Ultrathin Polymer Film Capacitor Composed of Poly(*N*-alkylacrylamide) Langmuir−Blodgett Films

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ABSTRACT: The capacitor properties of *N*-alkylacrylamide polymer Langmuir−Blodgett (LB) films were investigated as a function of number of layers with current−voltage measurement and ac impedance spectroscopy. Poly(*N*-dodecylacrylamide) (pDDA), poly(*N*-*tert*-pentylacrylamide) (ptPA), and poly(*N*-adamantylacrylamide) (pADA) were used as dielectric materials. The breakdown voltage of the LB films increased linearly with the number of layers. The breakdown electric fields were determined to be 0.27, 0.20, and 0.09 GV/m for pDDA, ptPA, and pADA, respectively. The large capacitance value of 1 μF/cm^2 is obtained at ptPA LB film capacitor with five layers (5.0 nm). The relative dielectric constants for ptPA, pADA, and pDDA are determined to be 5.7, 5.1, and 4.1, respectively, from ac impedance spectroscopy. The dielectric properties are found to be related with a relative ratio of highly polarized amide part to the alkyl side chain length of *N*-alkylacrylamide polymers.

Introduction

Polymer film capacitors are widely used in electronics because of the accuracy of capacitance compared with ceramic capacitors such as tantalum oxide capacitor.[1] However, the volume of the polymer film capacitors is larger than that of the ceramic ones because the film thickness of the polymer film capacitors is several micrometers, and the dielectric constant of polymers is smaller than that of the ceramic one. Reducing the film thickness of the capacitor has two points of merit, that is, larger value of capacitance and smaller size of capacitors. Smaller size of capacitors is recently required for miniaturizing cellular phones and portable computers. Furthermore, molecular size capacitor will be needed for realizing nanotechnology.

To achieve ultrathin film capacitor and molecular size capacitor, several efforts such as self-assembled monolayer (SAM) using alkanethiols on gold[2] and alkyl bromide on silicone,[3] the layer-by-layer deposition method,[4] and the Langmuir−Blodgett (LB) technique[5,6] have been carried out. Preparation of molecularly tunable nanoscale organic capacitor has been tried with self-assembled monolayers (SAMs) on gold,[7] Hg[2], and silicon[3] surfaces. These methods might be introduced to replace commercial polymer thin film capacitors with the thickness of micrometer order.[8] In most of the attempts using the SAM case, alkanethiols with different alkyl lengths must be needed to change the capacitance value by changing the thickness factor of the film. Since the sandwich structure with two metal electrodes is difficult to be prepared for those SAM capacitors, in general, the electrolyte solution or liquid metal such as mercury is employed to characterize the molecular tunable capacitor used in these SAM capacitors, which is not so close to the actual condition of use.

On the other hand, the LB technique has attractive features to prepare ultrathin films with molecular orientation and ordering at a molecular level.[5] Moreover, since LB films are built up by deposition of condensed monolayers at the air−water interface onto a solid support, the film thickness can be controlled by a molecular size, i.e., nanometer order. One of electrical properties of LB films is their electrically insulating property, for which they can be expected to be dielectric materials for thin film capacitors. However, as the LB films using low-molecular-weight amphiphiles such as stearic acid is mechanically and thermally weak, they have not been suitable in practical use so far. Meanwhile, polymer LB films using amphiphilic polymers are expected to realize the actual capacitors. We have found that *N*-alkylacrylamide polymers form stable monolayer on a water surface and LB films on solid substrates.[9−13] Therefore, we attempt to utilize the polymer LB films to polymer film capacitors in this study. In general, capacitance of films largely depends on the thickness of dielectric films. By using the LB technique, the film thickness can be precisely controlled by the thickness of monolayer (nanometer level) and the number of deposited layers; thus, we can make an ultrathin polymer film capacitor at a molecular level.

