CHEMISTRY LETTERS, pp. 1959-1962, 1988.

Electrically Induced Wettability Change of Polyaniline.
Potential Controlled Tensiometric Study

Masakatsu HATO
Research Institute for Polymers and Textiles,
1-1-4- Higashi, Tsukuba, Ibaraki 305

Electrically induced wettability change of polyaniline has been addressed by a potential controlled tensiometric method. Contact angle decreases with a change in the electrical potential toward more positive values. Wettability of polyaniline can be modulated by external electrical signals.

Wettability (or surface energy), of polymers is important in many technical problems such as adhesion, composite materials, biocompatible polymers, etc. and has been a subject of many studies.$^{1-4)}$ In conventional polymers, however, their wettability is primarily determined by their chemical structure and once they are processed, it is generally difficult to control it intentionally afterward. Recently developing electrically conductive organic polymers will provide us with a possibility of intentional control of their wettability. In this communication, we will report for the first time on in situ monitor of wettability changes of polyaniline in response to external electrical stimuli. Recently developed potential controlled tensiometry$^{5)}$ was applied to monitor changes in contact angle O at a polymer-water-air interface. The wettability of the electrical conductive polymers is also interesting in relation to their possible application to protective coating$^{6)}$ or a photo electric image process.$^{7)}$

A polyaniline film of 0.1 μm in thickness was synthesized on a platinum wire (99.99% purity; 0.5 mm in diameter) by electrochemical polymerization of aniline at a current density of 50 $\mu A/cm^2$ in a 1 M HCl aqueous solution containing 0.5 M of aniline under nitrogen atmosphere.$^{8)}$ Total electric charge passed was 50 mC/cm^2. Cyclic voltammogram between -0.2 and 0.8 V of the polyaniline was identical to that reported in the literature.[11)] SEM was used to determine film thickness and to confirm film integrity. Potential was measured with respect to an Ag/AgCl electrode with a 3 M KCl agar bridge. Contact angle under active potential controlled conditions was determined by a potential controlled tensiometry, where contact angle θ was determined from the measured force ΔF exerted by the meniscus formed at a solid-liquid-air interface, i.e., $\cos\theta = (\Delta F - F_b)/p\gamma$. F_b, p, and γ were a buoyancy force, a perimeter of the solid, and surface tension of liquid respectively.[5)] Test liquid was aqueous HCl. Experimental temperature was 20 ± 1 °C.

Figure 1 shows a typical example of wettability change (expressed by θ) of the polyaniline coated platinum electrode in response to a step change in the electrode potential E. In order to keep the meniscus under advancing angle conditions, a probe liquid container and hence the liquid level was moved upward at a constant velocity of 74 μm/min by a computer controlled electric drive throughout the experiment. Initially, E was controlled at -0.2 V. At this potential, ΔF was 1.4×10^{-5} N ($\theta = 75^\circ$). At time t=0, E was stepped from -0.2 V to +0.8 V. Upon the potential step, ΔF started to increase quickly (θ decreased). After 30 s it reached 6.5×10^{-5} N ($\theta=50^\circ$), and remained constant so far as the potential was kept at this value. At time t=3.8 min, E was stepped back to -0.2 V. In this case, ΔF slowly decreased and took ca. 4.0 min to return to the initial value of 1.4×10^{-5} N ($\theta=75^\circ$) and remained constant until a next potential step was applied at time t=10.4 min. Upon the potential step from -0.2 V to +0.6 V at time t=10.4 min, θ quickly decreased toward a new value of 54°. The contact angle could be restored to the initial value of 75° by the next potential step from +0.6 V to -0.2 V. The above mentioned changes in the contact angle were also visible to the naked eye as an increase or a decrease in the meniscus height H(θ), which were in qualitative agreement with a decrease or an increase in contact angles.

It is noted θ increased at a markedly slower rate than it decreased. This dose not mean a slower change in the polymer surface, but is attributable to direction-dependent meniscus motion. When θ decreases from θ_1 to θ_2 in response to a potential step (Fig.2), the meniscus height increases from $H(\theta_1)$

to $H(\theta_2)$ by spontaneous advancing motion of the solid-liquid-air three phase contact line (TPL) over previously non-wetted surface. On the other hand, when θ changes in the opposite direction, the TPL can not spontaneously recede over the previously wetted surface[9)] but is pinned at a position TPL in Fig. 2. Therefore, the change in θ from θ_2 to θ_1 is achieved only after the liquid level moves upward by $\Delta l\{=H(\theta_2)-H(\theta_1)\}$, and the meniscus takes such a shape as drawn by a dashed line in Fig. 2. Once the liquid level reaches this position, TPL starts to advance over the polymer surface with the constant contact angle θ_1, i.e., with a constant meniscus shape. This discussion is supported by a following calculation. The meniscus height on the electrode surface may be expressed by a following equation,[10)]

