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Super water-repellent poly(alkylpyrrole) films having environmental stability

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Abstract: We present electrochemical synthesis of super water-repellent poly(alkylpyrrole) films which exhibit excellent environmental stability in terms of contact angle ($> 150^\circ$) for water. The poly(alkylpyrrole) films synthesized under an optimized electrochemical condition consisted of thousands of micro-scaled ‘needles’ which densely aligned by shoulder to shoulder. The surface of the aligned ‘needles’ was analyzed by a box-counting method, to be a fractal structure with a dimension of 2.18.

Keywords: Super water-repellency; Fractal structure; Electrochemical polymerization; Conductive polymer

1. Introduction

Wettability of solid surface to a certain liquid is governed by two factors, i.e. a chemical factor and a geometrical factor of the solid surface.¹ Studies on the super liquid-repellency of solid surface is crucially important either in academic aspect or in technological one. Several such kinds of super water- or oil-repellent surfaces with contact angles larger than 150° have been realized by combination of the chemical factor and the geometrical one [2-14]. Main approach for the chemical factor is a coating of fluorinated compounds which show very low surface energy. On the other hand, main approach for the geometrical one is formation of fractal or rough surface structures.

Usually inorganic materials used for super water-repellent surfaces are inherently hydrophilic or relatively less hydrophobic ones with intrinsic contact angles less than 90° , and fluoroalkylsilane-

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coating was necessary in order to realize super water-repellency [6-9]. Tadanaga *et al.* have

succeeded in preparation of transparent super water-repellent glasses in which heptadecafluorodecyltrimethoxysilane was coated on rough alumina-layer [6,7]. Nakajima *et al.* reported preparation of boehmite and silica films whose surfaces showed super water-repellency after coating with fluoroalkylsilane [8]. Recently Hikita *et al.* successfully fabricated super liquid-repellent surfaces using colloidal silica nanoparticles and fluoroalkylsilane by one-step method in which roughness and low surface energy are simultaneously induced [9].

In contrast, usually organic compounds are relatively more hydrophobic. Only geometric approach, therefore, could realize the super water-repellency. Neinhuis and Barthlot [15] have investigated water-repellency of plant leaves in detail and pointed out the effect of roughness of the leaf surface on the super water-repellency. For instance, a leaf of some plant such as lotus, shows super water-repellency dominantly by the geometrical factor [15]. The surface of the leaf is a fractal or rough geometrically but chemically is just a wax whose composition is mainly esters of fatty acids and alcohols [15]. Legs of water striders also show super water-repellency dominantly by the geometrical factor [16]. By mimicry of the lotus effect in nature, several approaches were proposed in order to realize the super water-repellent surfaces [17,18]. Alkylketene dimer (AKD) surface which is geometrically a fractal with a dimension of 2.29 but chemically is just a wax, is first artificial super water-repellent surface with so large contact angle of 174° [2,3]. The series of studies on the AKD fractal structures provide much useful insights to explain theoretically the origins of super water-repellency of the leaves of plants or insects in nature. The AKD fractal surface, however, has a drawback of poor environmental stability from the standpoint of practical applications. The AKD surface is environmentally weak mainly because it is well soluble in organic solvents and its melting point is as too low as 67°C [3]. Therefore, creation of environmentally stable super water-repellent surfaces, which are geometrically fractal or rough, is crucially significant not only in academic aspect but also in technological one.

Conductive polymers have attracted great attention because of its interesting electrical properties and easy synthesis of film-shaped products coupled with good thermal stability [19-21]. For such conductive polymers, the synthetic methods have been well established [22,23]. Conventionally, the conductive polymers are electrochemically synthesized as films with versatile surface features

depending upon the electrochemical reaction conditions [22]. Yan *et al.* [24-26] reported that polypyrrole microtubes formed during electrochemical polymerization under a controlled reaction condition. Qu *et al.* [27] also reported the formation of polypyrrole microstructure with morphology like bowls, cups, and bottles during the electrochemical polymerization. Therefore, in principle the conductive polymer films with fractal structure or rough morphology are possibly synthesized by simple optimization of the reaction conditions. In addition, the conductive polymers usually consist of aromatic rings and conjugated π -bonds on the polymer main chains, and have enough thermal stability of chemical composition. Furthermore, the polymers are usually insoluble in organic solvent from the similar reason. Kossmehl *et al.* previously reported the wettability and thermal stability of poly(2,2'-bithienyl-5,5'-diyl) which is one of conductive polymers [28,29]. Yamamoto *et al.* have also reported wettability of conductive polymers [30]. Recently we have also reported super water-repellent conductive polymer, poly(alkylpyrrole) films (larger contact angle than 150 °), which showed excellent environmental stability to both temperature and organic solvents or oils [31]. Herein we report systematic studies on the super water-repellent poly(alkylpyrrole) films in terms of reaction conditions, characterization, fractal dimension, wettability, and environmental stability.