In this paper, we carried out current (*I*)−voltage (*V*) measurement and impedance spectroscopy of poly(*N*-dodecylacrylamide) (pDDA), poly(*N*-*tert*-pentylacrylamide) (ptPA), and poly(*N*-adamantylacrylamide) (pADA) polymer LB film capacitors, aiming at the application to nanoelectronic devices. We prepared the capacitors by deposition of the LB films between two electrodes, in a "dry system" without the existence of any solution, which are close to the actual condition of use of thin film capacitor. Since this work is our first step toward application of polymer LB films to dielectric materials, we hope that the results can provide us data for molecular designing to find an ideal structure in the future.

Experimental Section

Preparation of LB Film Capacitor. ITO (indium tin oxide)-coated glasses with 10 Ω/sq resistance were used as bottom electrodes of the capacitor. Patterned ITO substrates were prepared by etching ITO with concentrated hydrochloric acid except the middle parts of ITO covered by lacquer. After

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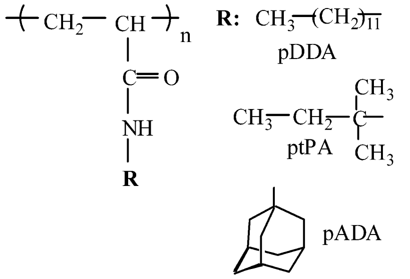

Figure 1. Chemical structures of *N*-alkylacrylamide polymers.

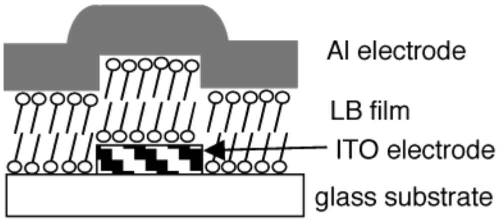

Figure 2. Schematic representation of the polymer LB film capacitor.

the etching process, patterned ITO substrates were cleaned with a mixture of ethyl acetate and methanol, cleaned with acetone, and then dried with nitrogen gas, successively.

We used three kinds of *N*-alkylacrylamide polymers: pDDA[9,10] as a polymer with long alkyl side chain, ptPA[11] as a polymer with short-branched alkyl side chain, and pADA[12] as a polymer with cyclic alkyl side chain, as shown in Figure 1. The synthesis and characterization of pDDA,[9,10] ptPA,[11] and pADA[12] were carried out as published previously.

These polymers were deposited on patterned ITO substrates with the Langmuir–Blodgett method. The deposition of polymer monolayers was carried out with an automatic Langmuir trough (FSD-50, USI) at a dipping speed of 10 mm/min under a surface pressure of 35 mN/m for pDDA, 25 mN/m for ptPA, and 15 mN/m for pADA at 15 °C. Distilled, deionized water was used for the subphase. The film thickness of these polymer LB films was determined by XRD measurement.

Aluminum was vapor-deposited onto the LB films deposited on ITO substrates through a mask with an evaporation rate of 2–3 Å/s measured with a quartz crystal thickness monitor. The deposition was performed under a vacuum of $(1-2) \times 10^{-5}$ Torr, and the thickness of Al electrode was obtained to be 800–1000 Å. During the evaporation, substrates were cooled to 5 °C to avoid the thermal damage of the LB film. Six pieces of polymer LB film capacitors with about 33 mm^2 area on ITO substrate were prepared (Figure 2).

Characterization of the polymer LB film capacitor. The $I-V$ characteristics were measured using Keithley 236 source measurement unit. An impedance analyzer (SI 1280B, Solartron Instrumentation) was used to apply a sinusoidal voltage signal of variable frequency to the electrodes. The current response of the system was analyzed in terms of the absolute value of the complex impedance $|Z|$ and the phase shift ϕ. The measurement was conducted in frequency range 0.1 Hz–2 kHz with amplitude of 0.1–1 V.

