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Light-tunable solvent drying in photo-responsive solution coatings

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ABSTRACT

Solvent drying rate of azobenzene/acetone solution coating was tunable by linearly polarized UV light. The light exposure promotes the photo-induced conformational change of azobenzene from its trans to its cis form, as well as the molecular alignment perpendicular to a polarization direction. Drying experiments of the photo-responsive solutions revealed that angled irradiation of s-polarized light showed a peculiar angle-dependent drying behavior, while no dependence was observed for the p-polarized light irradiation. The photo-induced solvent drying was observed in a particular range of azobenzene weight fractions and UV light intensities, suggesting a promising way to tune solvent drying rates by light.
1. Introduction

There has been much interest in liquid coatings whose properties are tunable by light. Light absorbed in such liquids can change microstructures on a molecular level, which in turn alter mechanical/electrical functions of the coatings. Despite the potential utilities of light-responsive fluids, previous drying studies have been restricted to photo-curable liquids, in which photosensitive monomers can polymerize via cross-linking reactions (1-3). Here we report the alternative case where light irradiation promotes an orientation and/or conformational change of a single, non-polymerizable molecule.

Azobenzene moieties are typical class of photo-responsive molecules, which undergo an intra-molecular rotation around the double bond N=N from its trans to its cis form via ultraviolet (UV) light irradiation (Figure 1). The non-planar cis form shows a higher surface energy and thus is more hydrophilic than the planar trans form (4). Furthermore, the long axis of azobenzene moiety is known to become oriented perpendicular to a polarized direction of light due to its angular-selective absorption. Based on these unique characteristics, extensive studies have been performed for photo-induced rapid mass transfer (5), morphology control in phase separating blends (6), light-guided reversible motion of a liquid droplet (4), anisotropic molecular orientation (7), structural change in monolayer on a liquid surface (8-9), and for creating photosensitive surfactants (10) and photo-rheological fluids with light-tunable viscosity.
(11). However, little attention has been paid for drying kinetics of photo-responsive solutions exhibiting the orientation and/or structural change on a molecular level. In this study, we demonstrate experimental evidence that an irradiation of angled, polarized UV light alters solvent drying rates of azobenzene/acetone thin film coatings.

2. Experimental apparatus and procedure

Experimental apparatus is shown schematically in Figure 2. We used trans-azobenzene (Wako, as purchased) dissolved in acetone (Wako, as purchased). The solution was deposited on a glass substrate with an initial film thickness of 400 microns. The coated area was specified to be 18 cm$^2$ by gluing 1.0 mm thick aluminum shim on the substrate. The coating was then mounted on an electronic balance (Sartorius LP1200S) to measure the decrease in film mass, which was stored in a personal computer at a sampling rate of 2.5 Hz. The coating was continuously heated by a glass conductive heater (Kitazato MP-10DMH) set beneath the substrate with an air clearance of 1 mm. The substrate temperature was maintained at 313.2 K by regulating the current through the heater. The solvent drying rate was calculated from each slope of the weight-loss curves as $r = -(1/A)dW/dt$ where $A$ is the film surface area, $t$ the time and $W$ the mass of the film during drying.

The coating solution was dried while being irradiated with UV light from a light source
(Keyence UV-400) with a wavelength of 365±5nm. A sheet polarizer (Sigma Koki NSPFU-30C) was placed in the beam path to produce linearly polarized UV light. The irradiation experiments were performed under two different configurations of s-polarized, in which the polarization direction is orthogonal to the irradiation plane, and p-polarized with the polarization direction parallel to the plane. The light intensity on the sample was measured using UV meter (Custom UV-340) and ranged between 0 and 5000 μW/cm². The light source was tilted against the coating surface at a certain angle, \(\theta\), in order to promote an orientation of azobenzene molecule in the liquid. Because the cis isomer can return to the trans isomer via visible light irradiation, all the equipments were set inside a dark box with an illuminance of 0.55 lx in order to minimize the reverse isomerization reaction.

3. Results and discussion

First, linearly s-polarized UV light was irradiated on to coatings with a tilt angle of 45 degrees at a light intensity of 500 μW/cm². The variation in the film weight with elapsed drying time is shown in Figure 3 for (a) pure acetone and (b) azobenzene/acetone=1/40 (wt/wt) binary solution coatings. In the former case, the measured weight-loss curve of the light irradiated coating agrees with that of the non-irradiated case, indicating that the UV light exposure promotes negligible variation in drying rate. This is consistent with the preliminary UV-vis
spectra measurement, which revealed that all UV light is transmitted through pure acetone at the wavelength of interest. For the azobenzene solution, on the other hand, the weight loss curve shows a slightly smaller slope compared with the non-irradiated case (Figure 3c), suggesting that the UV light exposure decreases the evaporation rate of acetone from the photo-responsive solution coating. Similarly suppressed solvent drying was observed for the p-polarized UV light exposure.