2. Experimental

2.1. Materials. Sodium *p*-toluenesulfonate (Ts) (Tokyo Kasei) and 1-octadecylpyrrole (ODP) (Wako), as well as organic solvents were of guaranteed reagent grade and used as received.

2.2. Electrochemical synthesis of poly(alkylpyrrole) films. The electrochemical synthesis was performed in a two-electrode cell containing acetonitrile solution of alkylpyrrole and Ts by using a constant current generator (Yokogawa Programmable DC source) at room temperature. In this work ODP was used as an alkylpyrrole. The reaction conditions were optimized by changing concentrations and molar ratios of ODP and Ts, applied voltage and reaction time. The obtained films were extensively washed with acetonitrile to eliminate remained reactants, finally dried at room temperature under a reduced pressure overnight.

2.3. Analyses of the films. Wettability of the films was evaluated with static contact angles for water. The contact angles of the films for water droplets (ca. 1 mm in diameter) were measured with

an optical contact angle meter (Kyowa DropMaster 300) at room temperature and humidity. Raman spectrum was measured using a JASCO NR-1800 Laser Raman Spectroscopic System with a microscope. Excitation light from an argon laser ($\lambda = 514.5$ nm) was focused on a surface of the film through the microscope. The wavenumber was calibrated by comparing with 520 cm^{-1} Raman band of silicon. Infrared spectrum was measured on a surface of the film using a reflectance mode through a microscope. Scanning electron microscopic (SEM) observations of the films were carried out on a field-emission SEM (Hitachi S-5200) after covering the film surface with a thin layer of sputtered alloy of gold and palladium. Analysis of fractal dimension of the films was carried out by box-counting method according to the procedures as previously reported [3,5]. In the analysis of length of irregular curve or area of irregular surface by the box counting method, one may divide the embedding space into boxes of side length ε and count how many boxes are occupied by the curve or the surface. Number of occupied boxes $N_{\text{box}}(\varepsilon)$ for $\varepsilon \rightarrow 0$ may grow like $N_{\text{box}}(\varepsilon) \sim \varepsilon^{-D}$. The exponent D is the fractal dimension by definition [32,33]. The surface area magnification factor, e.g., the ratio of the real surface area to the projected one can be written as $(L/l)^{D-2}$; where L , l and D are the upper and the lower limit lengths of fractal behavior and D the fractal dimension, respectively. Critical surface tension of the smooth poly(alkylpyrrole) film was determined from the Zisman plot by measuring contact angles for various liquids [34]. The values of $\cos\theta$ were plotted against γ_L , where θ is the contact angle of a liquid and γ_L the surface tension of the liquid, and the plot was extrapolated to the value of $\cos\theta = 1$. The critical surface tension was estimated as the surface tension of liquid at $\cos\theta = 1$.

2.4. Environmental stability of the films. Thermal stability was evaluated by treating the films at various temperatures for 2 h. After the thermal treatments the contact angles were measured at room temperature. The treatment at $80\text{ }^\circ\text{C}$ was carried out for various treating time. The durability to organic solvents or oils was evaluated as follows: The films were immersed in a certain organic solvent for 10 min, and then dried at $80\text{ }^\circ\text{C}$ under a reduced pressure. On the other hand, the oils were put on the films and then washed with acetone, finally dried similarly as above. Contact angle

for water was measured on the dried films. The morphological structure of the treated films with temperature and solvents was also observed by the SEM to check the stability of the films.

