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Direct Observation by Laser Scanning Confocal Microscopy of Microstructure and Phase Migration of PVC Gels in an Applied Electric Field

Hong Xia, Takamitsu Ueki, and Toshihiro Hirai*

Smart Materials Engineering, Faculty of Textile and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

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The fluorescent probe lucigenin was incorporated in poly(vinyl chloride) (PVC) gels, and laser scanning confocal microscopy (LSCM) was used to clarify the internal structures of the gels. From the two-dimensional and three-dimensional information by LSCM, we first observed the internal structure of the PVC gel at a wet status, where the PVC gels comprised a polymer-rich phase and a polymer-poor phase uniformly with a three-dimensional network structure. After an electric field was applied, an effect of the electric field resulted in the change of internal structure in the gels. The polymer-poor phase moved from the cathode to the anode and the polymer-rich phase formed linelike arrangement between electrodes due to the attraction force. On the other hand, the freeze-dried PVC gels with/without in-situ dc voltage casting were particularly fabricated to confirm above results by the field emission scanning electron microscopy (FE-SEM). It was found that many craters remained on the surface of the gel near the anode due to sublimation in freeze-drying. This phenomenon did not appear on the surface near the cathode. The results of in-situ dc voltage casting also suggested that a substantial amount of polymer-poor phase was moved and fixed at the anode. Thus, results of both LSCM and in-situ dc voltage casting corresponded to the effect of electric field on PVC gels and provided a convincing evidence for the interpretation of the deformation mechanism of PVC gel actuators by an applied electric field.

1. Introduction

The formation of poly(vinyl chloride) (PVC) physical gels is generally classified as crystallization-induced gelation,^{1–3} and microcrystals can be formed only by the association of syndiotactic sequences as junction points in the network structure of gels.⁴ Their internal structures are related to the characteristics of gels such as optical, mechanical, and thermal properties. PVC gels with more than 60 wt % dibutyl adipate (DBA) plasticizer have unique dielectric response behavior and creeping deformation^{5,6} that always occurs on the anode (see Supporting Information Figure 1). Using this asymmetric deformation behavior and designing boundary conditions such as the shape and size of electrode and gel, various PVC gel actuators have been developed in our group.^{7,8} In previous work we found a polarization phenomenon of PVC gel, in which PVC particles flocked together at the anode and adopted an arrangement of linelike tracks in the electric field due to the contribution of DBA as a solvent, while DBA moved from cathode to anode very quickly.⁹ This movement of the plasticizer DBA caused the mechanical properties and surface characteristics to be different in the gel near the anode and the

cathode. So, an asymmetric deformation, creeping motion would be engendered.¹⁰ To study the actuation mechanism and use PVC gel materials effectively, clarifying the internal structures of the gels in an applied electric field is indispensable, and it is still important focus in PVC gel actuators. However, the dielectric constants of the solute and solvent in a gel are generally similar and difficult to contrast in light.¹¹ PVC gel with a large amount of plasticizer is extremely flexible, with high viscosity and high transparency. Even highly precise and high-magnification devices such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), and scanning probe microscopy (SPM) may be difficult to use directly for analysis of internal structure and morphological evolution of untreated (wet) PVC gels. Recently, laser scanning confocal microscopy (LSCM) has attracted the attention of many researchers as a very powerful technique for observation of three-dimensional phase-separated morphology. Three-dimensional information on phase-separated structures from a series of sliced images can be obtained by moving the focal plane in the depth direction of the specimen (parallel to the incident beam axis). Jinnai et al. have constructed a three-dimensional image of bicontinuous phase-separated structures by computationally stacking such images.^{12,13} Takeno et al. used LSCM and light scattering (LS) to investigate the time evolution of the phase-separated morphology in a binary polymer mixture involving a percolation-to-cluster transition (PCT).¹⁴ Hirokawa directly observed the internal structure of

*To whom correspondence should be addressed. E-mail: tohirai@shinshu-u.ac.jp.

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poly(*N*-isopropylacrylamide) gel.¹⁵ Thus, the method of LSCM observation will be valuable to evaluate internal structure of the PVC gel. In the present study, we incorporated the fluorescent probe lucigenin in PVC gel and carried out LSCM to visualize the polymer-rich phase and the polymer-poor phase and their structure in wet PVC gels and their changes before and after application of an electric field. In addition, in order to inspect the movement of DBA by applied an electric field more definitely, we utilized in-situ dc voltage casting to keep the state of DBA migration and then used freeze-drying and field emission scanning electron microscopy (FE-SEM) to verify the results of LSCM observation.