In order to quantify the light-driven drying in detail, the drying rate difference between irradiated and non-irradiated cases was obtained for s- and p-polarized light irradiation. Figure 4 shows the variation in drying rate difference with the light tilt angle. For the p-polarized light, the difference in drying rates was found to be independent of angles. In contrast, the s-polarized light exposure showed a minimum drying rate at the tilt angle of 45 degrees, and agreed with p-polarized case at $\theta=10$ and 90 degrees, indicating a particular angle-dependent behavior even at the same light intensity.

This peculiar drying feature for the angled UV irradiation can be understood by considering photo-induced orientations of azobenzene molecules. As noted earlier, the azobenzene molecule rotates via UV light absorption and aligns perpendicular to the polarization direction. In p-polarized irradiation, a trans-azobenzene molecule can transform to cis form but its rotation is restricted to the horizontal plane parallel to the coating surface. Thus cis-azobenzene molecules
exhibit the same alignment even at different irradiation angles, leading to the angle-independent drying behavior. On the other hand, the angled s-polarized irradiation tends to tilt cis-azobenzene molecules perpendicular to the coating surface because its polarization direction is orthogonal to the irradiation plane. The tilted cis-azobenzene molecules align near the free surface, interact with surrounding solvent molecules to some extents and eventually alter evaporation rates of the solvent as shown in Figure 4. Note that, at the irradiation angle of 90 degrees, azobenzene molecules align only in the horizontal plane as they do in the p-polarized light irradiation. This is consistent with the fact that the same drying rate was observed between s-polarized and p-polarized light exposure at $\theta=90$ degrees.

In the second series of experiments, the solute mass concentration was varied while the light tilt angle and the polarized direction were kept constant. Figure 5 shows the variation in drying rate difference with weight ratio of azobenzene to acetone at two different light angles of 45 and 90 degrees. The two solid curves are guide to the eye. In dilute solution coatings, no distinguished difference in drying rate was observed between irradiated and non-irradiated cases. This is consistent with the fact that the drying rate in this regime agreed with that of pure acetone coating. An increase in azobenzene weight ratio leads to a regime where the irradiated coatings exhibit a particular decrease in solvent drying rate compared to non-irradiated coatings. Interestingly, a further increase in azobenzene tends to increase the drying rate, giving rise to an
enhanced drying via the s-polarized UV exposure.

A similar trend was observed for the drying results at different UV light intensities. As shown in Figure 6, little change in drying rate was observed in the absence of light exposure. A slight increase in light intensity gives rise to a particular decrease in the solvent drying rate at low intensity regimes, whereas the irradiated coating dries significantly faster than the non-irradiated case at higher light intensities. These facts suggest that the solvent drying rate is tunable by UV light in the photo-sensitive solution coating, and particularly suppressed at an intermediate range of light intensities and cis-azobenzene concentrations.

It is not immediately clear how the azobenzene isomers interact with the solvent to retard/enhance the solvent drying via the UV light irradiation. Here we simply note that the variation in drying rate stems from combined effects between the trans-cis isomerization reaction and the photo-induced molecular orientation. The former can suppress the solvent drying to some extent by simply irradiating the p-polarized UV light (see Figure 4) being independent of the light tilt angles. For the latter, on the contrary, the angle-dependent drying at s-polarized UV light provides direct evidence that the molecular alignment plays a significant role in azobenzene-acetone interactions at the evaporating surface, because the s-polarized light exposure not only leads to the photo isomerization but also contribute to the angle-selective rotation of each azobenzene molecules. Although further studies are needed to quantify the
photo-induced drying in detail, the present experiments provide a start toward a new route to achieve local, precise control of solvent drying rate via UV light exposure.

4. Conclusions

Photo-induced conformational change of azobenzene from its trans to its cis form promotes a particular change in solvent drying rate in azobenzene/acetone solution coatings. Linearly polarized UV light was irradiated on to the coating for promoting the photo-isomerization reaction as well as the molecular alignment perpendicular to a polarization direction. The UV-irradiated coatings dried slower than non-irradiated ones in dilute regimes and at low light intensities, showing a particularly suppressed drying via the light exposure. Furthermore, the angled irradiation of s-polarized UV showed an angle-dependent drying behavior, while no dependence was observed for the p-polarized light irradiation. These facts suggest that the solvent drying rate is tunable by light in the photo-sensitive solution coatings.

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