3. Results

3.1. Electrochemical synthesis of the poly(alkylpyrrole) films. The electrochemical synthesis of poly(alkylpyrrole) films was performed in various reaction conditions. The reaction condition was optimized in terms of water-repellency or larger contact angle for water. Fig. 1 shows that the contact angle increases with increasing applied voltage up to 22.5 V, but significantly decreases above 30 V. The contact angle was maximized at the ODP concentration of $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ when the ratio of $C_{\text{ODP}}/C_{\text{Ts}}$ is 10/1 in both cases of the applied voltage of 22.5 V and 30 V, as shown in Fig. 2. The contact angle of the obtained poly(alkylpyrrole) film behaved similarly to the above with changing concentration of ODP at constant concentration of Ts, as shown in Fig. 3. The contact angle suddenly increased between the concentration of $2.5 \times 10^{-3} \text{ mol dm}^{-3}$ and $5.0 \times 10^{-3} \text{ mol dm}^{-3}$, and then decreased. The contact angle, however, did not significantly change with the concentration of Ts (Fig. 4). Table 1 shows the small change of contact angle against reaction time. It is noteworthy that very low contact angles were usually observed in the films poorly covered on the ITO electrodes probably due to over-oxidation at very high applied voltage or due to lower concentration of reactants. Another possibility is due to the formation of smooth poly(alkylpyrrole) films instead of the needle-like ones, which is indeed observed in the films synthesized under the above conditions. Consequently, a super water-repellent poly(alkylpyrrole) film with a contact angle of 154° was synthesized in the following reaction conditions: ODP/Ts, 10:1 molar ratio; ODP, $5.0 \times 10^{-3} \text{ mol dm}^{-3}$; reaction time, 60 min; applied voltage, 22.5 V; working electrode, ITO glass. The poly(alkylpyrrole) films obtained under these conditions were used for studies on spectroscopic analysis, morphology, fractal dimension determination, and environmental stability. On the other hand, thin and flat films were synthesized at 3 V for 30 min for the measurement of critical surface tension by Zisman plot.

3.2. Chemical structure and morphology. Infrared spectrum clearly shows the absorption peaks due to pyrrole rings and to alkyl groups at 1596 cm^{-1} and 2922 cm^{-1} , respectively. Raman spectrum of the poly(alkylpyrrole) film shows several Raman bands, as shown in Fig. 5. The main Raman bands are as follows: C=C stretching at 1575 cm^{-1} , antisymmetrical C-N stretching at 1340 cm^{-1} , and ring deformation of pyrrole unit, associated with radical cation at 980 cm^{-1} . The Raman spectrum is consistent with that of conventional polypyrrole [24,35].

Fig.s 6a and b show SEM images of surface and cross-section of the super water-repellent poly(alkylpyrrole) film, respectively. “Needle”-like shaped poly(alkylpyrrole) grew perpendicularly to the surface of the indium-tin-oxide (ITO) electrode. It is interesting to note that thousands of the “needle”-like shaped poly(alkylpyrrole) in sizes of ca. $5\text{ }\mu\text{m}$ in diameter and ca. $40\text{ }\mu\text{m}$ in length, are arrayed densely and orderly on the surface of the ITO electrode.

3.3. Fractal analysis of the super water-repellent surfaces. Fractal structure of the solid surface is quite powerful to enhance the wettability [2,3], since the fractal surface has very large real surface area compared with the projected one. The poly(alkylpyrrole) film actually showed super water-repellency, and the fractal analysis was made on its surface. The fractal dimension of the trace of the surface was estimated by box-counting method for the cross-sectional view of the film. The fractal dimension of the surface itself can be obtained by adding 1 to that of the cross-section [33].

Fig. 7 shows electron microscopic photographs of the cross-sectional view of a super water-repellent poly(alkylpyrrole) film, and their trace figures of the film surfaces. The size of the traces is, of course, the same as that of the SEM image. The box-counting method was applied to this trace figures, and the $\log N(r)$ vs. $\log r$ plot was obtained as shown in Fig. 8, where r is the size of boxes, $N(r)$ the number of boxes to cover the trace object. The fractal dimension of the trace of the cross-section D_{cross} ($1 \leq D_{cross} < 2$) can be calculated from the slope of this plot. The fractal dimension, D ($2 \leq D < 3$), of the poly(alkylpyrrole) surface is, thus, obtained as $D \cong D_{cross} + 1$ [33].

The method was applied to several kinds of poly(alkylpyrrole) films prepared in different reaction time which resulted in different length of the microrods in the films. The fractal dimensions calculated for these samples are listed in Table 1.

3.4. Critical surface tension of the flat poly(alkylpyrrole) surface. Critical surface tension of a solid surface is a measure of its hydrophobicity. The Zisman plot was made in Fig. 9, and the critical surface tension of the flat poly(alkylpyrrole) surface was estimated to be about 26 mN/m.

3.5. Environmental Stability. The influences of treating temperature on the water-repellency are systematically investigated in order to evaluate the thermal stability of the films in terms of contact angle for water. The contact angle of the film was nearly constant even when the treating temperature increases, as shown in Fig. 10 and the inset therein [31].

The influences of organic solvent- and oil-treatment on the water-repellency are systematically investigated in order to evaluate the durability of the films to the organic solvents and oils in terms of contact angle for water. The contact angle of the film did not change even after the treatments with various solvents and oils, as shown in Fig. 11 [31].

