Polymer Films

Environmentally Stable Super Water-Repellent Poly(alkylpyrrole) Films**

Hu Yan, Kazutomo Kurogi, Hiroyuki Mayama, and Kaoru Tsujii**

It is well-known that the wettability of a solid surface by a liquid is governed by two factors: a chemical component and a geometric component of the solid surface.[1] Super liquid repellency is crucially important in daily life and in industry. Several kinds of super water- or oil-repellent surfaces with contact angles larger than 150° have been realized by a combination of chemical and geometric approaches.[2–12] The main approach for the chemical factor is a coating of fluorinated compounds with low surface energy, whereas the geometric factor is governed by the formation of fractal or rough surface structures.

In nature the leaves of some plants, such as the lotus, show super water repellency only by the geometric factor.[13] The surface of the leaf is geometrically a fractal, but chemically is a wax composed mainly of fatty acid esters and alcohols. The legs of water striders also show super water repellency by the geometric factor only.[14]

The alkylketene dimer (AKD) surface, which geometrically is a fractal with a dimension of 2.29 but chemically is just a wax, is only one artificial super water-repellent surface with a large contact angle, in this case 174°.[2,3] A series of studies on the AKD fractal structures provide much insight into the theoretical origins of the super water repellency that occurs in nature in plant leaves or insects. The AKD surface, however, has the drawback of poor durability from the standpoint of practical applications. The AKD surface is environmentally weak, mainly because it is soluble in organic solvents and its melting point is as low as 67 °C.[3] Therefore, creation of environmentally stable super water-repellent surfaces which do not contain any fluorinated compounds but are geometrically rough or fractal structures is crucially significant, from both the academic and practical aspects.

Conductive polymers have attracted great attention because of their unique electrical properties and the easy synthesis of film-shaped products coupled with good thermal stability.[15–17] Therefore, the synthetic methods are well-established.[18,19] Conventionally, conductive polymers are electrochemically synthesized as films with various surface features according to the reaction conditions.[19] Therefore, in principle, conductive polymer films with a fractal structure or rough morphology are easily synthesized by simple optimization of the reaction conditions. Kossmehl et al. reported poly(2,2′-bithienyl-5,5′-diyl) (PBT) layers, which were synthesized by an electrochemical method and showed super water repellency and good thermal stability.[20,21] Herein, we report on super water-repellent poly(alkylpyrrole) films (contact angle larger than 150°), which showed excellent environmental stability to both temperature and organic solvents or oils.

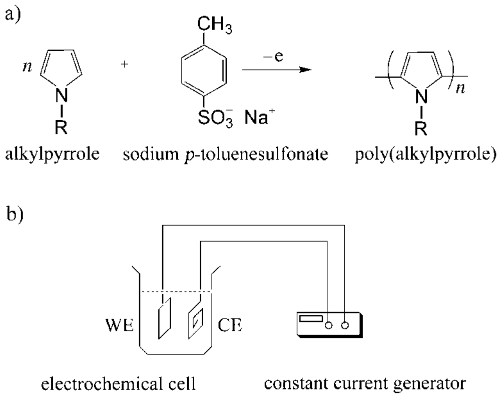

Figure 1. a) Chemical structures of monomeric alkylpyrrole, sodium *p*-toluenesulfonate electrolyte, and the polymer produced; b) setup of the electrochemical synthesis (WE = working electrode, CE = counter electrode).

