Photoactive Additives for Cross-Linking Polymer Films: Inhibition of Dewetting in Thin Polymer Films

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In this report, we describe a versatile photochemical method for cross-linking polymer films and demonstrate that this method can be used to inhibit thin polymer films from dewetting. A bifunctional photoactive molecule featuring two benzophenone chromophores capable of abstracting hydrogen atoms from various donors, including C−H groups, is mixed into PS films. Upon exposure to UV light, the bis-benzophenone molecule cross-links the chains presumably by hydrogen abstraction followed by radical recombination. Photoinduced cross-linking is characterized by infrared spectroscopy and gel permeation chromatography. Optical and atomic force microscopy images show that photocrosslinked polystyrene (PS) thin films resist dewetting when heated above the glass transition temperature or exposed to solvent vapor. PS films are inhibited from dewetting on both solid and liquid substrates. The effectiveness of the method to inhibit dewetting is studied as a function of the ratio of cross-linker to macromolecule, duration of exposure to UV light, film thickness, the driving force for dewetting, and the thermodynamic nature of the substrate.

Introduction

Polymer thin films have important applications in materials science and engineering including the fabrication of sensors and microelectronic, optoelectronic, and biomedical devices and the control of wettability, adhesion, barrier properties, and friction and wear.[1,2] A current problem in thin film technology involves stabilizing a polymer film on a given surface such that the polymer remains wetted on the substrate. A smooth surface is said to be wetted by an adsorbed species when van der Waals interactions at the substrate−liquid, liquid−air, and substrate−air interfaces allow the liquid to spread on the surface such that the contact angle is zero or very close to zero.[3] The effect of the interfacial tensions on the contact angle, θ, is described by the Young equation

$$\cos \theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \qquad (1)$$

where γ_{sv} is the solid−vapor interfacial tension, γ_{sl} is the solid−liquid interfacial tension, and γ_{lv} is the liquid−vapor interfacial tension. When a thin film is cast on a nonwettable surface for which the interfacial tensions do not favor wetting, dewetting can occur, a process in which the film retracts from the substrate, typically by forming holes, and organizes into structures that ultimately decay into a stable state.[4] In many cases, this is undesirable because it will compromise the function of any device for which the film is a component. Studies on PS films have

shown that the dewetting process generally occurs in three stages.[5] In the first stage, the film breaks up into holes with the mass of the film either redistributed evenly across the film or collected in a rim at the perimeter of the holes. In the second stage, the holes grow and coalesce to form a morphology consisting of a polygonal pattern of unstable ribbons. In the third stage, the ribbons break down into stable droplets.

Thin films can be cast on nonwettable substrates by spin-coating. The polymer chains become frozen in a vitrified state that stabilizes the film because the chains lose their mobility. Such glassy films are metastable[6] and will spontaneously dewet the substrate when the polymer chains gain enough mobility by heating above the glass transition temperature, T_g, or exposure to solvent vapor. The likelihood of wetting for a thin film is determined by the sign of the spreading coefficient, S[2]

$$S = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \qquad (2)$$

If S is positive, the liquid will wet the surface. If S is negative, the liquid dewets the substrate.

Numerous examples of systems that dewet have been reported. Polystyrene (PS) has been shown to dewet on various solid and liquid substrates including Si,[5] poly(dimethylsiloxane) (PDMS),[7] and poly(methyl methacrylate) (PMMA).[8] PDMS films with a thickness below 500 nm on silanized Si have been reported to dewet spontaneously.[9] Bilayers composed of polycarbonate deposited on poly (styrene-*co*-acrylonitrile) dewet when annealed above T_g.[10] Films composed of mixtures of deuterated oligomeric styrene and oligomeric ethylene−propylene were found to dewet

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gold substrates following phase-separation.[11] Further, it has been shown that some polymers display autophobicity, meaning the polymer will dewet a substrate coated with a monolayer of an identical polymer.[12,13] Inorganic materials such as gold films are also susceptible to dewetting.[14] Dewetting of some thin films after exposure to solvent vapor is a current problem in developing sensors to detect nerve agents. These examples and many others indicate that materials required for a given application may need to be stabilized by chemical or physical means in order to preserve functionality.