4. Discussion

4.1. Hydrophobicity of poly(alkylpyrrole) films. The critical surface tension of the flat poly(alkylpyrrole) surface is about 26 mN/m as mentioned before. This value is slightly higher than that of the CH₃- group of monolayer (~24 mN/m) or crystal surface (~22 mN/m) [36]. This result implies that the octadecyl groups of the poly(alkylpyrrole) are oriented to the surface of the film and are fairly aligned each other. This is not surprising matter taking into consideration that the film is synthesized in an organic solvent (acetonitrile).

The critical surface tensions of polyethylene, polystyrene and polypropylene are approximately 32, 34, and 23 mN/m, respectively. The poly(alkylpyrrole) is much more hydrophobic than polyethylene or polystyrene, and seems to show similar hydrophobicity to polypropylene.

4.2. The fractal morphology of the poly(alkylpyrrole) surface. The “needle”-like shaped array is quite similar with an array of polyacrylonitrile nanofibrils as previously reported by Feng *et al* [10]. The array of the polyacrylonitrile nanofibrils, however, was fabricated by using a template [10]. The surface of the array of the polyacrylonitrile nanofibrils showed super water-repellency with a contact angle of larger than 150 ° [10]. Martin *et al.* first reported a template-guiding synthesis of polypyrrole microtubes [31]. They synthesized an array of polypyrrole microtubes

electrochemically by using a porous polycarbonate membrane as a template [31]. The array of the poly(alkylpyrrole) in this work, however, grew without any template, and the single “needle”-like shaped poly(alkylpyrrole) might be microtube based on the expanded images of Fig. 6. Spontaneous formation of polypyrrole microtubes without any template during the electrochemical polymerization were previously reported [24-27]. In the cases, however, the microtubes do not array orderly and densely and the sizes of diameter and length are much larger than those in this work. Therefore, we believe that this work first showed the array of “needle”-like shape or capped-microtubes of conductive polymer synthesized electrochemically without template. The features of the array should show super water-repellency in principle like the case of polyacrylonitrile nanofibrils [11]. Furthermore, the array should show high stability in principle toward heating and organic solvents because the conductive polymers usually consist of long-range conjugated aromatic rings which are thermally stable and insoluble in usual organic solvents [23].

4.3. Super water repellency of the fractal surface. The contact angle θ_f of liquid droplet placed on a fractal solid surface is given by eq. (1) [2,3].

$$\cos \theta_f = \left(\frac{L}{l} \right)^{D-2} \cos \theta \quad (1)$$

where L and l are the upper and the lower limit lengths of fractal behavior respectively; D is the fractal dimension of the solid surface. It is assumed that 1) l is much larger than the diameter of molecules composing a liquid, and 2) L is much smaller than the diameter of a liquid droplet. This eq. (1) represents quite well the wettability of super water-repellent fractal surfaces of AKD [2,3].

The fractal parameters of L and l are not obtained in the present work from the plot of $\log N(r)$ vs. $\log r$ unlike the case of AKD. So unfortunately, we cannot apply the eq. (1) quantitatively to the experimental results of this work. But qualitatively, we can see the relationship between the fractal dimension and the contact angle of some poly(alkylpyrrole) samples as shown in Table 1. The contact angle of water on the poly(alkylpyrrole) films is smaller than that on the AKD surface (174°). This may be due to the smaller fractal dimension of the film compared with that of AKD, since the critical surface tension of the film is small enough. Further optimization of reaction conditions to make the surfaces with higher fractal dimension is the next challenge in future. If ones reduce the

surface tension of the fractal poly(alkylpyrrole) film (26 mN/m) by coating with fluorinated compounds it could simply realize high oil-repellency. Actually we have achieved high oil-repellent poly(alkylpyrrole) films with contact angle larger than 130° by this approach. The detail will be published elsewhere.

4.4. Environmental stability of the super water-repellent surfaces. The poly(alkylpyrrole) is one of the conductive polymers which usually consist of aromatic rings and conjugated π -bonds on the main polymer chains. Therefore, the polymer has enough thermal stability of chemical composition in the experimental range of the temperature and the treating time. If the films were treated at very high temperature, however, dedoping or decomposition which could influence the stability would occur [23]. On the other hand, needle-like shape of the poly(alkylpyrrole) may also have high thermal stability in the shape, similarly in the case of polypyrrole microtube [24]. The high thermal stability of the film in terms of contact angle can be, thus, explained by the thermally stable chemical factor and geometrical one.

The poly(alkylpyrrole) could be a doped conductive polymer which usually consists of conjugated π -bonds in which π -electrons are delocalized on the main polymer chains as indicated by the dark color of the film [23]. The doped conductive polymers usually are insoluble in any organic solvents [23]. Therefore, the film has enough durability of chemical composition and morphology to the organic solvents and the oils tested. The durability of the film to the organic solvents and oils in terms of contact angle can also be explained by the highly stable chemical factor and geometrical one. Fig.s 12 (top) and (bottom) show SEM images of the films after the thermal and oil treatment, respectively. The ordered surface structures of the films were kept unchanged even after the treatments of heating and organic solvents, which strongly supports our consideration of above.