2. Experimental Section

A. Preparation of the PVC Gels. Four PVC gels were prepared with 1:1, 1:5, 1:9, and 1:10 w/w % of the PVC (with degree of polymerization 3700):plasticizer dibutyl adipate (DBA). The gels are coded as PVC1, PVC5, PVC9, and PVC10, respectively. The DBA content is one of the important factors for morphology and properties of the gels. Thus, the different DBA contents of PVC5 and PVC10 without in-situ casting were prepared for LSCM tests. For in-situ dc voltage casting, PVC9 was prepared, while PVC10 was hard to be formed due to casting condition change. PVC1 with low DBA content was also prepared for the comparison of structure in freeze-drying.

PVC particles were dissolved in mixtures of tetrahydrofuran (THF) solvent and DBA plasticizer by blending for 3 days and then cast in a Teflon laboratory dish at room temperature. After evaporating THF for 5 days, a transparent PVC gel was formed.

To fix the state of the PVC gel in an applied electric field, we used the in-situ dc voltage casting setup (see Supporting Information Figure 2) to cast the gel. The distance was 5 mm between the two electrodes and about 2 mm from the top electrode (anode) to the surface of the PVC/DBA/THF solution. The dc power was turned on and the voltage maintained at 1 kV for at least 24 h at room temperature (about 30 °C). After a few days PVC9 gel (0.40 mm thick) was formed. For this special sample, the spectra of both surfaces (the anode and cathode sides) were investigated using attenuated total reflection Fourier transform infrared (Shimadzu Iprestige-21) spectroscopy.

B. Fluorescent Probe. Lucigenin (bis-*N*-methylacridinium), a fluorescent indicator for Cl^- , had molecular weight (M_w) 510.5 g mol⁻¹, light absorption wavelength (λ_{max}) 480 nm, and wavelength of maximum (bluish-green) fluorescence 505 nm. Lucigenin is soluble in water, ethanol, and acetone. In our previous work, we found that negative charges existed in PVC gel internal by the space charge measurement.⁹ It could be considered that the negative charges include the Cl^- and O_2^- . Lucigenin is an aromatic compound used in areas that include chemiluminescence; it can be used as a probe for superoxide anion in biology and has an extinction effect for chlorine anion. Therefore, the DBA-rich phase and the PVC-rich phase in PVC gel may be distinguished by the chemiluminescent properties of lucigenin. On the other hand, the fluorescent lucigenin was casted as a solid existed uniformly in the interior of gel and its size (with several benzene rings) is large. This may be considered that the fluorescent lucigenin is difficult to flow toward the cathode when an electric field is applied and will be suitable for PVC gel preparation. Herein, a dilute solution of lucigenin in THF (4–6 drops) was added to PVC/THF/DBA solution to make PVC5 and PVC10 gels for validation of the PVC gel structure and its variation in an applied electric field.

C. LSCM and Fluorescence Microscope Observation. A BX50-fluorescence microscope (Olympus) with WBV filter was used to observe actuation of the PVC gel. An FV1000-D laser scanning confocal microscope with a 60× objective lens was

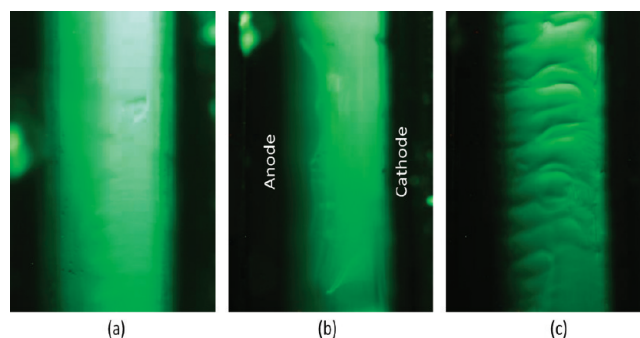


Figure 1. Fluorescence microscope images of the cross section of a PVC9 gel that was sandwiched between two electrodes (right: cathode; left: anode): (a) before, (b) during, and (c) after application of an 800 V dc electric field.