Results and Discussion

Monolayer Behaviors of *N*-Alkylacrylamide Polymers at the Air–Water Interface. Three kinds of *N*-alkylacrylamide polymers were spread onto water surface, and the monolayer behaviors were investigated from $\pi-A$ isotherms at 15 °C (Figure 3). The isotherms show a steep rise in surface pressure and high collapse pressure. The results indicate that these *N*-alkylacrylamide polymers form stable monolayer on the water surface. The collapse pressure for pDDA, ptPA, and pADA was 58, 35, and 20 mN/m, respectively. The collapse pressure would depend on the alkyl side chain length of the polymers. The monolayer of pDDA shows higher collapse pressure due to the stabilization of larger hydrophobic interaction between the dodecyl side chains of pDDA than the *tert*-pentyl and adamantyl side chains. The limiting molecular occupied surface area per monomer unit, which is obtained by extrapolation of the linear part of $\pi-A$ curves to zero surface pressure, is almost 0.28 nm^2 repeat unit^{-1} for all *N*-alkylacrylamide polymers. It is independent of the hydrophobic alkyl part of the amphiphile but dependent on the hydrophilic acrylamide moiety in the *N*-alkylacrylamide polymers. The occupied area of the acrylamide moiety, 0.28 nm^2, is larger than that of the alkyl moiety in the amphiphiles. The cross-sectional area of *n*-alkyl, *tert*-pentyl, and adamantly side chains is 0.19, 0.25, and 0.28 nm^2, respectively, from the CPK model. The monolayers for pDDA, ptPA, and pADA were transferred on ITO substrates under constant surface pressure of 35, 25, and 15 mN/m, respectivel, with a transfer ratio of about unity.

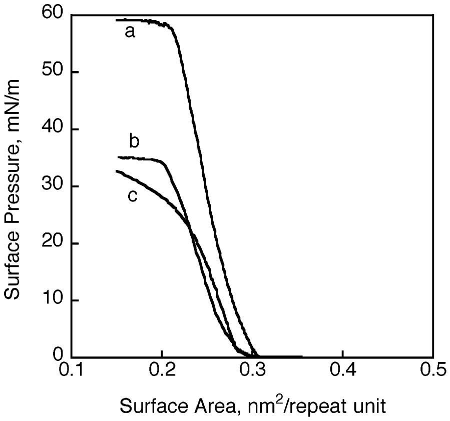

Figure 3. Surface pressure–area isotherms of *N*-alkylacrylamide polymer monolayers on a water surface at 15 °C: a, pDDA; b, ptPA; c, pADA.

***I*–*V* Characteristics.** The capacitor is known to break down over a certain bias voltage, which is defined as the breakdown voltage.[2,5] The relationship between the breakdown voltage and the film thickness of the LB film capacitors was investigated with $I-V$ measurement. The typical $I-V$ curves for ptPA LB film capacitors with different number of layers are shown in Figure 4. Current does not flow at small bias voltage, indicating that the ptPA LB films act as an insulator. Meanwhile, current drastically flows over a certain bias voltage, where the ptPA LB film capacitors break down and do not work as capacitors. The breakdown voltage, which is obtained by extrapolation of the linear part of $I-V$ curve to zero current, increases with the number of layers in the ptPA LB film capacitors. The same trends are obtained in the pDDA and pADA LB film capacitors. The relationship between the breakdown voltage and the film thickness of the polymer LB films is shown in Figure 5. The layer thickness from XRD measurement is reported to be 1.0 nm for ptPA,[11] 1.1 nm for pADA,[12] and 1.8 nm for pDDA.[10] The breakdown voltage is linearly proportional to the film thickness. This result means that the profile of electric field formed in the polymer LB film is formed uniformly. The breakdown voltage per film thickness, that is, breakdown electric field,[14] is calculated from the slope. The values of the breakdown electric field appear to be 0.27, 0.20, and 0.09