5. Conclusion

Super water-repellent poly(alkylpyrrole) films with a contact angle of larger than 150° were synthesized by electrochemical polymerization. The surface of the films consisting of perpendicular alignment of thousands of 'needle'-like shape of the poly(alkylpyrrole) was considered to be fractal with a dimension of 2.18, based on the analysis by box counting method. The critical surface

tension of the flat poly(alkylpyrrole) surface estimated from the Zisman plot is about 26 mN/m. It means that the poly(alkylpyrrole) shows similar hydrophobicity to polypropylene. It should be emphasized that differently from inorganic counterparts the poly(alkylpyrrole) films showed super water-repellency without fluorinated compound-coating, furthermore, exhibited excellent environmental stability to both heating and organic solvent treatments in terms of the contact angle for water and the morphological structure of the surface. The results of this research may considerably be of significance as both fundamental and industrial guiding principles. Moreover, the feature of the film which consists of vertical alignment of 'needle'-like conductive polymer can be extended to nanotechnological or biotechnological applications such electronic devices [37] and substrates for biological studies [38,39].

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Table 1: Fractal dimension and contact angle of the poly(alkylpyrrole) films prepared in different reaction time.^{a)}

Reaction time/min	Fractal dimension ^{b)}	Contact angle of water ^{c)/°}
0.5	2.03	125
1.0	2.13	138
60	2.18	154

a) Other conditions: applied voltage 22.5 V; concentration of ODP 0.005 mol dm⁻³; ODP/Ts 10:1 molar ratio; electrode ITO. b) Error margin: ±0.05. c) Error margin: ±1.6 °.

Figure captions

Figure 1. Applied voltage-dependent contact angle of the produced film (error margin: $\pm 1.6^\circ$).

Figure 2. C_{ODP} -dependent contact angle of the produced film (error margin: $\pm 1.6^\circ$).

Figure 3. C_{ODP}/C_{TS} -dependent contact angle of the produced film (error margin: $\pm 1.6^\circ$).

Figure 4. C_{TS} -dependent contact angle of the produced film (error margin: $\pm 1.6^\circ$).

Figure 5. Raman spectrum of the poly(alkylpyrrole) film produced under optimized conditions.

Figure 6. Scanning electron microscopic (SEM) image of surface (a) and cross-section (b) of the produced poly(alkylpyrrole) film. Inset is a digital camera image of a water droplet on the film.

Figure 7. Cross sectional SEM images (a-1, a-2, a-3) and their trace curves of the poly(alkylpyrrole) film surface (b-1, b-2, b-3).

Figure 8. $\log N(r)$ vs $\log r$ (r in μm) plot of the poly(alkylpyrrole) film surface. The data (closed circles) were obtained by treating the trace curves of Figure 8 (b-3, b-2, b-1) with the box-counting method.

Figure 9. Contact angles of various kinds of liquid on the fractal and flat poly(alkylpyrrole) film.

Figure 10. Thermal stability of the super water-repellent poly(alkylpyrrole) film treated at various temperatures for 2 h (error margin: $\pm 1.6^\circ$). Inset shows thermal stability of the film treated at 80°C for various treating time (error margin: $\pm 1.6^\circ$).

Figure 11. Durability for the organic solvent-, oil-, and water-treatment of super water-repellent poly(alkylpyrrole) film (error margin: $\pm 1.6^\circ$).

Figure 12. Scanning electron microscopic (SEM) image of surface of the super water-repellent poly(alkylpyrrole) film after treated by heating at 80°C (top) and by immersing in acetone (bottom).

