Tuning the Surface Free Energy of Polybenzoxazine Thin Films

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A novel approach to manipulate the surface free energy and wettability on polybenzoxazine thin films can be achieved simply by varying the time of thermal treatment or UV exposure. A fraction of the intramolecular hydrogen bonding of the as-cured sample will convert into intermolecular hydrogen bonding upon thermal treatment or UV exposure and, thus, results in an increase in the hydrophilicity and wettability. This UV approach provides a simple method to generate wettability patterns or wettability gradients on the surface of a polybenzoxazine film. In addition, we have applied this technique to the preparation of a large-area periodic array of CdTe colloidal nanocrystals on polybenzoxazine thin films.

The surface and interfacial properties of materials are directly related to their surface energies. Current approaches toward engineer-tunable surfaces include light irradiation[1,2] and UV[3] thermal treatment,[4,5] acidification,[6-8] and applying electrical potentials,[9,10] among others.[11] Intra- and intermolecular interactions play important roles in determining the surface properties of polymers. For example, Jiang et al.[4] found that at temperatures above its lower critical solution temperature (LCST), the compact, collapsed conformation of poly(*N*-isopropylacrylamide) (PNIPAAm), induced by intramolecular hydrogen bonding between the C=O and N−H groups of the main chains, results in a low surface free energy and a high contact angle for water. When the temperature is below the LCST, however, intermolecular hydrogen bonding between the PNIPAAm main chains and water molecules predominates, leading to a higher surface free energy and a lower water contact angle. Similarly, Chung et al.[12] reported that the presence of amide groups in a fluorinated-main-chain liquid-crystalline polymer system induces strong intermolecular hydrogen bonding, resulting in higher surface free energies and higher degrees of hydrophilicity.

Structured surfaces that exhibit lateral patterns of varying wettability have received extensive attention because it can apply as preparing fluid microchips[13] and the periodical arrangements of metallic nanoparticles[14,15] or nanowires[16] and self-assembly of block copolymer[17] or carbon nanotubes.[18] In addition, a gradient surface displays a gradual change in the chemical and physical properties along its length and has a wide range of applications in material science.[19-22] A gradient in a surface can induce the net mass transport of liquids, which affords a driving force for operation of microfluidic devices and for biological cell motility in vitro. Therefore, a simple method to

create a wettabilty pattern or wettability gradient on a polymer thin film needed to be developed.

Polybenzoxazines (PBZs), feature strong intramolecular hydrogen bonds that result in extremely low surface free energies, even lower than that of pure Teflon.[23] In PBZ systems, strong intramolecular hydrogen bonding between the hydroxyl groups and the amino groups in the Mannich bridges tends to decrease the surface free energy, whereas intermolecular hydrogen bonding between hydroxyl groups results in higher surface free energies. We are unaware, however, of any previously available methods that allow precise control over the surface free energies of PBZ films. In this paper, we present a simple strategy for obtaining wettability patterns and wettability gradients on PBZ thin films by using UV irradiation to modify the extent of intra- and intermolecular hydrogen bonding. We have applied this technique to the preparation of a large-area periodic array of CdTe colloidal nanocrystals on PBZ thin films.

After optimizing its thermal curing conditions, B-ala PBZ contains predominantly intramolecular hydrogen bonds and, therefore, possesses an extremely low surface free energy. Figure 1 displays the advancing contact angles and surface free energies (γ_s) of three test liquids on B-ala PBZ films after various curing times at 210 °C. The lowest surface free energy we obtained for a B-ala film was 14.4 mJ m^{-2}, calculated using van Oss and Good's three-liquid method,[24] which is substantially lower than that of pure Teflon (21 mJ m^{-2}). The surface free energy in this B-ala PBZ system decreased initially and then increased steadily upon increasing the curing time. This phenomenon can be explained in terms of changes in the ratio of intra- and intermolecular hydrogen bonds (Figure S1 of the Supporting Information).[23] Therefore, the surface free energy of this PBZ is tunable from 14.4 to 46.3 mJ m^{-2} merely by controlling the length of time that it is subjected to thermal curing. Nevertheless, this technique would be very difficult to use to fabricate a