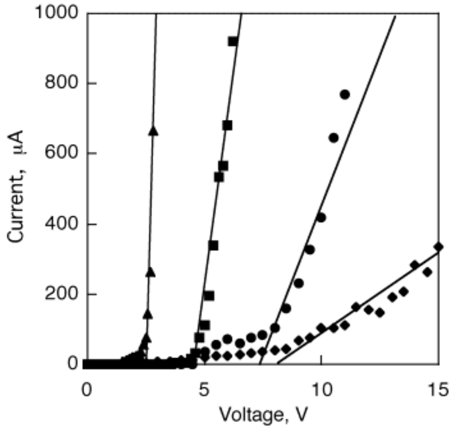

Figure 4. Current−voltage plots of ptPA LB film capacitors with different numbers of layers: ▲, 11 layers; ■, 21 layers; ●, 41 layers; ◆, 61 layers.

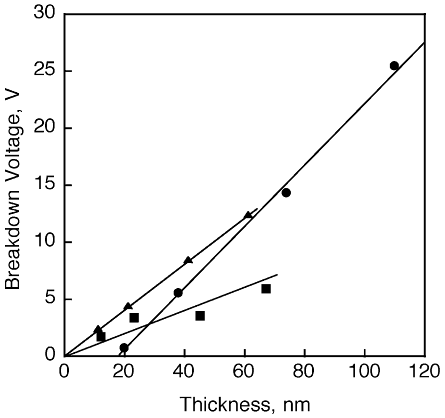

Figure 5. Plots of breakdown voltage vs film thickness of the *N*-alkylacrylamide polymer LB film capacitors: ●, pDDA; ▲, ptPA; ■, pADA.

GV/m for pDDA, ptPA, and pADA, respectively. They are compared to the maximum value of commercial polyethylene, 0.6−0.75 GV/m.[15] Although the present polymer LB films seem to be weaker in strength toward bias voltage than commercial polyethylene, the thickness of the sample films is quite different. The polyethylene value was measured for 1 μm thickness, while our measurement was conducted by the thickness range from 11 nm (11-layer ptPA LB film) to 110 nm (61-layer pDDA LB film). Importantly, the ptPA LB film capacitor bears about 3 V of applied voltage with thickness as thin as 11 nm. We do not know exactly why the breakdown voltage of pDDA LB film is almost zero until a thickness of 20 nm. One of possible reason is that *n*-alkyl chains might be weaker in heat during aluminum vapor deposition than *tert*-pentyl and adamantyl chains. Therefore, a defect in the pDDA LB film might be produced, resulting in the breakdown voltage of almost zero at a thickness of 20 nm.

Impedance Spectroscopy. Impedance measurement was carried out to obtain dielectric characteristics and capacitance value of the polymer LB films. Ac amplitudes below the breakdown voltage, 0.1 and 1 V in the frequency range from 0.1 Hz to 20 kHz, were applied for the impedance measurements. The typical Bode plots for pDDA LB film capacitors with different numbers of layers are shown in Figure 6. The logarithm of the absolute impedance value $|Z|$ is linearly proportional to the logarithm of frequency with the slope of −1 for all pDDA LB film capacitors. This result indicates that the pDDA LB film capacitors behave as an ideal capacitor. However, $|Z|$ became a saturated value in the low-frequency range for the 11-layer capacitor. The result shows that the membrane resistance of pDDA LB film with 11 layers would be smaller than that of the thicker one. Therefore, the impedance behavior of the polymer LB film capacitor can be represented by a simple equivalent circuit consisting of a capacitance C connected in parallel with a membrane resistance R.[6] Since the equivalent circuit is a parallel between a capacitance C and a resistance R, the total impedance should be expressed as eq 1[16]