Fig. 1: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

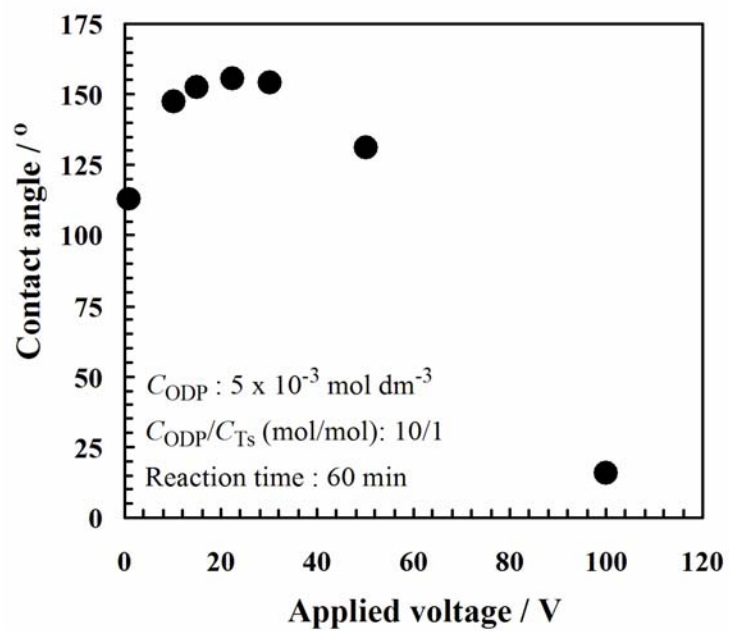


Fig. 2: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

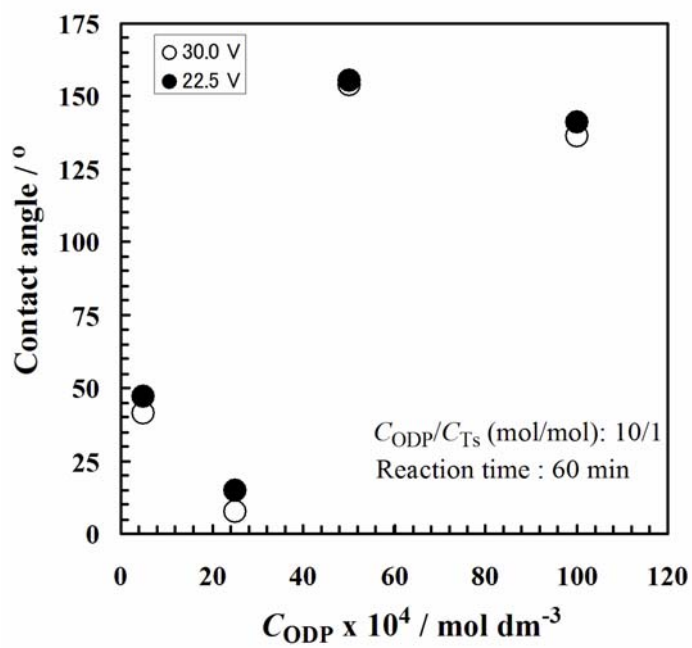


Fig. 3: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

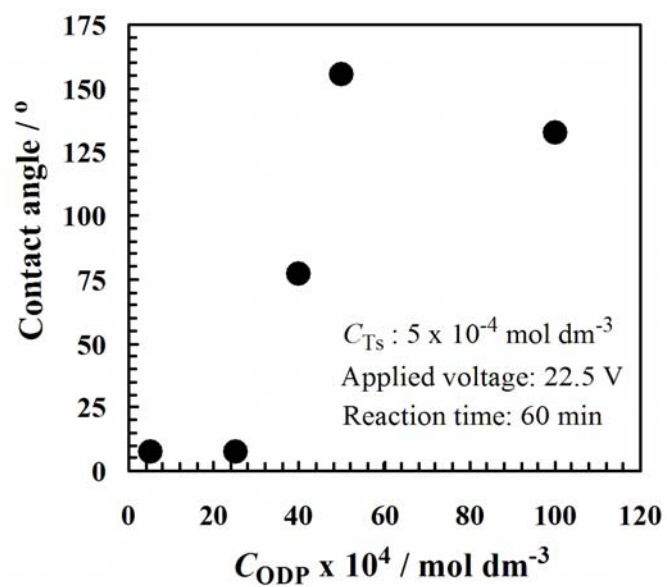


Fig. 4: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

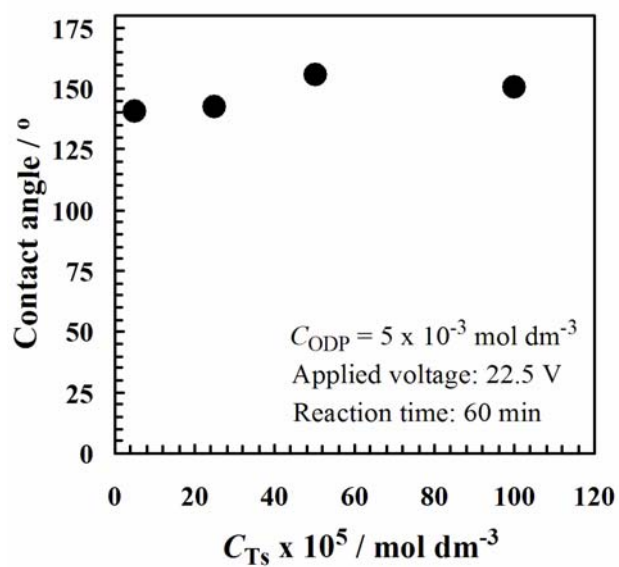