Developing methods to prevent dewetting is a current challenge in materials science. Film impurities have been reported to catalyze dewetting,[15] however, in some cases additives have been shown to suppress dewetting. Buckminster fullerene,[16] dendrimers,[17] and PS nanoparticles[18] have all been shown to inhibit dewetting. Decreasing the liquid−air interfacial tension through the use of low energy end groups has also been shown to suppress dewetting.[19] An oligostyrene liquid was stabilized on Si by grafting PS to the substrate and mixing PS chains into the liquid.[20] Other film stabilization techniques include the incorporation of branched molecules into the film [21] and blending random functional copolymers into unstable films.[22]

In this report, we demonstrate a new photochemical-based technique for cross-linking polymers and show that this technique can be applied to inhibit dewetting. The new method involves the addition of bifunctional benzophenone additives that cross-link the polymer thin film upon exposure to appropriate radiation. Methods of polymer thin film stabilization with cross-linkers have been demonstrated previously; however, they require the incorporation of cross-linkable units within the polymer chain at the synthesis stage. For example, random copolymers containing benzocyclobutene functional monomers can be cross-linked thermally.[23] The present method is more direct and universal because preexisting polymers are cross-linked by simply incorporating a photoactive additive within the polymer thin film. To illustrate the new method of dewetting inhibition, we report the results for two rather standard but distinct systems whose dewetting properties are well studied and are reproducible: PS on Si wafers and PS on PMMA.

Results and Discussion

Our strategy for developing a versatile method for inhibiting dewetting follows three stages: (1) design of a bifunctional photoactive cross-linker that can react with any polymer containing hydrogen atom donors including C−H, Si−H and

S−H groups; (2) analysis of infrared (IR) spectroscopy and gel permeation chromatography (GPC) to show that the photoactive molecule embedded in a polymer film undergoes a photochemical reaction that cross-links the macromolecules in the film; (3) imaging polymer films with optical and atomic force microscopy to show that the photoactive cross-linker can inhibit dewetting and to subsequently investigate how dewetting inhibition depends on irradiation time, film thickness, concentration of photoactive additive, the driving force for dewetting, and the thermodynamic and chemical nature of the substrate. We selected a system employing two distinct substrates for our investigations that can be considered as classic cases for polymer dewetting and can be conveniently imaged with optical microscopy: PS on Si and PS on PMMA.[5,19,24−27] Note that it has been shown that PS does not dewet Si under certain cleaning conditions. We found that cleaning the Si wafer with piranha followed by UV/ozone treatment did not prevent dewetting and therefore provided a convenient and reproducible system by which to study how our technique inhibits dewetting.

A bifunctional photoactive molecule containing benzophenone chromophores[28] was selected as the initial design for the cross-linker additive because these chromophores are known to undergo hydrogen abstraction reactions with hydrogen atom donors such as C−H groups and thus are capable of cross-linking a wide variety of different polymer types. The bis-benzophenone derivative employed, bis-3-benzoyl benzoic acid ethylene glycol (**1**; see Figure 1), was synthesized by dicyclohexylcarbodiimide (DCC) coupling of 3-benzoyl benzoic acid to ethylene glycol.

A plausible mechanism for the photoinduced cross-linking reaction is presented in Figure 1. Irradiation is expected to produce an excited n−π* state that intersystem crosses to the triplet.[28] One of several deactivation pathways includes hydrogen abstraction of a nearby C−H group on a PS chain (step 1). Hydrogen abstraction will form radicals that can recombine to form covalent bonds. Two potential recombination pathways can result in cross-links. First, radical centers on the PS chains can recombine with each other (step 2). This requires that the photogenerated PS radicals are located sufficiently close to each other. This pathway may be limited in that the chain motion can be hindered by the solid-state reaction conditions used to cross-link the film. Second, the inclusion of two benzophenone chromophores supplies an additional cross-linking pathway that circumvents the need to have two macroradical centers in close proximity. Recombination of two benzophenone ketyl radicals at the ends of a single molecule of **1** with PS macroradicals results in cross-links without the need for two interacting PS radicals. The main possible side reactions include recombination of the ketyl radicals to produce pinnacol derivatives that may or may not act as extended cross-link bridges and disproportionation products. Our benzophenone derivative is particularly well suited to this study because the excitation wavelength occurs around 340 nm, sufficiently separated from the adsorption band of the PS phenyl rings that falls below 280 nm.

