and Electroconductive Characteristics of a Charged Polypeptide Gel in Organic Medium

Takuji Nishide, J. P. Gong, Hidekazu Yasunaga, Norio Nishi,[†] and Yoshihito Osada*

Division of Biological Sciences, Graduate School of Science, Hokkaido University, Sapporo 060, Japan

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ABSTRACT: A novel electroconductive polypeptide gel based on a formation of a charge-transfer (CT) complex between poly(L-lysine) (PLL) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) was prepared. The PLL gel extensively swelled in dimethyl sulfoxide (DMSO) containing TCNQ and showed a dark green color to give PLL^+TCNQ^-. Differential scanning calorimetric (DSC) measurement showed a significant depression of the melting temperature. The electrical conductivity of the PLL^+TCNQ^- gel below melting temperature of DMSO was nearly 3 orders of magnitude higher than the corresponding solution. These phenomena were explained in terms of the extensive association of DMSO molecules with the charged network through strong electrostatic interaction.

Introduction

In previous papers from our laboratory we have reported a new class of electroconductive organogels swollen in a nonvolatile organic solvent: *N,N*-dimethylformamide (DMF).[1,2] These gels are made of an electron-donating polymer network, cross-linked poly[*N*-[3-(dimethylamino)propyl]acrylamide] (PDMAPAA), and a low molecular electron acceptor, TCNQ subsequently doped to the polymer network in DMF. The PDMPAA gel showed extensive swelling and exhibited a green color when TCNQ was doped. The spectrophotometric and kinetic studies revealed that swelling and coloration are due to formation of the charge-transfer complex between a polymeric network and TCNQ, to give fully ionic species in DMF.

The doped acceptors underwent electrophoretic migration toward the anode under an electric field to give a two-dimensional orientation in the gel and showed anisotropic electroconductivity.[2] This class of organogels also showed the photo voltaic phenomenon when irradiated visible light and the efficiency were 4 orders of magnitude higher than that of the corresponding solution.[3] A repetitive oscillation and entrainment occurred in PDMAPAA–TCNQ gel when dc voltage was applied.[4]

This paper deals with the thermal and electrical properties of the cationic polypeptide gel swollen in DMSO. A significant depression of the melting point of the gel was observed.

The electrical conductivity of the gel was nearly 3 orders of magnitude higher than that of the corresponding solution below the melting point of DMSO. These phenomena were explained in terms of a strong association of DMSO molecules along the charged network through electrostatic interaction.

Experimental Section

Material. Poly(L-Lys(Z)) was synthesized from N^ϵ-carbobenzoxy-L-lysine (Lys(Z)) (from Peptide Laboratories) using diphenylphosphoryl azide (DPPA) (from Nakalai Tesque Inc.) and triethylamine (from Wako Jyunyaku Co., Ltd.) by reacting for 3 days in DMF according to the literature.[5] Poly(L-Lys) methanesulfate was derived from poly(L-Lys(Z)) using methanesulfonic acid (MSA) (from Wako Jyunyaku Co., Ltd.) and methoxybenzene (anisol) (from Wako Jyunyaku Co., Ltd.) at room temperature,[6,7] which was then transformed to poly(L-Lys) hydrochloride (PLL·HCl) by using anionic ion exchange resin (Amberlite IRA-400).

TCNQ was purified by repeated recrystallization in acetonitrile. Poly(ethylene diglycidyl ether) (Denacol EX830) was used as a cross-linking reagent without further purification. DMF (from Wako Jyunyaku Co., Ltd.) and DMSO were distilled *in vacuo*.