Fig. 5: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

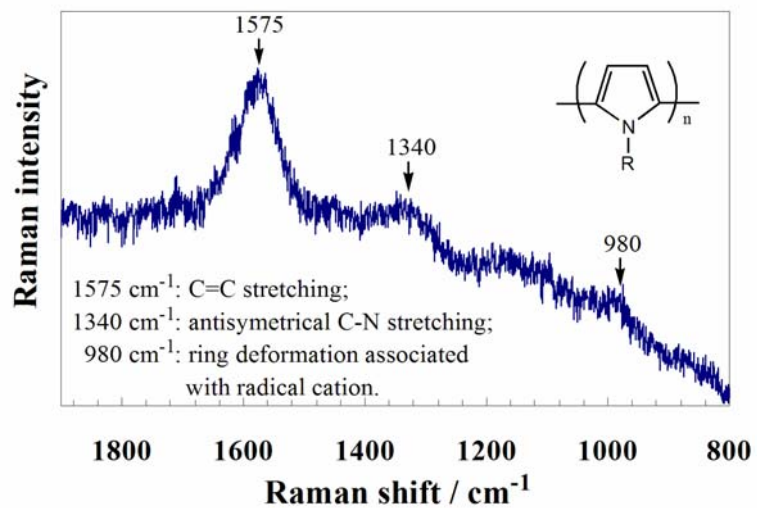


Fig. 6: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

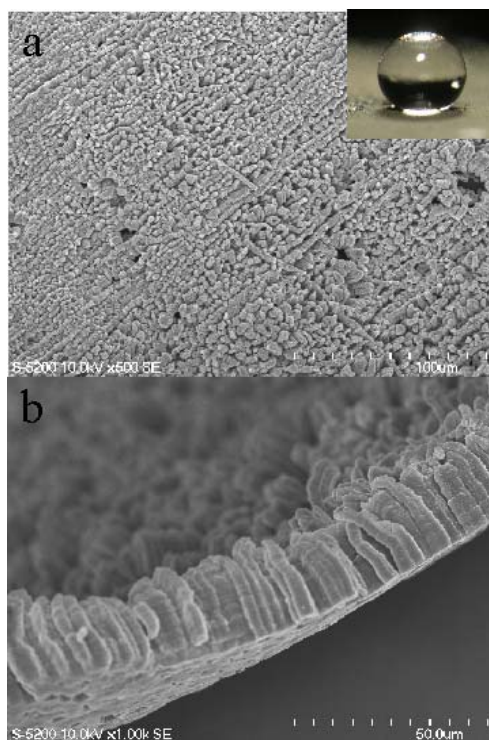


Fig. 7: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

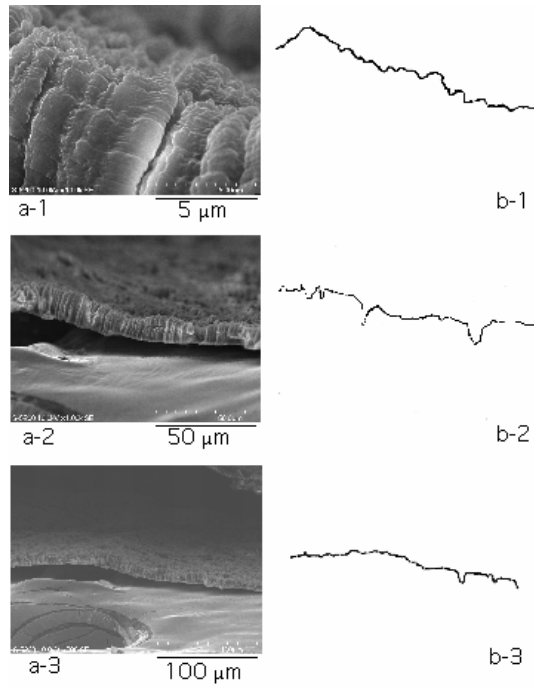


Fig. 8: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