To verify the ability of **1** to induce a photocrosslinking reaction in a PS film, irradiated films containing **1** were examined by IR spectroscopy and GPC. Hydrogen abstraction is expected to occur at the aromatic ketone as shown in Figure 1. Examination of the corresponding peak in the IR spectrum indicates whether this chromophore can participate in a photochemical reaction when

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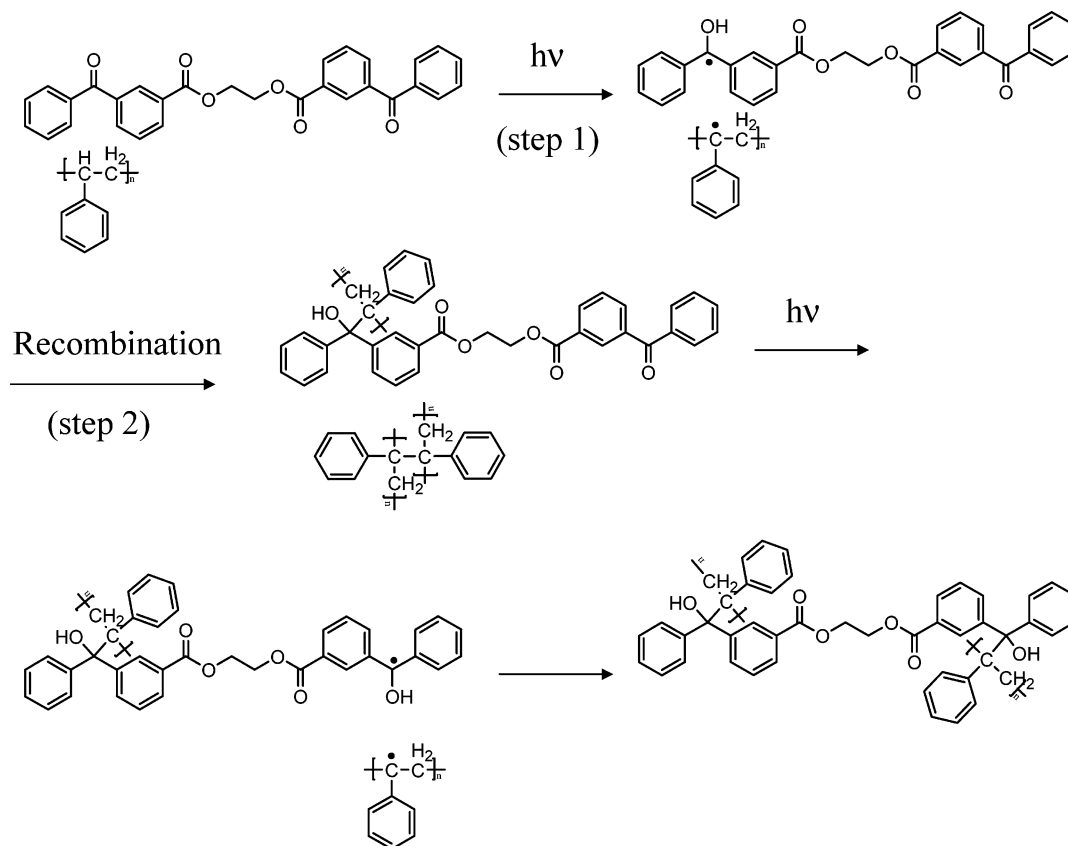
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Figure 1. Two pathways are proposed for cross-linking PS by **1**. In the first, after **1** abstracts hydrogen atoms from PS chains, recombination between a PS radical and a benzophenone ketyl radical results in a covalent bond. When this happens on both benzophenone chromophores, a cross-link will result. In the second, radicals created on PS chains by hydrogen abstraction can recombine to form cross-links.

mixed within the polymer matrix. IR spectra of a PS film containing **1** taken after intervals of irradiation with UV light shows that the aromatic ketone at 1661 cm^{-1} decays relative to the ester groups at 1725 cm^{-1} over time (see the Supporting Information). The observed decrease in the aromatic ketone absorbance as a function of time demonstrates that **1** can undergo a photochemical reaction while confined in a polymer matrix.