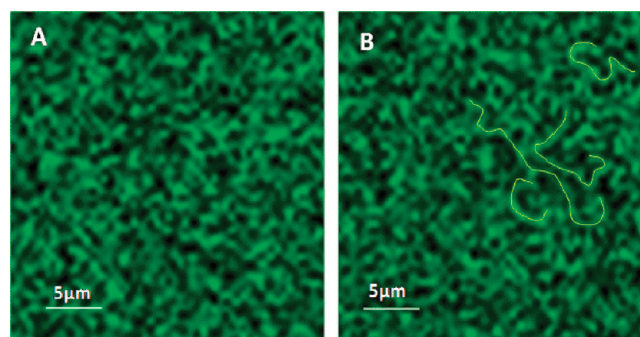


Figure 2. LSCM 2D images of PVC10 gel before and after application of a 1 kV electric field.

used to investigate the internal gel structure and variation by 3D scanning. The incident laser beam travels along the *z*-direction. Three-dimensional images of the PVC gel domains are obtained by shifting the focal plane (*x*–*y* plane) along the *z*-direction and computationally stacking the LSCM sliced images taken from the respective focal planes (see Supporting Information Figure 3). PVC5 and PVC10 gels were observed and compared before and after application of a 1 kV dc voltage within 5–10 min, in which the structure is in a relatively stable state.

D. Freeze-Drying and FE-SEM. In order to conduct FE-SEM observation, freeze-drying was used to preprocess the PVC gels which were casted with and without an applied electric field. A 15 × 24 mm² test piece of PVC9 gel included two parts: part A subjected to the 1 kV electric field and part B that was not subjected to the electric field. Both parts were freeze-dried (FDU-1200, EYELA) at –49 °C trap temperature and 8.7 Pa vacuum pressure for 218 h. To compare gels with different DBA contents, PVC1 (0.15 mm thickness, 15 × 15 mm²) was also prepared by freeze-drying. The surfaces and cross sections of the samples were observed using a Hitachi S-5000 field emission scanning electron microscope.

3. Results and Discussion

A. LSCM Observation. Figure 1 shows the results of PVC gel actuation. The sample was set between the electrodes under the fluorescence microscope. It is apparent from Figure 1a that the cross section of the gel was uniformly bright. When 800 V dc voltage was applied (see Figure 1b), the gel was attracted to the anode, and the thickness reduced to 80% of the original thickness. After the electric field was turned off, a wrinkle pattern appeared in the direction of the electric field in the cross section of the gel, and 90% of the thickness was recovered (Figure 1c). In the previous study, we have confirmed that a polarization phenomenon