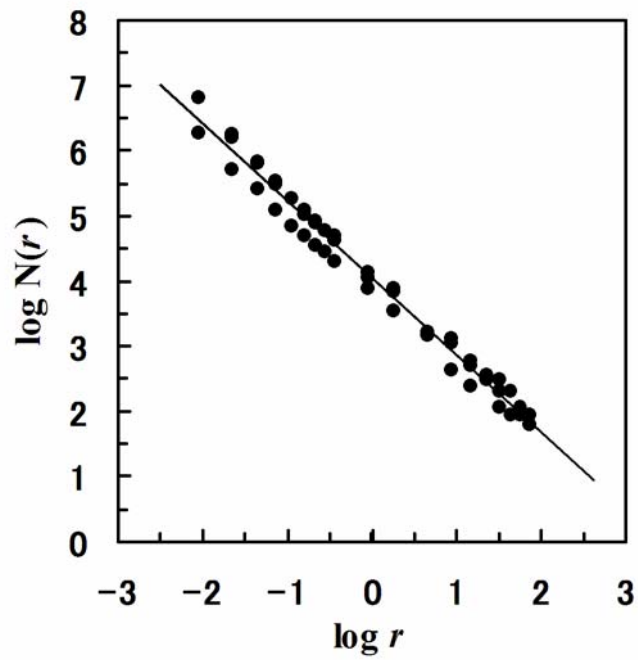


Fig. 9: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

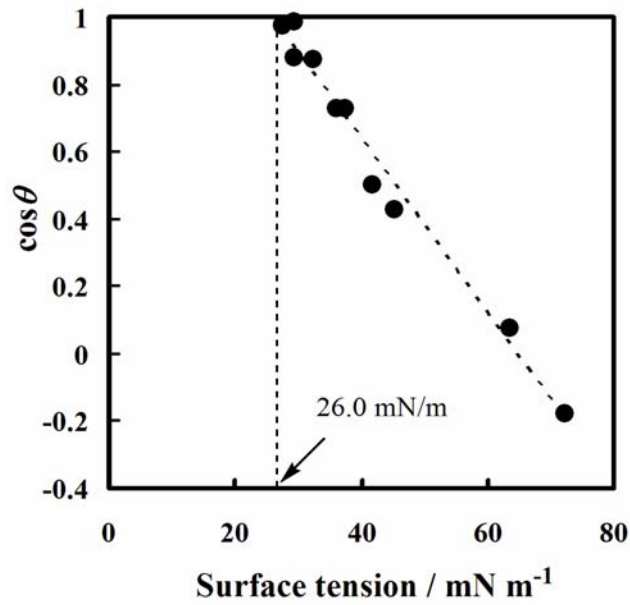


Fig. 10: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

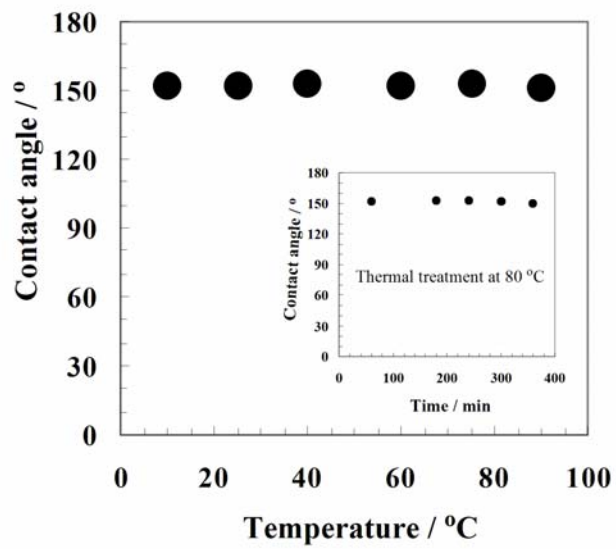


Fig. 11: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

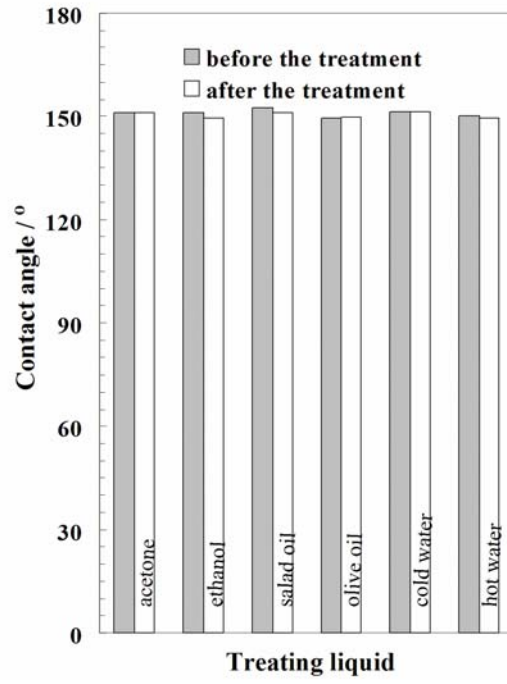


Fig. 12: K. Kurogi, H. Yan,* H. Mayama, and K. Tsujii*