Analysis of the IR spectrum only indicates that a photochemical event takes place but does not specify the nature of the photochemical event, although H abstraction is the most plausible primary photochemical process occurring. H abstraction by compound **1** does not guarantee cross-linking. To determine if PS chains can be photochemically cross-linked by photoexcitation of **1** in a PS matrix, films containing **1** and PS ($M_n = 2600$) were analyzed by GPC. It should be noted that GPC is not suitable for quantitatively characterizing the effect of the concentration of **1** on the degree of crosslinking because of the possibility for forming insoluble gels. In any case, we performed the experiment using various concentrations of **1** to qualitatively demonstrate that cross-linking occurs at various concentrations. Analysis of the GPC curves in Figure 2 shows that the lowest molecular weight peak, which occurs at comparable retention times in all of the samples, shifted to higher molecular weight after irradiation. In some cases, the shift was accompanied by the growth of new peaks corresponding to higher molecular weights. The formation of higher molecular weight species suggests that irradiation of **1** within the polymer film results in cross-linked (i.e., branched) PS chains. It is possible that insoluble higher molecular weight networks were created that cannot be detected using GPC. The decay of the aromatic carbonyl and an increase in the molecular weight of the PS chains after irradiation are consistent with the hypothesis that **1** photochemically cross-links the PS chains as the result of photoinduced H abstraction.
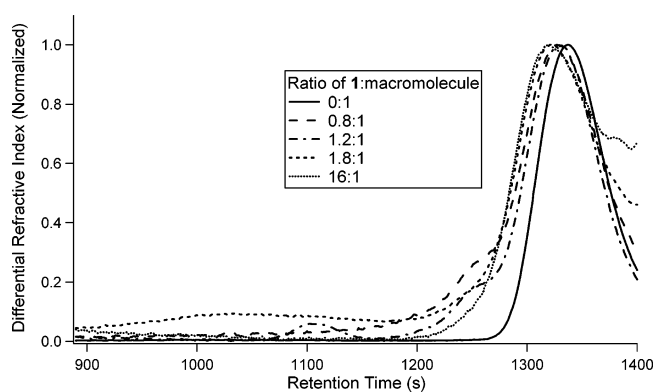
Figure 2. GPC traces (normalized) of irradiated PS films containing varying ratios of **1** to macromolecule.

After demonstrating that **1** can photochemically cross-link PS, we examined the effect of cross-linking on the dewetting behavior of PS. To gain insight into the factors influencing the utility of our method, we varied a number of parameters in our system that are expected to affect dewetting. These include the concentration of **1** embedded in the film, irradiation time, thickness of the film, the driving force for dewetting, and the surface thermodynamics of the substrate. We used a combination of optical microscopy (OM) and atomic force microscopy (AFM) measurements to obtain qualitative and quantitative data. Although less convenient than OM, AFM is required when films are too thin to resolve the features and to visualize three-dimensional dewetting morphologies. In addition, AFM was used to quantitatively compare the degree of dewetting in our samples based on the determination of the average surface roughness. We also compared samples by calculating the mean height of the surface features.
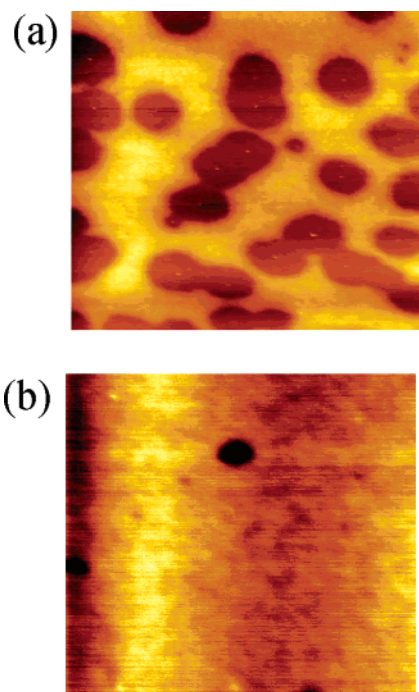
Figure 3. AFM images (5 × 5 um) of PS films after annealing at 170° C overnight. (a) Pure PS film (b) Irradiated PS film containing a ratio of **1** to PS of 29:1.