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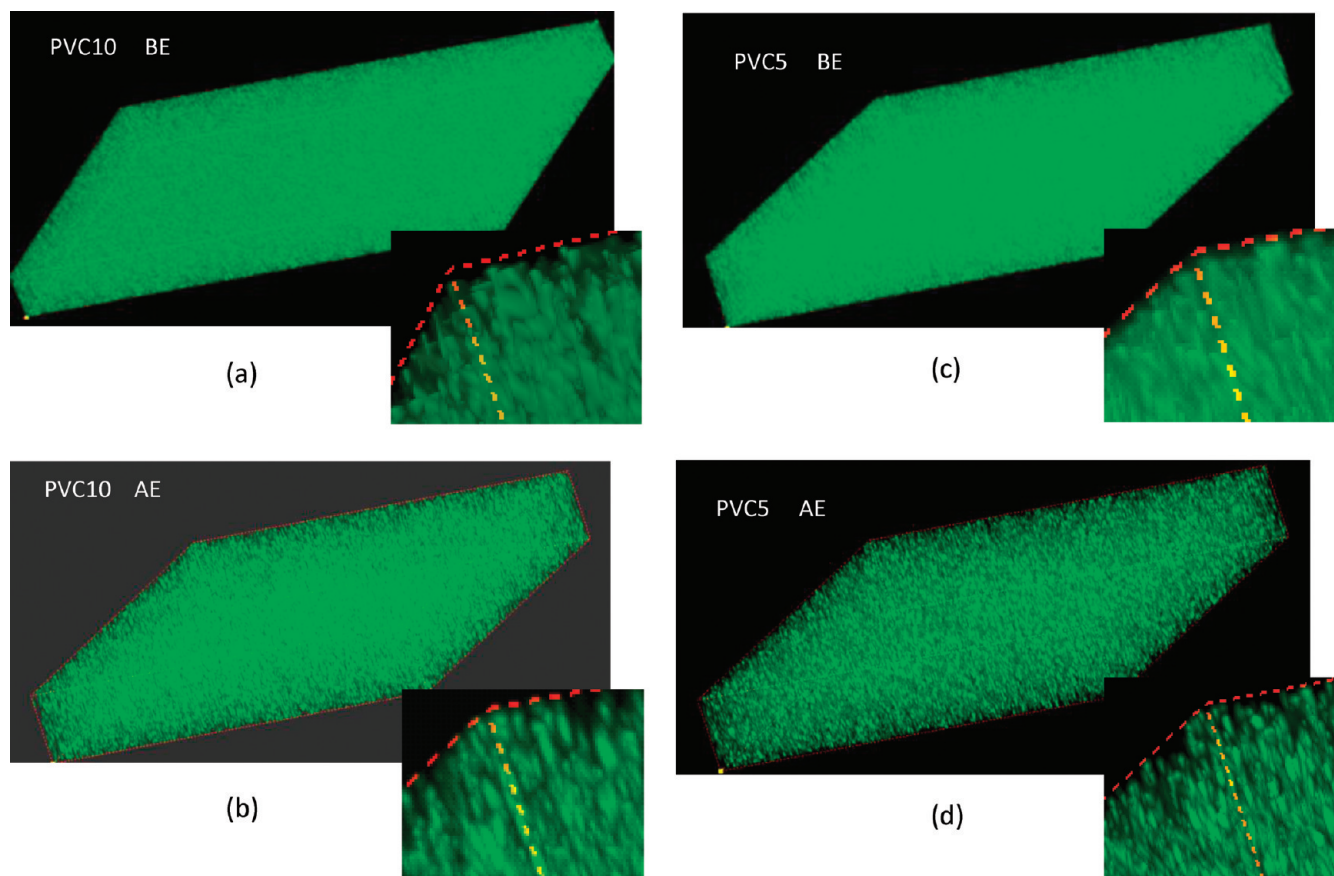


Figure 3. LSCM 3D images ($318 \times 318 \times 100 \mu\text{m}$) of PVC10 and PVC5 gel before (a, c) and after (b, d) application of a 1 kV electric field. The insets are higher magnification images.

in PVC polymer with DBA appeared when an electric field was applied.⁹ PVC polymers will be arranged as linelike in a parallel direction to applied electric field, and DBA moved to the anode. Thus, the internal structure of the PVC gel was changed by applying the electric field, and then the wrinkle pattern in gel cross section remained.

Figure 2 shows a 2D LSCM image of PVC10 gel in the x – y plane before and after application of a 1 kV electric field. The phase structure of PVC gels appeared clearly: the light green area showed the DBA-rich phase, and the dark area marked the PVC-rich phase since emitted light of lucigenin may be quenched by Cl^- . By comparison with the LSCM image of PVC5 and PVC10, the dark area of PVC5 was larger than that of PVC10. The DBA-rich phase was interconnected and surrounded by the PVC-rich phase with many string shapes less than $1 \mu\text{m}$ in width and different lengths to form fringed micelle microcrystals as junction points in the network structure.^{16–23} Some dark domains were isolated by light green domains. After application of 1 kV dc voltage, the light domains became longer (see Figure 2, image B). It may be considered that the DBA-rich phase was moved and easily connected by applying the electric field.

Figure 3a,b shows three-dimensional images of the samples in Figure 2. Ten of the x – y plane slices were overlapped to form the three-dimensional structure of a $100 \mu\text{m}$ thick gel. Figure 3b shows that the dc voltage induced changes such that the dark domain (PVC-rich phase) was changed more perpendicular to the electrode, and the structure of the gel had a more regular arrangement than that of the original gel (before application of the electric field). The specimen with lower DBA content (PVC5) displayed a similar result (Figure 3c,d), and the differences with and without the applied electric field seem clearer than for PVC10 because the recovery ability of the PVC5 gel was lower than that of the PVC10 gel when the dc voltage was removed. These results correspond to the polarization phenomenon of PVC particles.⁹ Regardless of gel state (amount of plasticizer), the results discussed above indicate that a polarization phenomenon of PVC polymer occurred, in which PVC molecules tended to flock together at the anode and adopt an arrangement of linelike tracks in the electric field due to the contribution of DBA plasticizer. Moreover, the polarization phenomenon facilitates the plasticizer moving to the anode and causing the creeping deformation.

