Communications to the Editor

Electrophoretic Orientation of Phthalocyanine Molecules in Polymer Gel

Introduction. Polymer gel consists of an elastic cross-linked polymer network and a fluid filling the interstitial space of the network. We recently synthesized a new class of electroconductive organogels swollen in nonvolatile organic solvent, *N,N*-dimethylformamide (DMF).[1] This gel is composed of an electron-donating polymeric network and a low molecular weight electron acceptor, subsequently doped to the polymer network.

We found that 2,3,9,10,16,17,23,24-phthalocyanineoctacarbonitrile (octacyanophthalocyanine; OCPc) doped as an electron acceptor in poly[(dimethylamino)propylacrylamide] (PDMAPAA) gel undergoes electrophoretic migration toward the anode and makes a two-dimensional orientation in the gel. The polymer gel thus obtained as well as the dried one showed anisotropic electroconductivity as large as 3 orders of magnitude. This electrophoretic orientation in the electroconductive polymer gel provides a new method to synthesize electroconductive organic materials with organized structure.

Experimental Section. Preparation of the Gel. A cross-linked PDMAPAA gel was prepared by radical polymerization of a 3 M DMF solution of (*N,N*-dimethylamino)propylacrylamide (DMAPAA) in the presence of a calculated amount of *N,N*-methylenebis(acrylamide) (MBAA) and azobis(isobutyronitrile) (AIBN). The polymerization was carried out in an ampule (10 mm in diameter, and 100 mm in length) at 60 °C for 10 h under nitrogen atmosphere. Doping of OCPc was made by immersing PDMAPAA gel into a large amount of a DMF solution of OCPc.

OCPc was synthesized according to the literature,[2] i.e., via polycyclotetramerization of 1,2,4,5-benzenetetracarbonitrile through an intermediate, 4,5-diiminoisoindolinecarbonitrile.

Measurement. The conductivity of the gel was measured with a pair of platinum plate electrodes (1 × 0.5 cm^2) in N_2 atmosphere at room temperature using an electrometer (HA-501, Hokutodenko Co.). The conductivity of the solutions was measured with a pair of platinum-black plate electrodes using a conductmetric meter (CM-30, Shimadzu). The conductivity of the film of dried gel was measured with four vacuum-evaporated gold electrodes in vacuo. X-ray diffraction patterns of the gel were taken with nickel-filtered Cu Kα radiation using an X-ray diffractometer (XD-610, Shimadzu).

Results and Discussion. PDMAPAA gel swollen in DMF is transparent and slightly yellow. However, when OCPc was doped, the gel showed significant contraction and became blue. For example, PDMAPAA gel cross-linked with 0.3 mol % MBAA contracted to half of the initial volume by doping of 0.2 mol % OCPc in DMF. *OCPc has two absorption peaks in DMF, at 630 and 690 nm, and their intensity ratio is 6:7.*[3] However, when OCPc solution is mixed with a DMF solution of PDMAPAA, the absorption maximum of OCPc at 690 nm becomes weaker and a new absorption peak appears at 598 nm (Figure 1). *This spectral change is commonly observed when OCPc undergoes interaction with electron-donating polymers, such as poly(vinylcarbazole) or polyimide.*[4] *The reduction potential of OCPc also shifts from 0.3 to 0.2 V by the presence of these electron-donating polymers*[5] *These experimental data indicate that OCPc makes an electronic interaction with PDMAPAA as shown in eq 1.* If the relative intensity of absorption at 690 and 598 nm is plotted against the molar ratio of PDMAPAA to OCPc, a straight line bending near PDMAPAA/OCPc = 0.1 is obtained (Figure 2). In contrast, DMAPAA, a low molecular weight analogue of PDMAPAA, shows little absorption change and hardly interacts with OCPc. Absorptions of OCPc in the range of 550-700 nm have been characterized as a Davydov splitting manifesting $\pi-\pi$ interactions between neighboring phthalocyanine molecules.[6] Since the splitting seen in the spectra for OCPc is likewise due to Davydov splitting, this result indicates that the PDMAPAA involved has decreased $\pi-\pi$ interaction between adjacent OCPc molecules.