As an initial test to see if **1** had an effect on the dewetting characteristics of PS films, ultrathin films were spin-cast from a solution containing a ratio of molecules of **1** to PS of 29:1 and a solution without **1**. The thickness of the film without **1** is approximately 2.5 nm (thickness determined by ellipsometry). After irradiation with a 350 nm lamp for 1 h and baking overnight at approximately 170°, well above T_g for PS, the samples were analyzed by AFM. The features on the surface of the films were too small to be seen with OM. Figure 3 shows AFM images for these samples (Figure 3, panels a and b) along with a PS film without **1** annealed under the same conditions (Figure 3a). These images display holes, which are diagnostic of the first stage of dewetting. The film containing **1** shows a lesser amount of holes. Note that for this particular sample the substrate was not imaged until a hole could be found, biasing the experiment against a positive result. Even with this handicap, the film appears to be qualitatively less damaged than the control. The ultrathin films used in this experiment are expected to result in a quasi-two-dimensional network. The degree of dewetting is inhibited; however, it is not clear whether the elastic properties of this low-dimensional network are able to resist the capillary forces responsible for dewetting. The effect of film thickness is discussed below. The average roughness of the film containing **1** is 0.3 nm compared to the roughness value of 1.9 nm for the sample without **1**, a decrease by more than a factor of 6. Annealing a film containing **1** without irradiation did not show a large effect on the dewetting characteristics (data not shown). It should be noted that we found that direct irradiation of pure PS films with 254 nm lamps, a condition that cross-links PS,[29] similarly inhibits dewetting. Irradiation of pure PS films with the 350 nm lamp used to activate compound **1** in this study showed no effect on the dewetting behavior. These results suggest that irradiation of films containing **1** results in cross-links that inhibit the polymer chains from reorganizing on the surface.

To understand the dependence of the concentration of **1** on the dewetting characteristics of photocrosslinked PS films,

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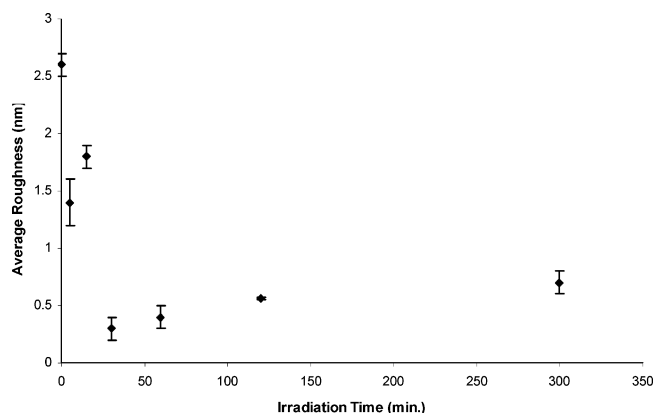
Figure 4. As the dosage of photons is increased, the surface roughness of irradiated PS films containing **1** annealed overnight at 170 °C decreases. The ratio of molecules of **1** to PS in each film is 60:1. The thickness of these films without addition of **1** is approximately 2.5 nm.

additional films were cast containing intermediate concentrations of **1** relative to the above two samples. Assuming the mechanism for dewetting retardation involves a photochemical cross-linking reaction that limits the mobility of the polymer chains needed to form holes, changes in the surface roughness should correlate with the amount of **1** in the sample. We measured the average roughness of the baked films as a function of the ratio of molecules of **1** to molecules of PS in the films (see the Supporting Information). As expected, the roughness decreases as the amount of **1** is increased. A similar trend is found when the corresponding heights of the PS films are plotted against the amount of **1** in the spin-cast solution (see the Supporting Information). The average height of the annealed films decreases as the amount of cross-linker increases, suggesting that the irreversible expansion accompanied by heating a thin film above T_g is attenuated.[6] By adjusting the concentration of compound **1** in the films, the surface topography can be controlled. These trends support the idea that **1** acts as a cross-linker that impedes the movement of the chains, inhibiting the film from redistributing its mass.

Another way to control the surface topography is to adjust the dosage of UV light. Prolonging the irradiation time should result in a higher concentration of cross-links. Figure 4 presents a graph of the average roughness vs the irradiation time for a PS film containing **1**. The observed dependence of surface roughness on irradiation time is in accord with surface modification via photochemical means. We used a rather high concentration (60:1 mol of **1** to PS) to ensure a strong effect on the dewetting characteristics. It is uncertain whether the resulting material can be classified as cross-linked PS. In any case, our intent is to demonstrate the effect of irradiation time on dewetting inhibition regardless of the cause of inhibition. At this particular concentration of **1**, no further decrease in the roughness of the films can be seen after about 30 min of irradiation.