The top sliced and bottom sliced 3D scanning images of PVC5 gel after application of 1 kV dc voltage are compared in Figure 4. To easily distinguish images, we did image processing for (a) and (d) and obtained the edge extraction results of light domains in (b) and (e) and the invert colors images in (c) and (f). Comparing the top (a, b, c) and bottom sliced (d, e, f) images, the light domain in the top sliced sample (near the anode) is much greater than in the bottom sliced image (near the cathode). In particular, the density in the edge extraction image (b) was much higher than in (e), and the dark domain in the invert colors image (c) was larger

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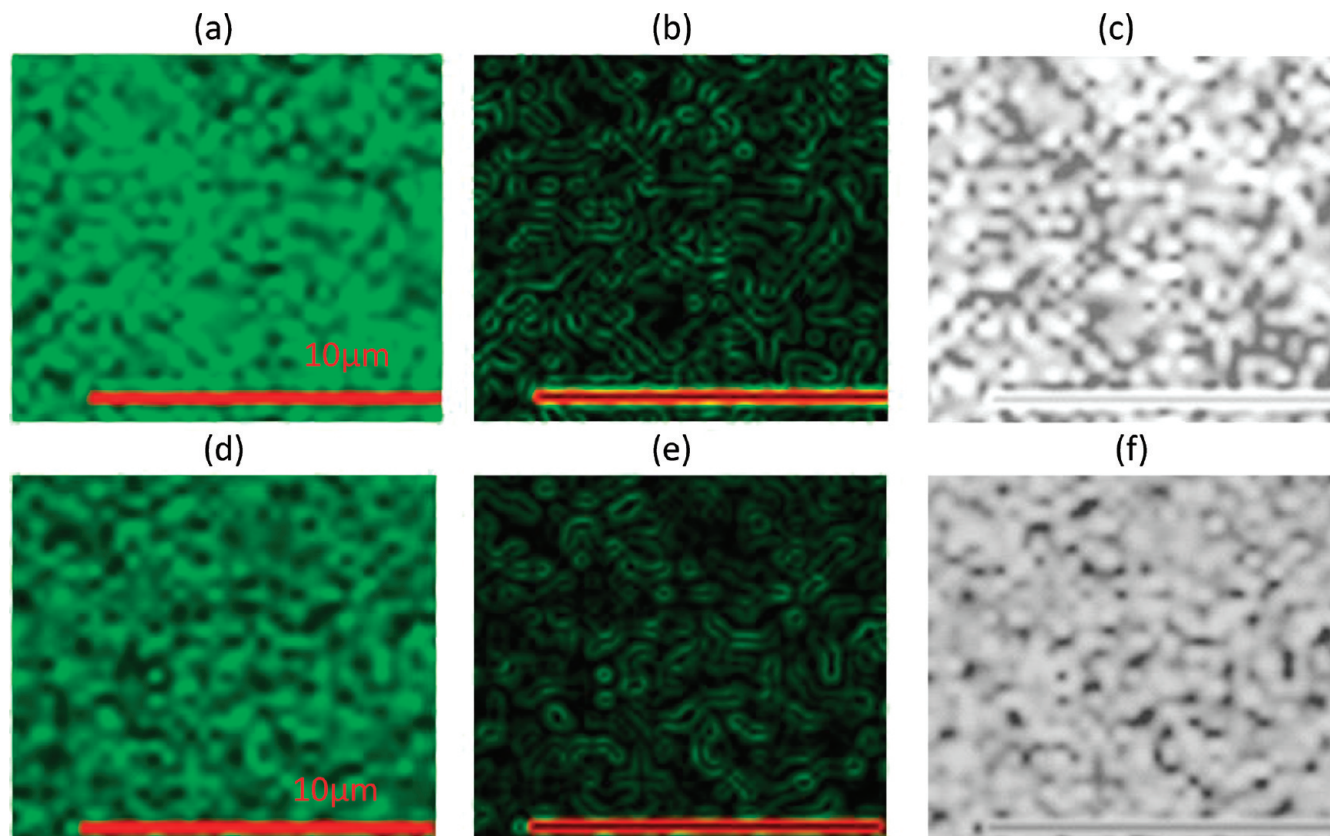