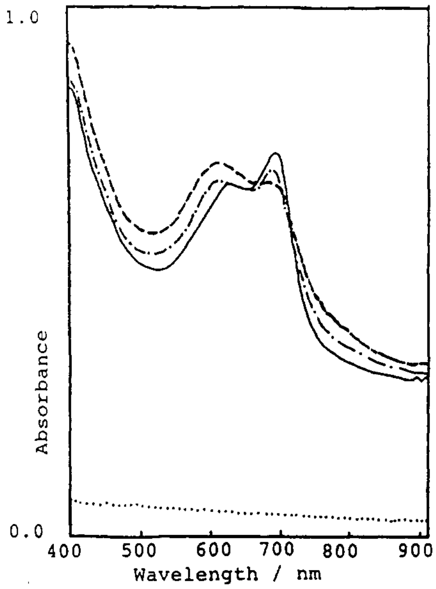

Figure 1. Electronic spectra of OCPc and PDMAPAA in DMF: (—) OCPc = 10^{-5} mol/L; (– –) OCPc in the presence of PDMAPAA (OCPc = 10^{-5} mol/L, PDMAPAA = 10^{-4} mol/L); (–·–) OCPc in the presence of DMAPAA (OCPc = 10^{-5} mol/L, DMAPAA = 10^{-4} mol/L); (···) PDMAPAA 10^{-4} mol/L.

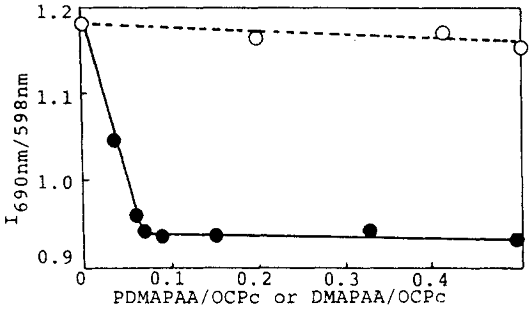

Figure 2. Plot of relative absorption intensity at 690 and 598 nm against the molar ratio of PDMAPAA to OCPc: (-●-) PDMAPAA/OCPc; (- -○- -) DMAPAA/OCPc. Concentration of PDMAPAA, 10^{-4} mol/L in DMF.

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Table I
Conductivity of PDMAPAA/OCPc Gel before (Wet Gel) and after (Dry Gel) Drying (S/cm)[a]

OCPc/PDMAPAA	wet gel σ_0	wet gel σ_x	wet gel σ_z	dry gel σ_0	dry gel σ_x	dry gel σ_z
0.02	5.0×10^{-6}	3.8×10^{-5}	1.8×10^{-8}	2.0×10^{-7}	3.8×10^{-4}	4.0×10^{-7}
0.05	3.3×10^{-5}	4.2×10^{-4}	1.2×10^{-7}	6.5×10^{-7}	1.1×10^{-4}	2.7×10^{-7}
0.25	2.1×10^{-3}	1.3×10^{-2}	8.1×10^{-4}	2.3×10^{-3}	1.2×10^{-5}	2.3×10^{-6}

[a] σ_0, before application of the electric field. σ_x, parallel to the electric field. σ_z, perpendicular to the electric field.