Film thickness has been shown to influence a variety of physical properties in polymer thin films.[30−32] In terms of dewetting, it has been suggested that the mechanism is dependent on the thickness of the film. In one report,[33] for a film of less than 10 nm, spinodal dewetting[34] has been suggested as the mechanism, a process in which height-fluctuating undulations caused by

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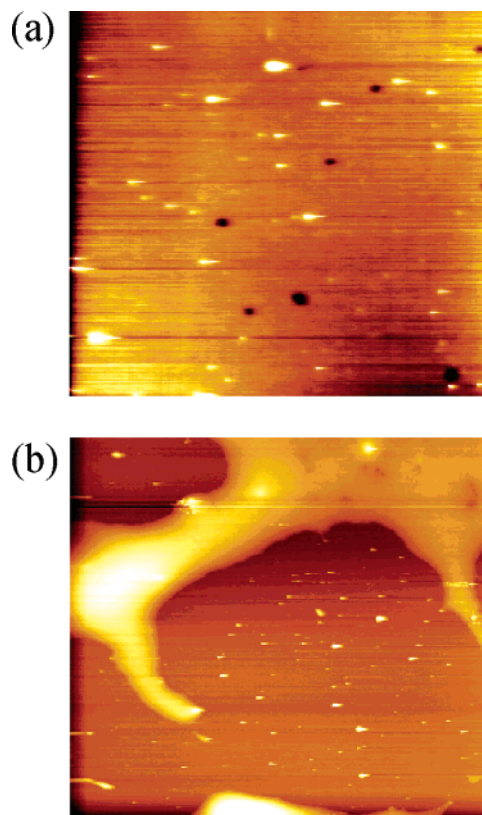(33) Xie, R.; Karim, A.; Douglas, J. F.; Han, C. C.; Weiss, R. A. *Phys. Rev. Lett.* **1998**, *81* (6), 1251−1254.
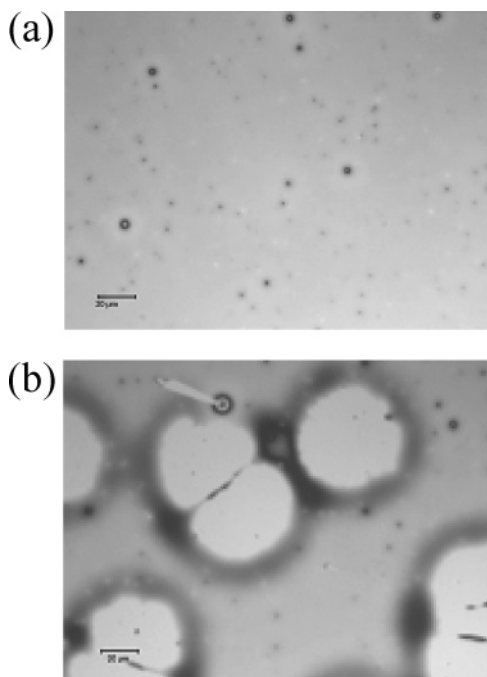
Figure 5. Optical microscope images of 25 nm PS films after annealing overnight at 170° C: (a) irradiated PS film containing a ratio of **1** to PS of 3:1; (b) PS film without **1**.

thermal energy develop on the film. When the size of the undulations reaches the size of the original film, contact points are created where the air, solid, and liquid interfaces all meet, resulting in the rupture of the film by the formation of holes and the initiation of dewetting. When films thicker than 10 nm are used, a nucleation mechanism[33,35] induced by impurities such as air bubbles has been attributed as the mechanism of dewetting. To demonstrate the applicability of our system to films of different thickness and the varying dewetting mechanisms that may result, we spin-coated additional films with thicknesses greater than that of the ultrathin films described above. The thickness values of the films without **1** added are 7 and 25 nm. Figure 5 presents OM images of the 25 nm film after 1 h of irradiation and annealing at 170 °C overnight. The molar ratio of **1** to PS chains is 3:1. The pure PS film shows large holes with a diameter of approximately 40 μm. The dark rings around the holes are rims, some of which have begun to coalesce. Some of the coalescing rims have ruptured, possibly by a drainage process in which the matter collected between two holes is transported to the perimeter to create a larger hole. The irradiated sample containing **1** shows no such features. The spots on the image are most likely dust or microphase separation of **1** and PS after heating. Occurrence of the latter process is supported by the fact that, as the concentration of **1** is increased, the number of spots increases with no traditional dewetting features becoming apparent.