Preparation of PLL Gel. A 20 wt % aqueous solution of PLL·HCl containing Denacol equivalent to 25 mol % of the number of residues of PLL was prepared and adjusted to pH 12 by adding an appropriate amount of NaOH. This procedure was made on cooling using an ice bath. Cross-linking of PLL·HCl was made by heating the solution for 12 h at 40 °C, and a water-swollen PLL hydrogel was obtained. The gel was dried *in vacuo* at room temperature and then immersed in a large amount of DMSO containing an equimolar amount of TCNQ. The mixture was left standing for a prolonged period of time (10–15 days) until an equilibrium was reached. The PLL gel was gradually colored due to formation of a CT complex with TCNQ and swelled in DMSO. All experiments were carried out in a nitrogen atmosphere to prevent TCNQ from degradation with oxygen.[1,8]

The corresponding polymer solution was prepared in a similar manner to that of the gel but without Denacol.

Measurement. The degree of swelling, *q*, was determined by measuring the weight of the PLL(TCNQ) gel swollen in DMSO and the dried gels;

$$q = W/W_0$$

where W and W_0 are the weights of the swollen and dried gels, respectively. The polymer concentration of the gel which is identical to the network density was evaluated as follows:

$$\text{polymer concentration (wt \%)} = 100/q$$

The electrical conductivity (σ) of a PLL(TCNQ) solution and its gel was measured using an LCZ meter (2330A, NF Electronic Instruments) under an ac electric field (1 V, 1 kHz), whereupon a pair of 5 × 5 mm platinum black plates were used as electrodes. The electrical conductivity was calculated according to the following equation:

$$\sigma = (1/R)(L/S)$$

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* Author to whom correspondence should be addressed.

[†] Graduate School of Environmental Earth Science.

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where R is the resistance of the gel, L is the distance between the two electrodes, and S is the area of the electrode. The cell constant of the solution was calculated using a KCl solution as a standard sample solution. Conductivity measurement was made using a cryostat (Sinku Ichikawa Ltd.) in the range of 213−333 K under a nitrogen atmosphere.

The melting point of the gel and the corresponding solution was measured using a differential scanning calorimeter (DT-40 Shimadzu Co., Ltd.). Samples were hermetically sealed in aluminum pans and scanned under a helium atmosphere from 173 to 343 K with a heating rate of 5 K/min. Temperature and energy calibration were made using the melting transition peak of spectroscopic grade cyclohexane. The sample weight was varied between 7 and 10 mg, and no weight loss was recorded during the experiments.

Results and Discussion

We have found that PLL·HCl is not soluble in DMSO alone but dissolves slowly if DMSO contains an appropriate amount of TCNQ. The PLL(TCNQ) solution as well as the corresponding gel showed a dark green color having absorption maxima at 751 and 852 nm and other weak peaks and was assigned as a TCNQ anion radical.[1] From spectrophotometric measurement we assume that a charge-transfer complex according to the following equation has been formed:

$$\mathrm{PLL} + \mathrm{TCNQ} \rightleftharpoons \mathrm{PLL}^{+}\mathrm{TCNQ}^{-}$$

From the degree of swelling of the gel, it has been found that the PLL(TCNQ) complex is in a fully ionized state in DMSO, as PDMAPAA and other amino-containing polymers are,[1] to give a cationic PLL and TCNQ anion radical ($\mathrm{PLL}^{+}\mathrm{TCNQ}^{-}$).

As is well established,[9] poly(L-lysine) forms an α-helix structure in an aqueous alkali solution and we have confirmed this by the negative absorption peak at 225 nm by circular dichroism. We assume the gel keeps its helical conformation since the cross-linking was made by keeping the pH 12 throughout the reaction. Unfortunately, we failed to measure the CD spectrum of the PLL(TCNQ) gel because of its extensive absorption of DMSO and lack of reproducibility. However, there is a paper describing that poly(L-lysine) takes a helix conformation in DMSO,[10] and we assume the PLL(TCNQ) gel still keeps its helical conformation in DMSO.