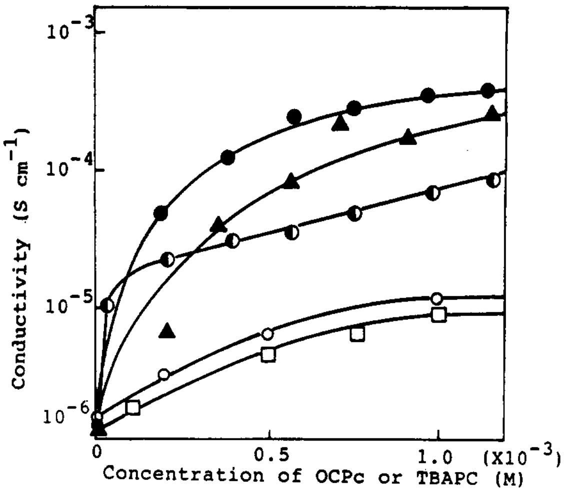

Figure 3. Dependences of conductivity on the concentration of OCPc or TBAPC in DMF: (▲) PDMAPAA/OCPc gel; (●) PDMAPAA/OCPc solution; (◐) DMAPAA/OCPc solution; (○) OCPc; (□) TBAPC. PDMAPAA = DMAPAA = 10^{-2} mol/L.

These spectrophotometric results as well as contraction of the PDMAPAA/OCPc gel indicate the possibility that OCPc has made specific interaction with the PDMAPAA network, which can be schematically shown as follows:

$$\text{PDMAPAA} + \text{OCPc} \rightleftarrows (\text{PDMAPAA}^{\delta+}\cdots\text{OCPc}^{\delta-}) \rightleftarrows (\text{PDMAPAA}^{\bullet+} + \text{OCPc}^{\bullet-}) \quad (1)$$

At present, we have no conclusive evidence as to whether or not OCPc has been fully ionized in DMF as 7,7,8,8-tetracyanoquinodimethane (TCNQ) does with PDMAPAA.[1] *This is the subject of further investigation.*

An addition of OCPc to a PDMAPAA solution or a PDMAPAA gel results in a dramatic increase in their conductivity as shown in Figure 3. The conductivity of DMAPAA (monomer) increased as well by addition of OCPc, but the enhancement of the conductivity of the PDMAPAA gel or the solution exceeded that of DMAPAA, indicating more strong interaction of PDMAPAA with OCPc to give a more ionized form in eq 1 than DMAPAA. Note that the conductivities of both PDMAPAA/OCPc solution and PDMAPAA/OCPc gel are nearly 2 orders of magnitude higher than that of the DMF solution of tetrabutylammonium perchlorate (TBAPC). Since TBAPC is a strong electrolyte and is supposed to be fully ionized in DMF, it can be assumed that OCPc is also ionized in DMF at least in part.

This was proven by the fact that OCPc makes an electrophoretic migration toward the anode in the PDMAPAA gel. When this gel is inserted between a pair of platinum electrodes and dc voltage is applied in a sweeping range of ±10 V, the current decreases rapidly by repeated sweeping. At the same time, one can observe that the blue of OCPc gradually moves toward the anode and the gel near cathode becomes almost transparent. If the dc voltage is turned off, the gel recovers the initial conductivity and uniform blue color. However, if sweeping is continued for a long period of time, more than 60 min, the gel cannot recover the initial conductivity any more and stays at a low conductivity of 15% of the initial value. The blue color also stays near the anode in the gel. This electrophoretic movement of OCPc toward the anode strongly suggests that OCPc molecules are negatively ionized, probably due to formation of a CT complex with PDMAPAA. It would be worth noting that OCPc unless doped in the gel makes no electrophoretic movement in DMF under the same electric field.