The electrochemical polymerization of alkylpyrrole was performed in a beaker by using two electrodes (Figure 1; see Experimental Section). Figure 2 shows the poly(alkylpyrrole) film that was electrochemically synthesized with 1-*n*-octadecylpyrrole and sodium *p*-toluenesulfonate as monomer and electrolyte, respectively. "Needle"-like poly(alkylpyrrole) structures grew perpendicularly to the surface of the indium tin oxide (ITO) electrode. Thousands of the poly(alkylpyrrole) needles, which were approximately 5 μm in diameter and 40 μm in length, were arrayed in an orderly manner on the surface of the ITO electrode. The needle-shaped array is similar to an array of polyacrylonitrile nanofibrils previously reported by Feng et al.[8] However, these nanofibril arrays were fabricated by using a template. The surface of the array of polyacrylonitrile nanofibrils showed super water repellency, with a contact angle larger than 150°. Martin et al. first reported the template-guided electrochemical synthesis of an array of polypyrrole microtubes by using a porous poly-

---

[*] Dr. H. Yan, Dr. H. Mayama, Prof. Dr. K. Tsujii
Research Institute for Electronic Science (RIES)
Hokkaido University
Sapporo 001-0021 (Japan)
Fax: (+81) 11-706-9357
E-mail: yanhu@es.hokudai.ac.jp
tsujik@es.hokudai.ac.jp

Prof. Dr. K. Tsujii
CREST, JST (Japan)

K. Kurogi
Faculty of Science
Hokkaido University (Japan)

[**] H.Y. acknowledges fellowship support from the 21st century COE program "Center of Excellence for Advanced Life Science on the Base of Bioscience and Nanotechnology" of Hokkaido University, Japan. This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 16310077) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, and was partly supported by NOASTEC, Japan. We thank Dr. S. Shibuichi of Kao Corporation for his preliminary but pioneering investigation and helpful advice on this work.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200500266

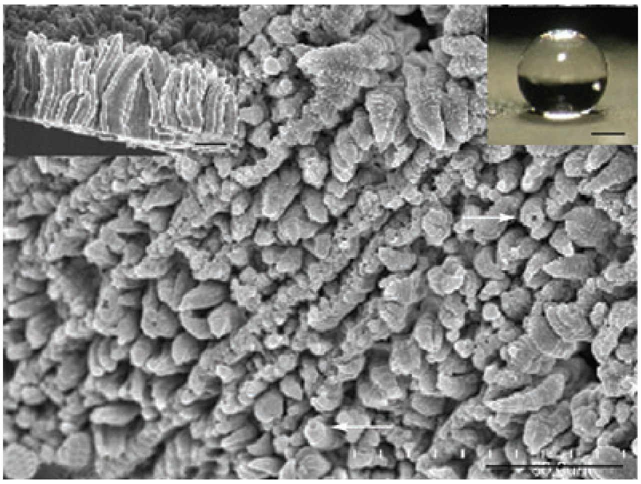

Figure 2. Scanning electron microscopic (SEM) image of the super water-repellent poly(alkylpyrrole) film (scale bar: 15 μm). Left inset: SEM image of the cross section of the film (bar: 15 μm). Right inset: digital camera image of a water droplet on the film (bar: 500 μm). The synthetic conditions were as follows: 1-*n*-octadecylpyrrole/*p*-toluenesulfonate (10:1 molar ratio); 1-*n*-octadecylpyrrole (0.005 mol dm^{-3}); reaction time, 60 min; applied voltage, 22.5 V; working electrode, ITO glass.

carbonate membrane as a template.[22] In the work described herein, the poly(alkylpyrrole) array grew without any template and, on close inspection, the single needle-like poly(alkylpyrrole) structures may be microtubes (arrows in Figure 2). Qiu et al. previously reported that microtube-like polypyrrole is formed in the electrochemical polymerization of pyrrole without template materials.[23] Recently Yan et al. also independently reported the formation of polypyrrole microtubes during the electrochemical polymerization of pyrrole without a template.[24–26] However, in these two cases, the microtubes do not array in an orderly and dense fashion, and the diameters and lengths are much larger than those reported herein.[22–25] Therefore, we believe that our work is the first to show an array of needle-like or capped microtubes of conductive polymer that was electrochemically synthesized without a template. The features of the array indicate that it should show super water repellency in principle, as in the case of polyacrylonitrile nanofibrils.[9] Furthermore, the array should show high stability to heating and organic solvents, because conductive polymers normally consist of long-range-conjugated aromatic rings which are thermally stable and poorly soluble in the usual organic solvents.[19]

Actually, the surface of the poly(alkylpyrrole) film showed super water repellency with a contact angle larger than 150° (right inset of Figure 2). The surface of a cross section of the poly(alkylpyrrole) film was subjected to a preliminary analysis by a box counting method,[2,3] and was found to be a fractal with a dimension of 2.23 (left inset of Figure 2).