Figure 1 shows typical DSC curves of DMSO (a), a DMSO solution of PLL(TCNQ) (b,c), and a PLL(TCNQ) gel swollen in DMSO (d). The thermogram of DMSO shows a sharp endothermic peak due to melting at 16.8 °C. This value is somehow lower than the reported one (18.5 °C),[11] probably due to presence of residual water. Melting temperatures of the polymer solution and gel were lower than that of DMSO, and their peaks were much broader. If one compares the polymer gel with the linear polymer solution, one notices easily that the gel melts at a lower temperature (gel, 4.3 °C; solution, 9.9 °C) with a wide satellite peak beginning at temperature as low as −50 °C. The wide endotherms observed here suggest that there exists a distribution of melting temperatures in the sample.

Figure 2 shows the PLL(TCNQ) concentration (network density in the case of the gel) dependence of the melting temperature of the solution and the gel in DMSO. The melting temperature of the solution and the gel decreased extensively with an increase in concentration, whereupon the gel decreased more sharply.

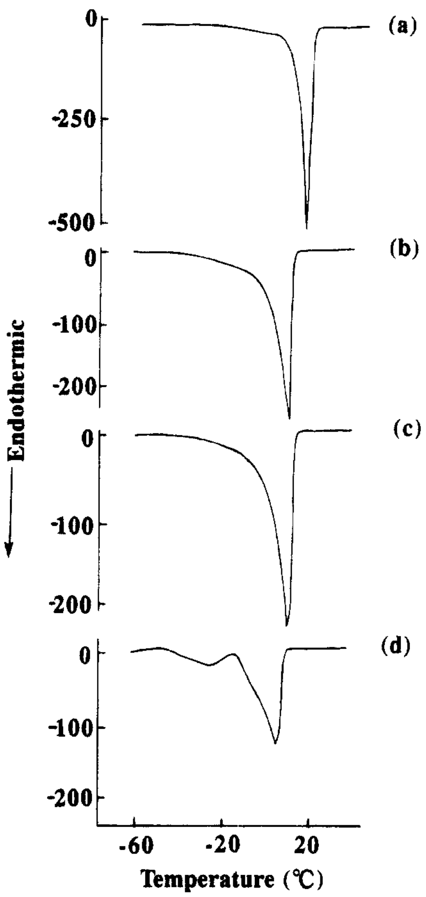

Figure 1. Typical endothermic DSC curves of DMSO (a), a PLL(TCNQ) solution in DMSO (b,c), and a PLL(TCNQ) gel swollen in DMSO (d). Sample amount and PLL(TCNQ) concentration: (a) 8.3 mg; (b) 6.9 mg, 3.0 wt %; (c) 9.9 mg, 15 wt %; (d) 8.0 mg, 14 wt % (q = 7).

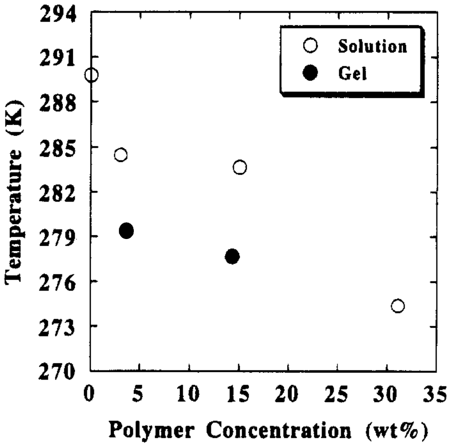

Figure 2. Concentration dependencies of the melting temperature of the PLL(TCNQ) solution and the gel in DMSO. The concentration of the gel is calculated from the network density (per repeating unit) in DMSO.

The enthalpy changes of melting for various polymer concentrations of the solution and the gel were calculated from the peak intensity in Figure 1; it was found that the enthalpy of melting decreases with an increase in the polymer concentration for both cases, but the decrease was more extensive for the gel. These results indicate the presence of a considerable amount of unfrozen DMSO in the gel below −60 °C.

Similar phenomena of a melting temperature depression and a board satellite peak have been observed in several neutral (noncharged) hydrogels swollen in water, and the phenomenon was attributed to the strong association of water molecules through hydrogen bounding.[12,13] Water molecules in aqueous biopolymer solutions and hydrogels are, in general, classified into three categories:[14] free water which freezes at 0 °C, water molecules which show a first-order phase transition below 0 °C (bound water), and those which do not crystallize even at temperature as low as 130 K (nonfreezing water).