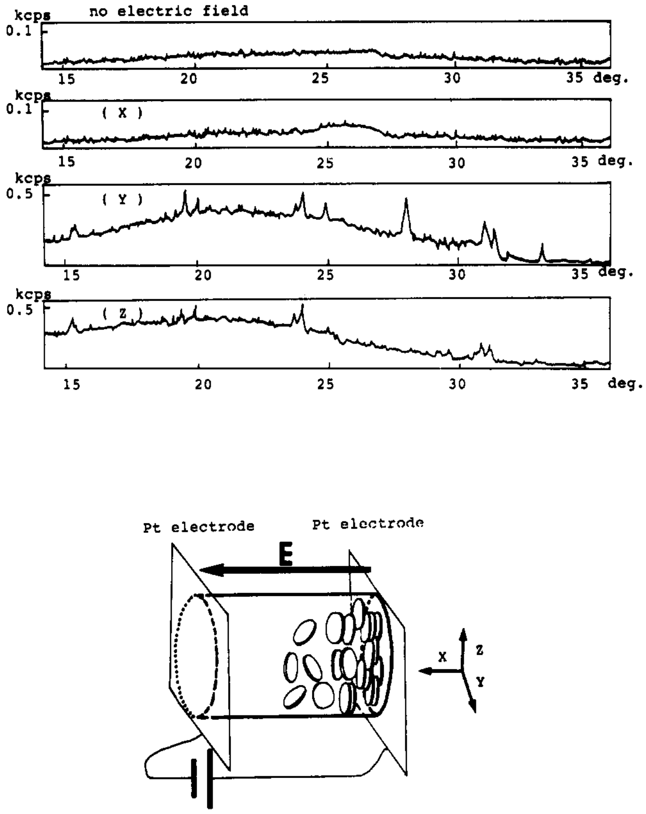

Figure 4. X-ray diffraction patterns of PDMAPAA/OCPc gel. *X*, *Y*, and *Z* indicate the direction of X-ray exposed, and *E* is the direction of the electric field applied.

An interesting feature here is that a prolonged application of electric field results in an orientation of OCPc molecules in PDMAPAA gel to give anisotropic conductivity.

Figure 4 shows X-ray diffraction patterns of the gel near the anode. It is seen that after application of the electric field the gel becomes crystalline, showing biaxial orientation perpendicular to the electric field. Since the polymer gel is amorphous unless an electric field is applied and also unless the gel contains OCPc, the orientation of the gel is apparently due to electrophoretic migration of OCPc toward the anode to give a regularly organized structure of OCPc.

Two-dimensional orientation of OCPc molecules in the PDMAPAA gel results in an anisotropic electroconductivity. As shown in Table I the conductivity of the polymer gel parallel to the electric field was 3 orders of magnitude higher than the conductivity perpendicular to the electric field applied. Enhanced conductivities to this direction were observed in all gels with different doping ratios, and this can presumably be associated with more favorable ionic and/or electronic conduction between neighboring OCPc rings well-organized in the polymer gel.

When this gel is evacuated and dried in vacuo, a dark brown solid film consisting of PDMAPAA and OCPc is obtained. This film also shows an anisotropic conductivity as shown in Table I, indicating that no disordering of OCPc occurs by drying. Drying of the amorphous gel (no electric field was applied) decreased the conductivity by a factor of 1 or 2 orders of magnitude, whereas those of the oriented one, in some cases, increased. Since the electric conductivity of dried film is apparently dominated by the electronic conduction mechanism, it can be assumed that ionic conduction of the solvent-swollen gel has transformed to electronic conduction in the course of drying, and this transition point, if both mechanisms are not sharing, depends on the amount of solvent in the gel.

Similar electrophoretic organization of dopant molecules in the gel and anisotropic conductivity was found in PDMAPAA/tetracyanobenzene gel. However, no orientation and anisotropic conductivity was observed in PDMAPAA/tetraphenylporphiline gel. PDMAPAA/tetracyanoethylene showed electrophoretic movement in the PDMAPAA gel, but no anisotropy of the conductivity was observed. Thus, the preparation of an electroconductive organogel based on the polymer CT complex and subsequent application of dc current can provide a new method to synthesize electroconductive organic materials with organized molecular structure.

Detailed analyses of the structure and the conduction mechanism of the gels are currently underway.

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References and Notes

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Y. Osada* and S. Ohnishi

Department of Chemistry
Ibaraki University, Mito 310, Japan

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