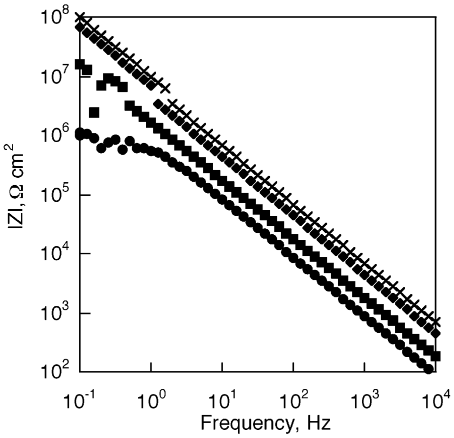

Figure 6. Bode plots of pDDA LB film capacitors with different number of layers: ●, 11 layers; ■, 21 layers; ◆, 41 layers; ×, 61 layers.

$$Z^{-1} = R^{-1} + j\omega C \tag{1}$$

where Z, R, C, j, and ω are total impedance, resistance component of the capacitor, capacitance component of the capacitor, complex number ($j^2 = -1$), and radial frequency $\omega = 2\pi f$ (f: frequency applied), respectively. Thus, from this equation, the absolute value of the impedance $|Z|$ can be written as eq 2:

$$|Z| = R/(1 + \omega^2C^2R^2)^{1/2} \tag{2}$$

At high frequency, $(\omega CR)^2$ will be much larger than unity; eq 2 is simplified to eq 3

$$|Z| = (\omega C)^{-1} \tag{3}$$

and the logarithm of eq 3 is expressed by

$$\log |Z| = -\log(2\pi C) - \log f \tag{4}$$

Equation 4 shows that the log $|Z|$ vs log f plot gives a straight line with a slope of −1, and capacitance C can be calculated from $|Z|$ at log $f = 0$.

On the other hand, at low frequency and finite value of R, $(\omega CR)^2 \ll 1$, eq 2 is simplified to eq 5, which becomes a constant value, that is, resistance (R).

$$|Z| = R \tag{5}$$

Most of the curves shown in Figure 6 did not reach a plateau region, indicating that the membrane resistance of the pDDA LB film capacitors were large enough to function as an ideal capacitor in the measured frequency range. However it should be noticed that the capacitor with ultrathin film (11-layer pDDA LB film) showed

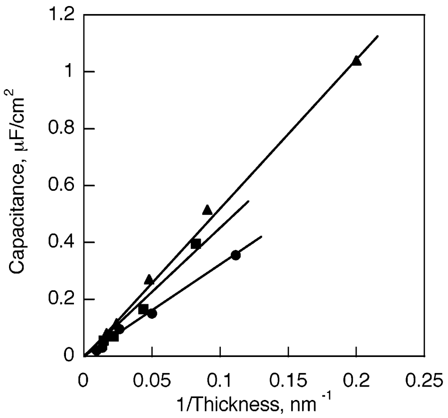

Figure 7. Plots of capacitance vs the inverse of film thickness of the *N*-alkylacrylamide polymer LB film capacitors: ●, pDDA; ▲, ptPA; ■, pADA.

transition to the horizontal region at low frequency. This means that the membrane resistance of the pDDA LB film with 11 layers would be a finite value of ca. 1 MΩ cm^2.

The calculated C of each capacitor is plotted against the inverse of the film thickness of the LB films, as shown in Figure 7. The capacitance for all *N*-alkylacrylamide polymer LB films is linearly proportional to the inverse of the film thickness of the LB film. The capacitance for the flat plate capacitor sandwiched with two electrodes is shown in the following equation:

$$C = \epsilon_0 \epsilon_r A/d \tag{6}$$

where ϵ_0 is the permittivity of the free space, ϵ_r is the dielectric constant of the insulating medium (i.e., the LB polymer), A is the electrode area, and d is the distance between electrodes (i.e., the LB film thickness). Thus, from the slope of each polymer LB film in Figure 7, the dielectric constants for pDDA, pADA, and ptPA LB films are determined to be 4.1, 5.1, and 5.7, respectively.