Figure 4. LSCM 2D images of PVC5 gel after application of a 1 kV electric field: (a) is top slice (near the anode) and (c) is the bottom slice (near the cathode) of the 3D images in Figure 3; (b) and (e) are edge extraction results of (a) and (d); (e) and (f) are invert colors results of (a) and (d), respectively.

than in (f). We calculated using image analysis software that the area of the light domain (DBA-rich phase) was 58.6% in the top sliced image and 46.1% in the bottom sliced image. It is concluded that the DBA-rich phase moved to the anode side to cause an asymmetric distribution of the internal structure of PVC gel between the two electrodes when an electric field was applied.

B. Freeze-Drying and FE-SEM Observation. Before freeze-drying, the FT-IR spectra were recorded of the anode and cathode surfaces of PVC9 gels with and without dc voltage casting. The intensity of the carbon–chlorine (C–Cl) band in the 690–710 cm^{-1} region^{10,24} varied considerably (Figure 5). The intensity of the 690–710 cm^{-1} band at the cathode was much stronger than at other locations, and that band can scarcely be observed at the anode surface. It is considered that the electric field has an influence on the content of the surface components due to a migration of the plasticizer DBA.

After freeze-drying for 218 h, the PVC9 gel shrank to about $9 \times 12 \text{ mm}^2$ area with 23.4 mg weight, and the area size of PVC1 gel reduced to $12.5 \times 11.5 \text{ mm}^2$ with 8.1 mg weight. The shrinkage rate (δ) can be calculated using the following equation:

$$\delta = \frac{A - A_0}{A_0} \times 100\% \quad (1)$$

where A is the area of dried PVC gel and A_0 is the area of the wet PVC gel. The shrinkage rates of PVC9 and PVC1 samples were about 70% and 36%, respectively. It is interesting to note that the thicknesses of both parts with and without applied electric field were quite different after freeze-drying. For the PVC9 gel, the

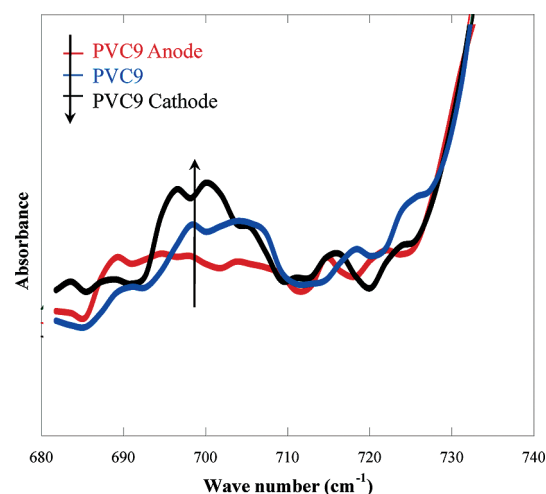


Figure 5. FT-IR spectra for PVC9 gel at the anode and cathode with and without in-situ dc voltage (1 kV) casting.

thickness of part A subjected to the applied electric field was 0.146 mm, while it was 0.268 mm in part B. It may be deduced that the plasticizer moved to the anode and then was sublimed. Moreover, the amount of sublimation increased with increasing content of plasticizer due to the change of polymer network mesh size.

Figure 6 shows FE-SEM images of PVC9 gel on the surface near the anode (a) and cathode (b) by 1 kV dc voltage casting. Figure 6a displays many craters with different sizes on the gel surface, while Figure 6b shows a flatter surface. It is surmised that some of the ingredients of the DBA-rich phase were sublimed by freeze-drying, since the DBA-rich phase was moved to the anode

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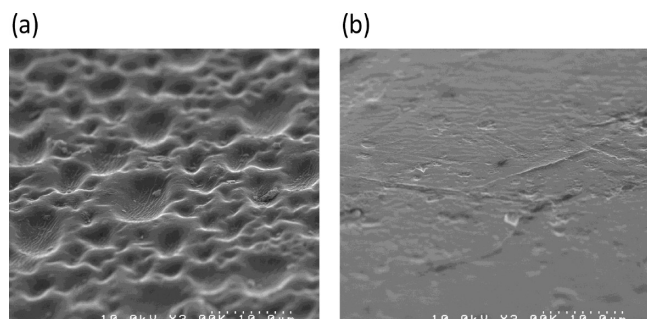


Figure 6. FE-SEM images of freeze-dried PVC9 by in-situ dc casting (in part A): (a) a top surface near the anode; (b) a bottom surface contacting the cathode.