Figure 6 presents AFM images of the 7 nm film after annealing overnight at 170 °C. The pure PS film (Figure 6b) shows coalescing holes that appear to have formed a ribbon. In the irradiated sample, the molar ratio of **1** to PS chains is 17:1. Decreasing the ratio to 8:1 gave similar results. In contrast to the 25 nm film, we found that a ratio of 3:1 is unable to prevent the formation of dewetting morphologies in the 7 nm film as evidenced by OM. Note that for the 2 nm film higher concentrations of **1** were also required. A greater amount of

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Figure 6. 30 × 30 μm AFM images of 7 nm PS films after annealing at 170° C overnight: (a) irradiated PS film containing a ratio of **1** to PS of 17:1; (b) PS film without **1**.

cross-linker is required to stabilize the thinner films because thinner films have a stronger tendency to dewet than thicker ones. In addition, the number of possible cross-links is expected to decrease as the film thickness decreases due to a lower chain density for thinner films. We expect that as the film thickness increases beyond what we tested an increasingly lower concentration of **1** in the film will prevent dewetting.

Exposure of a thin film to a vapor can also lead to dewetting. This is an important limitation to overcome in terms of developing surface acoustic wave devices that use polymer films as sensors for detecting vapors. To determine if **1** can also inhibit dewetting in films that are exposed to solvent vapor, we placed 7 and 25 nm PS films with and without **1** in a flask of saturated toluene vapor at room temperature. The resulting optical microscope images are shown in Figure 7. Figure 7a shows a 7 nm PS film containing **1** after irradiation and exposure to vapor. Figure 7b shows a pure 7 nm PS film after exposure to vapor. Films containing irradiated **1** formed holes but did not reach the stage of droplet formation, whereas films without **1** or unirradiated films containing **1** (data not shown) formed droplets, the final stage of dewetting. For the 25 nm film, the inhibition of dewetting is more pronounced. Figure 7c shows an image of a 25 nm PS film containing **1** after irradiation and exposure to toluene vapor. Figure 7d shows the corresponding pure PS film. Once again, droplet formation is observed in the pure film. Only small imperfections appear in the irradiated film. As the amount of **1** is decreased, the frequency of occurrence of these features decreases, indicating that the features may be microphase-separated domains. The ability of the photocrosslinked film to inhibit film rupture in response to vapor suggests that our method may show potential in stabilizing thin film devices that respond to chemical stimuli.

It is desirable to have a technique for stabilizing a film on a variety of substrates, regardless of the surface energy. As stated
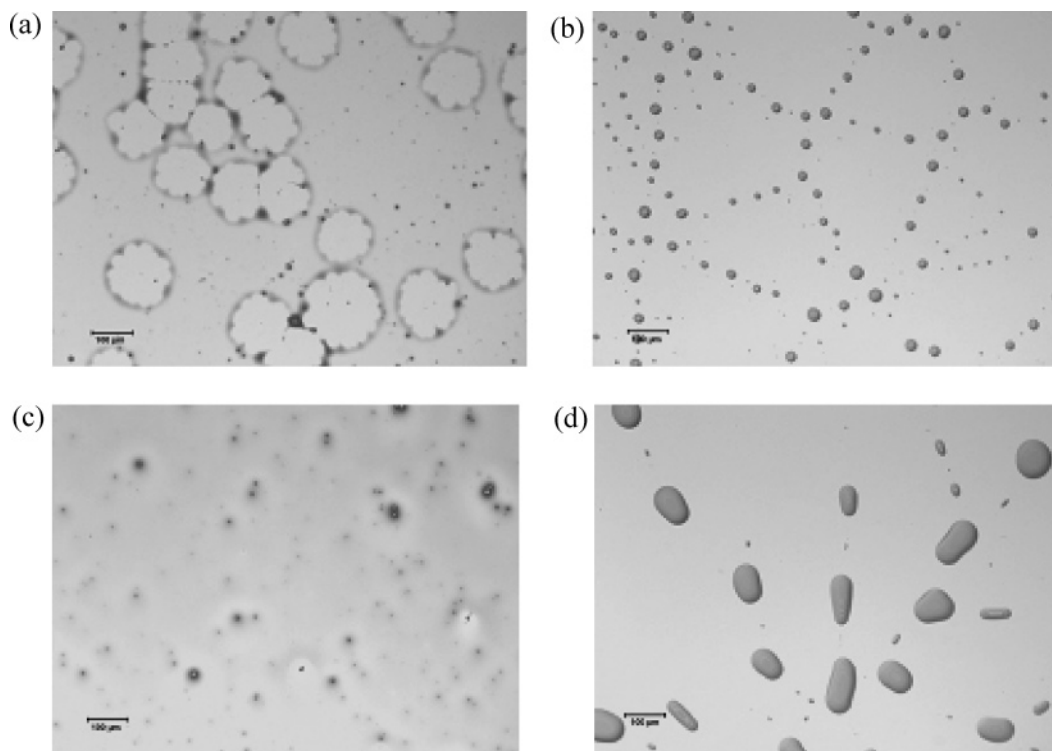
Figure 7. Dewetting induced by exposure of PS films to toluene vapor: (a) irradiated 7 nm PS film containing a ratio of **1** to PS of 18:1; (b) 7 nm PS film without **1**; (c) irradiated 25 nm PS film containing a ratio of **1** to PS of 4:1; (d) 25 nm PS film without **1**.