The reaction conditions such as concentration and molar ratio of the reactants, applied voltage, reaction time, and working electrode significantly influence the surface structure, that is, the water repellency of the poly(alkylpyrrole) film. Detailed results will be reported elsewhere.

The influence of treatment temperature on the wettability was systematically investigated to evaluate the thermal stability of the films in terms of contact angle to water (Figure 3). The contact angle of the film was nearly constant even when the temperature was increased. The inset of Figure 3 shows the effects of the treatment time at 80 °C on the film. Similarly, the contact angle of the film was also nearly constant when the treatment time was increased. Poly(alkylpyrrole) is one of the conductive polymers that usually consist of aromatic rings and conjugated π bonds on the main polymer chain. Therefore, the polymer has enough thermal stability of chemical composition in the experimental range of temperature and treatment time. The needle-like shape of the poly(alkylpyrrole) structures may also have high thermal stability, similar to the case of polypyrrole microtubes.[26] We consider that the high thermal stability of the film in terms of contact angle can be explained by the thermally stable chemical and geometric factors (see Supporting Information).

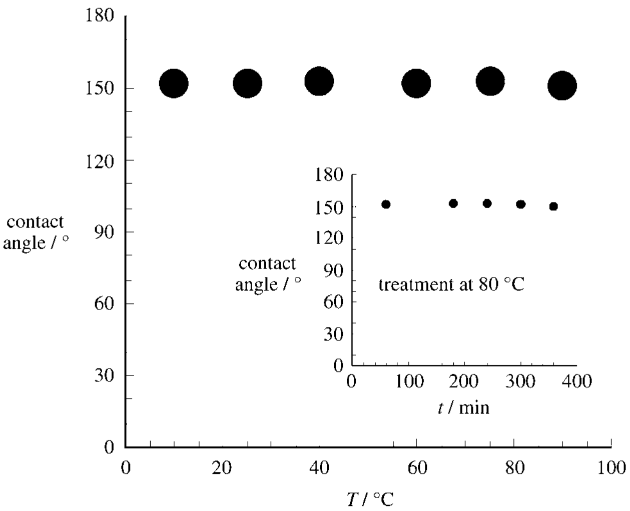

Figure 3. Thermal stability of the super water-repellent poly(alkylpyrrole) film treated at various temperatures for 2 h. The inset shows the thermal stability of a film treated at 80 °C for various treatment times.

Similarly, the influence of treatment with organic solvents and oils on the wettability was systematically investigated to evaluate the durability of the films to these substances in terms of contact angle to water. Figure 4 shows the effects of various organic solvents and oils on the water repellency of the film. The contact angle of the film did not change even after treatment. On the basis of the dark color of the film, the poly(alkylpyrrole) could be a doped conductive polymer, which usually consists of conjugated π bonds with π electrons that are delocalized on the main polymer chains.[19] Doped conductive polymers are normally insoluble in any organic solvents.[19] Therefore, the film has sufficient durability of chemical composition and morphology when treated with organic solvents and oils. We consider that the durability of the film in terms of contact angle can also be explained by the highly stable chemical and geometric factors.