We discuss a relationship between the dielectric constant and the chemical structure of the *N*-alkylacrylamide polymers. The dielectric constants changed in the order ptPA (5.7) > pADA (5.1) > pDDA (4.1). This order is related to the length of the alkyl chain attached to the amide group; that is, pDDA has the longest alkyl chain. The amide part of the polymers has the main contribution of the whole dipole moment so that it has the biggest contribution to the dielectric constant. The dielectric constant is determined by the ratio of the polar amide part to the nonpolar alkyl part. As ptPA has the largest ratio of amide part in *N*-alkylacrylamide polymers, it has the largest dielectric constant. Since pDDA has the lowest amide ratio, its dielectric constant appeared the lowest among them. The dielectric constants of *N*-alkylacrylamide polymers are larger compared with those of commercial polyethylene ($\epsilon_r = 2.3$),[17] heptadecanethiol SAM on gold ($\epsilon_r = 2.6$),[7] and hexadecanethiol SAM on Hg ($\epsilon_r = 2.4$).[18]

When voltage is applied to a capacitor with dielectric material inside, some power loss happens. Dielectric loss might be caused by electric conduction, relaxation of polar materials, etc. If ac voltage is applied to a capacitor, the phase difference between voltage and current should be 90°. However, if there is dielectric loss in the capacitors, the phase angle deviates from 90°. It is expressed as the ratio of dielectric loss ϵ'' and dielectric constant ϵ', $\tan \delta = \epsilon''/\epsilon'$. Tan δ is called dielectric loss tangent and is an indicator for dielectric loss of dielectric materials. For a system with equivalent circuit of parallel with C and R, it could be written as $\tan \delta = (\omega RC)^{-1}$.

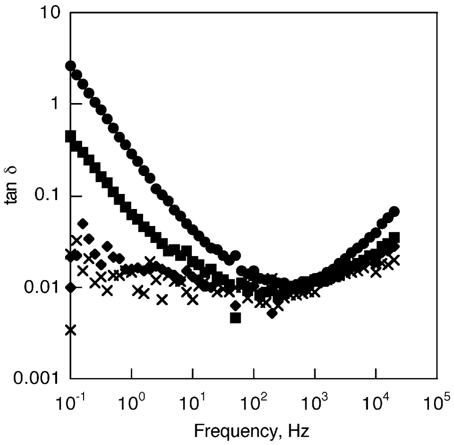

Figure 8. Plots of tan δ vs frequency of pADA LB film capacitors with different number of layers: ●, 11 layers; ■, 21 layers; ◆, 41 layers; ×, 61 layers.

To investigate the dielectric loss of the polymer LB film capacitors, a typical tan δ plot against frequency for pADA LB film with different numbers of layers is shown in Figure 8. Tan δ for pADA LB film capacitors with 41 and 61 layers is independent of frequency while for ones with 11 and 21 layers depend on frequency. The increase in tan δ with decreasing frequency would be due to the influence of contribution of the membrane resistance against the capacitance. Thus, the value of tan δ becomes independent of frequency in the thicker capacitors. On the other hand, the increase in tan δ with increasing frequency might be due to the relaxation of the polar amide group in the polymers. The results are in good agreement with Bode plot and $I-V$ measurement. The minimum value of tan δ for pDDA, ptPA, and pADA is determined to be 4×10^{-3}, 10×10^{-3}, and 8×10^{-3}, respectively. As the tan δ value for commercial polyethylene[17] is 1×10^{-3}, the dielectric loss of the *N*-alkylacrylamide polymers is similar to that of polyethylene to make a capacitor.

Conclusion

A capacitor consisting of *N*-alkylacrylamide polymer LB films as dielectric materials has been prepared, and its dielectric properties have been investigated by $I-V$ measurements and impedance spectroscopy. From $I-V$ measurements we determined the breakdown voltage of each polymer LB films and found out that the ptPA LB polymer has a breakdown electric field of 0.2 GV/m. The ptPA LB film capacitor with 11 layers, which is a thickness as thin as 11 nm, bore 3 V of applied voltage, shows that it might be a good candidate for an ultrathin polymer film capacitor. The results gave us an idea for constructing molecular thin film capacitors using dielectric polymer materials in our future work.

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