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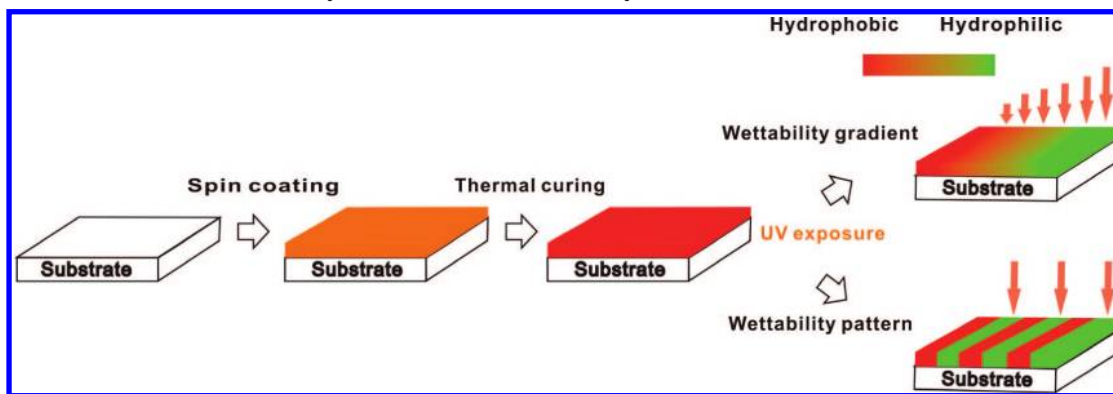† National Chiao Tung University.
‡ I-Shou University.
§ National Nano Device Laboratories.
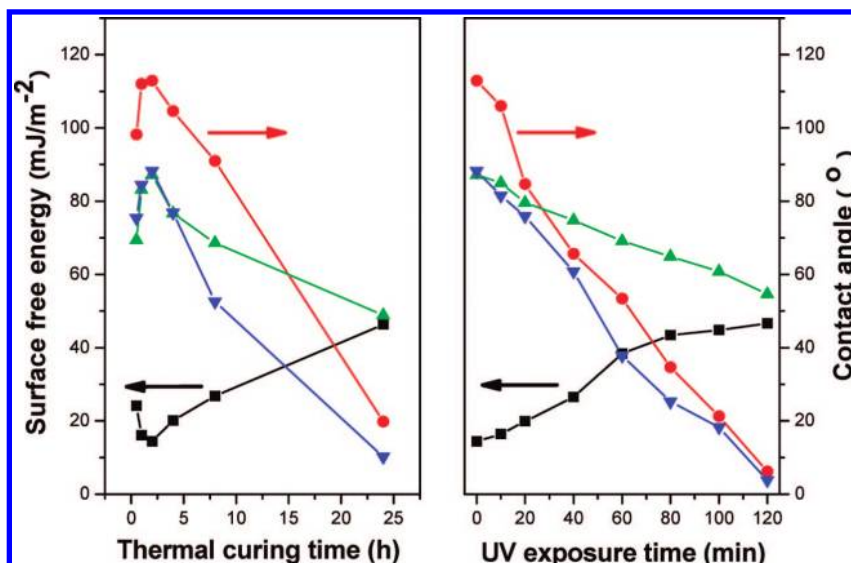
Figure 1. Advancing contact angles of (●)water, (▲)diiodomethane, and (▼)ethylene glycol and the respective surface free energies (γ's) (■) of B-ala PBZ films.

SCHEME 1: Fabrication of Wettability Gradients and Wettability Patterns on B-ala PBZ Films


gradient in the surface free energy or provide a wettability pattern on PBZ.

Ishida et al.[25,26] determined that C=O-containing species are formed when a bisphenol A-based PBZ resin is exposed to UV radiation under ambient conditions. The isopropylidene linkages of PBZ are the reactive sites where oxidation and cleavage occur upon UV exposure, forming 2,6-disubstituted benzoquinone units. The presence of these benzoquinone moieties decreases the extent of intramolecular hydrogen bonding while increasing

the extent of intermolecular hydrogen bonding. Because radical formation and oxidation reactions induced by UV radiation are usually concentrated at polymer surfaces, we suspected that the surface properties of PBZ thin films would be greatly affected by their length of UV exposure.