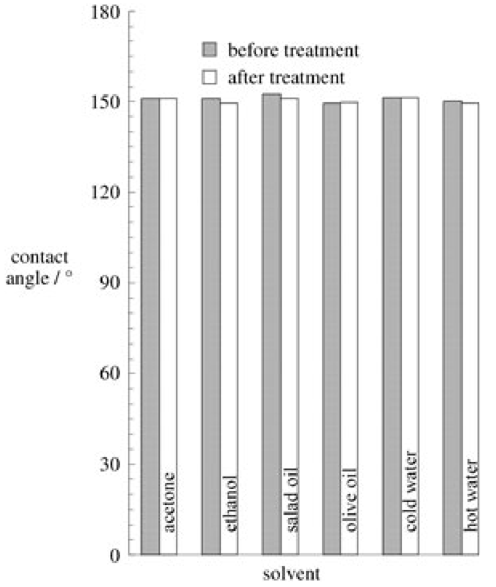

Figure 4. Durability of the super water-repellent poly(alkylpyrrole) film on treatment with organic solvent and oil. See text for the treatment conditions.

In conclusion, we have succeeded in the electrochemical synthesis of super water-repellent poly(alkylpyrrole) films with a contact angle larger than 150°. The SEM images show that the surface of the film consists of a perpendicular alignment of thousands of "needle"-like poly(alkylpyrrole) structures. On the basis of a preliminary analysis by a box counting method, the surface was considered to be a fractal with a dimension of 2.23. In contrast to AKD, the super water-repellent poly(alkylpyrrole) films had excellent environmental stability to both heating and organic solvent treatments in terms of the contact angle to water. These results may be of considerable significance as both fundamental and industrial guiding principles. Moreover, the feature of the film which consists of a vertical alignment of needle-like conductive polymer can be extended to nanotechnological or biotechnological applications, such as electronic devices[22] and substrates for cell culture.[27]

Experimental Section

Synthesis of poly(alkylpyrrole) films: The electrochemical synthesis was performed in a two-electrode cell containing an acetonitrile solution of alkylpyrrole and sodium *p*-toluenesulfonate, by using a constant-current generator (Yokogawa programmable DC source) at room temperature (Figure 1). The alkylpyrrole chosen was 1-*n*-octadecylpyrrole. Synthesis was carried out under the following conditions: working electrode, ITO glass; 1-*n*-octadecylpyrrole (5 mmol); sodium *p*-toluenesulfonate (0.5 mmol); applied voltage, 22.5 V; reaction time, 60 min. The films obtained were extensively washed with acetonitrile to eliminate reactants, and finally dried overnight at room temperature under reduced pressure. The reaction conditions were optimized in terms of contact angle of the film to water by changing the concentrations and molar ratios of alkylpyrrole and sodium *p*-toluenesulfonate, and the applied voltage, time, and working electrode.

Environmental stability of the films in terms of contact angle: Thermal stability was evaluated by treating the films at various temperatures for 2 hours. After the thermal treatments the contact angles were measured at room temperature. The treatment at 80 °C, however, was carried out for various treatment times. The durability to organic solvents or oils was evaluated by immersing the films in an organic solvent and then drying at 80 °C under a reduced pressure. The oils were placed on the films, which were then washed with acetone and finally dried as above. The contact angle was measured on the dried films.

SEM and contact angle measurements: Scanning electron microscopy (SEM) of the films was carried out with a field-emission SEM (Hitachi S-5200) after covering them with a thin layer of sputtered alloy of gold and palladium. The contact angles of the films to water droplets (≈1 mm in diameter) were measured with an optical contact angle meter (Kyowa DropMaster) at room temperature and humidity.