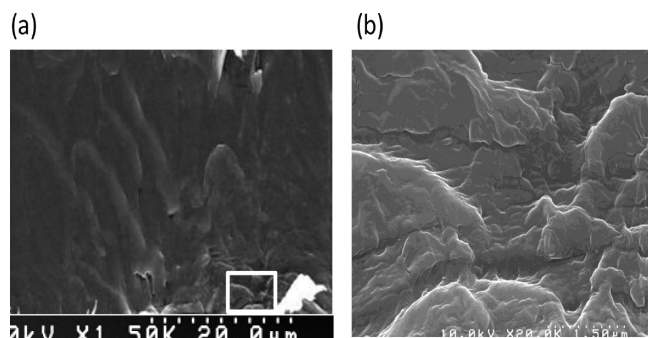


Figure 7. FE-SEM images of the cross section of freeze-dried PVC9 by in-situ dc casting (in part A). Image (a) resembles the inset of Figure 3a. (b) is a higher magnification image of the area in the white frame in (a).

and possibly fixed on the gel surface during in-situ dc voltage casting. Thus, more components of the DBA-rich phase will exist on the gel surface near the anode than at the cathode. We also compared the other part (part B) of the dried PVC9 gel without applied electric field and PVC1 gel. The sample shown a similar state on both surfaces of the samples where a wrinkle pattern appeared with some cracks due to the freeze-drying (see Supporting Information Figure 4). It can be considered that the phase structures of the PVC gels made by the general casting method are uniform, and no difference can be observed between upper and bottom surfaces.

Figure 7 shows FE-SEM images of the cross section in freeze-dried PVC9 (part A) by 1 kV dc casting. It is apparent that the polymer-rich phase was formed by countless swelled colloid particles, and we deduce that the hollow parts resulted from the

positions of sublimed solvent-rich phase (in part b). It seems that many connected tunnels were distributed through the interior of the gel. When the electric field was applied, the solvent-rich phases moved to the anode through the tunnels and caused a creeping deformation of the gel. In particular, the FE-SEM images completely supported the LSCM results in relation to the internal structures of PVC gel.

4. Conclusion

Using the fluorescent probe lucigenin incorporated in PVC gel and the technique of laser scanning confocal microscopy (LSCM) with sliced images and 3D image, we successfully observed the internal structure of the gel in the wet state. It was confirmed that PVC gel comprises a polymer-rich and a polymer-poor phase with a three-dimensional network structure. After an electric field was applied, we observed that the polymer-poor phase in the top sliced image (near the anode) was more than that in the bottom sliced image (near the cathode) and the polymer-rich phase was changed more perpendicular to the electrode; this indicated that the polymer-poor phase moved from the cathode to the anode and the polymer-rich phase formed linelike arrangement between electrodes.

Moreover, using in-situ dc voltage casting, freeze-drying, and FE-SEM observation, we found that many craters remained on the surface near the anode after polymer-poor phase sublimation, which was quite different from the surface near the cathode. The results also illustrated that polymer-poor phase was moved and fixed at the anode due to electric field stimulation. The effects of an electric field and phase migration phenomenon in the PVC gel interior were testified by both results from LSCM and in-situ dc voltage casting. All of the results provided strong evidence for the interpretation of the deformation mechanism of PVC gels by an applied electric field. These powerful methods, LSCM and in-situ dc voltage casting, in clarifying internal structure and phase separation would be valuable not only for gel materials but also for other polymer materials.

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Supporting Information Available: Examples of the actuation behavior of PVC gel (Figure S1), experimental methods of LSCM (Figure S2), in-situ dc voltage casting (Figure S3), and FE-SEM images of freeze-dried PVC9 and PVC1 without in-situ dc voltage casting (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.