Figure 1 reveals that the advancing contact angles of the three test liquids decreased upon increasing the UV exposure time of B-ala PBZ films (cured 2 h at 210 °C). This behavior is consistent with a partial destruction of intramolecular hydrogen
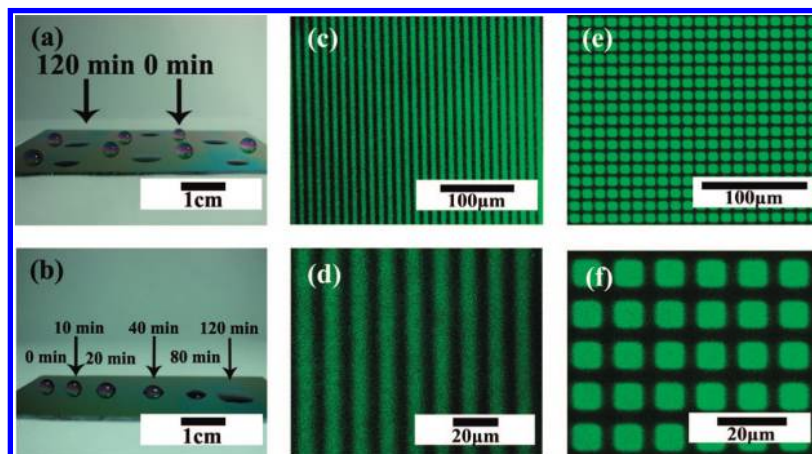
Figure 2. (a) Wettabilty pattern, (b) wettablity gradient, and (c−f) periodic arrangement of CdTe colloidal nanocrystals on B-ala PBZ films.

Letters

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bonding and a corresponding increase in the extent of intermolecular hydrogen bonding after UV exposure, resulting in higher surface free energies and higher degrees of hydrophilicity. The advancing contact angles of the polar test liquids (water, ethylene glycol) decreased substantially after UV exposure; the decrease in the advancing contact angle of the nonpolar liquid (diiodomethane) was less pronounced. To determine the interactions occurring between these liquids and the PBZ thin film, we used the two-liquid geometric method[27] to determine the corresponding values of γ_s, γ^d, and γ^p (Table S3 of the Supporting Information). The values of γ^d and γ^p can be calculated from the measured contact angles; the superscript "d" refers to the London dispersion forces, whereas the superscript "p" refers to polar forces, including all of the interactions established between the solid and liquid, such as Keesom dipole−dipole, Debye dipole−induced dipole, and hydrogen bonding interactions. The value of γ^p increased rapidly upon increasing the UV exposure time, but the change in γ^d was relatively insignificant; these phenomena imply that the polar forces between the PBZ thin film and the testing liquids increased substantially after UV exposure. The presence of new polar quinone C=O functional groups on the irradiated surface led to stronger polar forces between the PBZ film and the testing liquid, resulting in lower advancing contact angles for both water and ethylene glycol. The ESCA results in Table S3 of the Supporting Information reveal that the atomic fraction of oxygen, an indication of the degree of photo-oxidation of the surface, increased dramatically after UV exposure.

The relationship between the surface free energy of B-ala PBZ thin films and the UV exposure time suggested that we could manipulate the surface free energy at selected regions merely by varying the UV exposure time to create wettability patterns or wettability gradients. Scheme 1 provides an illustration of the procedures used to control the surface free energy of PBZ thin films. In the procedure, we controlled the surface free energy of the B-ala PBZ thin films through thermal curing and then created hydrophilic regions on them through UV exposure. Figures 2a and 2b present photographic images of a wettabilty pattern and a wettablity gradient formed upon two PBZ films after UV exposure. Furthermore, we also deposited CdTe colloidal nanocrystals through direct evaporation of a nanocrystal solution[28] in periodic arrangements on PBZ thin films exhibiting patterned lyophobicity (Figure 2c−f).

In conclusion, the surface free energy and hydrophilicity of PBZ films can be controlled through a combination of thermal treatment and UV exposure to change the ratios of intra- to intermolecular hydrogen bonds. This simple method allows wettability patterns and wettability gradients to be produced on the surfaces of PBZ films. In addition, we used this technique to pattern periodic arrangements of CdTe colloidal nanocrystals on PBZ thin films.

Supporting Information Available: Synthetic details, FTIR spectroscopic and ESCA analyses, and surface energies of the PBZ thin films after UV exposure. This material is available free of charge via the Internet at http://pubs.acs.org.

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