$$H(\theta)/r=\cos\theta[\ln\{4/ar(1+\sin\theta)\}-0.57721]$$

$$a = (g\Delta\rho/\gamma)^{1/2}$$

where, r, $\Delta\rho$ and g are a radius of a solid, the difference in density between probe liquid and air, the gravitational constant, respectively. From the equation, one can calculate the distance Δl necessary for the liquid level to move to change θ from θ_2 to θ_1. The calculated Δl for the E step from +0.8 V to -0.2 V or +0.6 V to -0.2 V are 259 μm and 219 μm respectively, i.e., the time required are 3.5(=259/74) and 3.0(=219/74) min indicating reasonable agreement with the experimental values of 4.0 and 3.5 min. Slightly longer experimental time may be due to a slight slipping motion of the TPL. Fig. 3 shows the advancing contact angles vs. E curve in an aqueous HCl at pH=2. Though absolute values of θ were somewhat variable from sample to

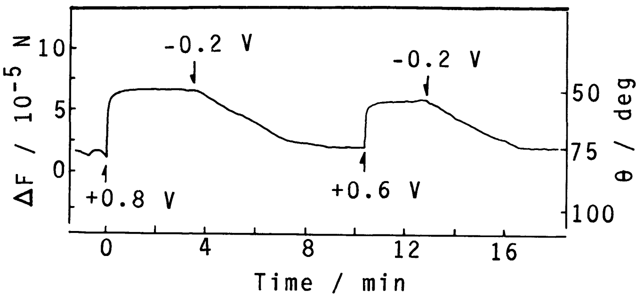

Fig. 1. Potential controlled tensiometry of polyaniline in an aqueous HCl solution at pH=1.

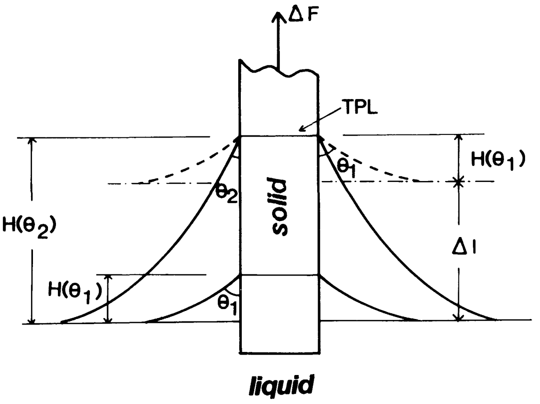

Fig. 2. Meniscus shape at a solid-liquid-air interface. Meniscus height H(θ) depends on contact angle θ.

sample, general features of the curve were the same for all samples studied, i.e., contact angles decreased with a change in the electrode potential toward more positive values.

The change may be explained by a decrease in the interfacial tension between polymer-solution interface due to an increase in positive charge in the polymer as E changes toward more positive values.[11]

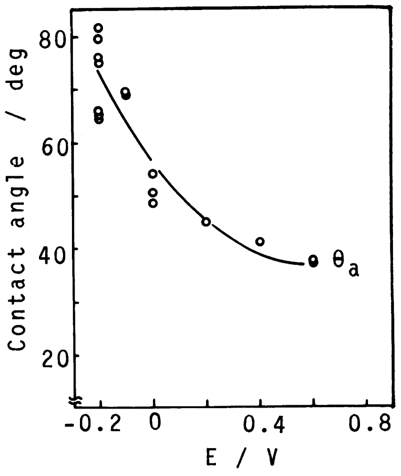

Fig. 3. Advancing contact angles of polyaniline as a function of electrode potential.

References

1) W.A. Zisman, Adv. Chem. Ser., 43, 1 (1964).

2) F.M. Fowkes, J. Phys. Chem., 66, 682 (1962).

3) R.E. Johnson, Jr., and R.H. Dettre, "Surface and Colloid Science," ed by E. Matijevic, and F.R. Eirich, Academic Press, N.Y. (1969), Vol.2, p.85.

4) P.G. de Gennes, Rev. Modern Phys., 57, 827 (1985).

5) M. Hato, J. Colloid Interface Sci., in press (1988).

6) R. Noufi, A.J. Nozik, J. White, and L.F. Warren, J. Electrochem Soc., 129, 2261 (1982).

7) H. Masuda, N. Shimizu, and S. Ohno, Chem. Lett., 1984, 1701.

8) T. Kobayashi, H. Yoneyama, and H. Tamura, J. Electroanal. Chem., 161, 419 (1984).

9) E. Bayramli, T.G.M. van de Ven, and S.G. Mason, Can. J. Chem., 59, 1954 (1981).

10) D.F. James, J. Fluid Mech., 63, 657 (1974).

11) W. Huang, B.D. Humphrey, and A.G. MacDiarmid, J. Chem. Soc., Faraday Trans. 1, 82, 2385 (1986).

(Received August 25,1988)