Received: January 24, 2005

Keywords: fractals · hydrophobic effect · polymers · surface chemistry · thin films

---

[1] K. Tsujii in *Surface Activity: Principles, Phenomena, and Applications* (Ed.: T. Tanaka), Academic Press, New York, **1998**, pp. 52 – 54.
[2] T. Onda, S. Shibuichi, N. Satoh, K. Tsujii, *Langmuir* **1996**, *12*, 2125 – 2127.
[3] S. Shibuichi, T. Onda, N. Satoh, K. Tsujii, *J. Phys. Chem.* **1996**, *100*, 19512 – 19517.
[4] K. Tsujii, T. Yamamoto, T. Onda, S. Shibuichi, *Angew. Chem.* **1997**, *109*, 1042 – 1044; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1011 – 1012.
[5] S. Shibuichi, T. Yamamoto, T. Onda, K. Tsujii, *J. Colloid Interface Sci.* **1998**, *208*, 287 – 294.
[6] K. Tadanaga, N. Katata, T. Minami, *J. Am. Ceram. Soc.* **1997**, *80*, 1040 – 1042.
[7] K. Tadanaga, N. Katata, T. Minami, *J. Am. Ceram. Soc.* **1997**, *80*, 3213 – 3216.
[8] L. Feng, S. Li, Y. Li, H. Li, J. Zhai, L. Zhang, Y. Song, L. Jiang, D. Zhu, *Angew. Chem.* **2002**, *114*, 1269 – 1271; *Angew. Chem. Int. Ed.* **2002**, *41*, 1221 – 1223.
[9] L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, *Adv. Mater.* **2002**, *14*, 1857 – 1860.
[10] L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, D. Zhu, *Angew. Chem.* **2004**, *116*, 2046 – 2048; *Angew. Chem. Int. Ed.* **2004**, *43*, 2012 – 2014.
[11] T. Sun, G. Wang, L. Feng, B. Liu, Y. Ma, L. Jiang, D. Zhu, *Angew. Chem.* **2004**, *116*, 361 – 364; *Angew. Chem. Int. Ed.* **2004**, *43*, 357 – 360.
[12] H. Yan, K. Tsujii, JP patent, Application No. P2004-378147.
[13] C. Neinhuis, W. Barthlott, *Ann. Bot.* **1997**, *79*, 667 – 677.
[14] X. Gao, L. Jiang, *Nature* **2004**, *432*, 36.
[15] S. Asavapiriyanont, G. K. Chandler, G. A. Gunawardena, D. Pletcher, *J. Electroanal. Chem.* **1984**, *177*, 229 – 244.
[16] P. G. Pickup, R. A. Osteryoung, *J. Am. Chem. Soc.* **1984**, *106*, 2294 – 2299.
[17] R. E. Noftleand, D. Pletcher, *J. Electroanal. Chem.* **1987**, *227*, 229 – 235.
[18] M. Satoh, K. Kaneto, K. Yoshino, *Synth. Met.* **1986**, *14*, 289 – 296.
[19] *Handbook of Conjugated Polymers* (Eds.: T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds), Marcel Dekker, New York, **1996**.
[20] G. Kossmehl, M. Niemitz, *Synth. Met.* **1991**, *41–43*, 1065 – 1071.
[21] M. Niemitz, G. Kossmehl, *Angew. Makromol. Chem.* **1991**, *185*, 147 – 154.
[22] C. R. Martin, L. S. Van Dyke, Z. H. Cai, W. B. Liang, *J. Am. Chem. Soc.* **1990**, *112*, 8976 – 8977.

[23] L.-T. Qiu, G.-Q. Shi, J.-Y. Yuan, G.-Y. Han, F.-E. Chen, *J. Electroanal. Chem.* **2004**, *561*, 149 – 156.
[24] H. Yan, T. Ishida, N. Toshima, *Chem. Lett.* **2001**, 816 – 817.
[25] H. Yan, M. Inokuchi, S. Ariyoshi, M. Kinoshita, N. Toshima, *Synth. Met.* **2003**, *135–136*, 269 – 270.
[26] H. Yan, M. Inokuchi, M. Kinoshita, N. Toshima, *Synth. Met.* **2005**, *148*, 93 – 98.
[27] H. Yan, H. Shiga, E. Ito, K. Tsujii, *Int. J. Nanosci.* **2005**, in press.