As reported previously,[1,2] polymers having amino group are fully ionized in DMSO or DMF, forming a CT complex with TCNQ, and behave as strong polyelectrolytes.

An enhanced depression in the melting temperature, the broader endothermic peak, and a decreased enthalpy of fusion observed for the polymer gel indicate that DMSO molecules are more strongly bound with the macroions of the network through electrostatic interaction.

Endotherms of a polymer gel at 4.3 °C and a wide satellite peak might be assigned to free and freezing bound DMSO molecules, respectively. From the sample amount of PLL(TCNQ) gel and peak area of these two peaks, one could roughly calculate the amounts of unfrozen DMSO filling the network as 40% and 22% for the gel with a PLL(TCNQ) concentration of 14 wt % ($q = 7$) and 3.5 wt % ($q = 28$), respectively. While the amounts of unfrozen DMSO were calculated as 18% and 13% for the solution with a PLL(TCNQ) concentration of 30 wt % and 15 wt %, respectively.

On the basis of the Poisson-Boltzmann distribution, we have previously proposed a one-dimensional capillary model and a three-dimensional network model to simulate the electrostatic potential energy distribution of fully-ionized polyelectrolyte gels.[15,16] The simulation result revealed that there exists deep electrostatic potential wells at every cross-linking point and potential valleys around the polymer chains, thus making a strong electrostatic field, especially around the cross-linking points. The electrostatic potential and the electric field steeply increase with a decrease in the distance from the charged network, and the water molecules located within several nanometrs of the network exist in an electrostatic potential field as high as 10^7 V/m. In a similar manner, the enhanced electrostatic field observed in the gel should make the DMSO (molecules) in a polarized state, thus lowering the freezing point of the DMSO molecules.

Figure 3 shows temperature dependencies of the electrical conductivity of the polymer gel as well as the corresponding polymer solution. An abrupt increase in the electrical conductivity in the range of 240–280 K should be associated with the melting of DMSO. The electrical conductivity increased 5 orders of magnitude for the polymer gel and 4 orders of magnitude for the solution in this temperature range. An abrupt increase in the conductivity begins at a temperature as low as 228 K for the polymer gel and 258 K for the solution, and this result well coincides with the experimental data showing the decreased melting–freezing transition temperature of the polymer gel than the corresponding solution shown (Figure 1).

An enhanced electrical conductivity of the gel in a lower temperature range may be associated with enhanced mobilities of carrier ions in the network. In other words, unfrozen TCNQ anion radicals (and in part the cationic PLL network) have a high enough mobility to transport charges in the gel below the melting temperature of DMSO, and the reason should be attributed to the deep potential well at the cross-linking point,[15,16] which is the intrinsic nature of the network. A more detailed study of the role of the network on the enhanced conductivity is in progress and will be reported later.

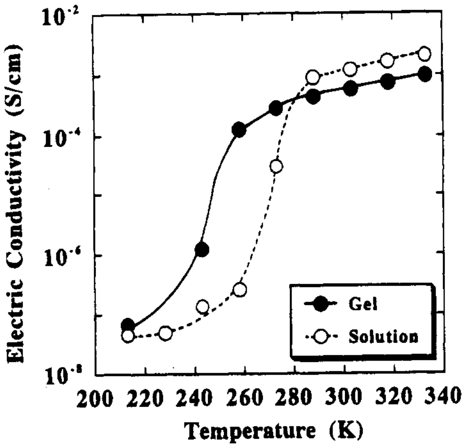

Figure 3. Temperature dependencies of the electrical conductivity of the PLL(TCNQ) solution and the gel in DMSO. PLL(TCNQ) concentration: solution, 15 wt %; gel, 14 wt % ($q = 7$).

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