in the Introduction, the thermodynamic nature of a substrate determines whether a given liquid will dewet a given substrate. The spreading coefficient of PS on a surface can be modified by spinning a thin layer of another polymer on the substrate before applying the PS. To test the ability of our method to stabilize PS films on a surface displaying different physical properties than Si, we prepared films of poly(methyl methacrylate) (PMMA) on silicon. The contact angle of PS on Si has been reported[36] to be 7.5°, whereas the contact angle on PMMA has been reported[19] to be 11.3°. The PMMA layer provides both a change in the wettability of PS on the substrate and a change from a solid−liquid to a liquid−liquid interface. After spin-coating PS films containing varying amounts of **1**, we applied the usual irradiation and annealing procedure. Figure 8 presents optical and atomic force micrographs of PS films on PMMA. For the PMMA surface, inhibition of dewetting is clearly seen in the irradiated sample when a molar ratio of **1** to PS of about 17:1 is used. The average roughness of the un-cross-linked film is 16 ± 3 nm, much higher than the value of 0.90 ± 0.01 nm for the cross-linked film. The average height of the un-cross-linked film is 60 ± 18 nm in comparison with 12 ± 8 nm for the cross-linked film. Higher amounts of **1** relative to the number of polymer molecules were required in order to see a noticeable inhibition of dewetting in comparison with the silicon surface. This is most likely due to a change in wettability; however it is also possible that the cross-linker additive migrates into the underlying PMMA film or causes interfacial cross-linking between PS and PMMA. It should also be noted that the viscous properties of the liquid−liquid interface will influence dewetting.[8] A very small concentration range was found to inhibit dewetting in this sample. This may be due to a driving force for **1** to mix into the PMMA layer or assemble at the polymer−polymer interface at a critical concentration. Further work will be performed to understand how **1** organizes in these films.

(36) Seemann, R.; Herminghaus, S.; Jacobs, K. *J. Phys.: Condens. Matter* **2001**, *13* (21), 4925−4938.

Conclusion

We have shown that a bis-benzophenone derivative, **1**, can be used to photochemically cross-link PS chains. The degree of cross-linking can be controlled by changing the amount of **1** in the films or by adjusting the dosage of UV light. Cross-linking thin films inhibits dewetting induced by various mechanisms and in various environments. Other potential applications of this reaction include photogeneration of gels and grafting polymers to polymer surfaces.

Methods

Synthesis of 1. To a solution of 6.7 g (0.03 mol) of 3-benzoyl-benzoic acid (Aldrich) in 250 mL of methylene chloride and 50 mL of ether in a 500 mL three necked round-bottom flask which was equipped with a reflux condenser and sealed with argon was added 0.4 g (0.003 mol) of 4-pyrrolidinopyridine (Aldrich) and 6.1 g (0.03 mol) of dicyclohexylcarbodiimide (Acros). The solution was stirred for 5 min, and then 0.93 g (0.015 mol) of ethylene glycol was added. The reaction mixture was stirred overnight and then refluxed for 5 h to complete the esterification. After cooling to room temperature, the *N,N*-dicyclohexyl urea byproduct was removed by filtration. The filtrate was washed with water (3 × 100 mL), 5% acetic acid solution (3 × 100 mL), water (2 × 100 mL), and NaCl saturated water (100 mL). The solution was dried with anhydrous Na_2SO_4. After removing the solvent on a rotoevaporator, the product was chromatographed on silica gel with ethyl acetate/hexane (v/v = 1/3). A white powder (6.5 g) was obtained (90% yield) and used without further purification. ^{1}H NMR: ($CDCl_3$) δ 8.44 (s, 2H), 8.25 (d, $J = 8$ Hz, 2 H), 8.01 (d, $J = 8$ Hz, 2H), 7.79 (d, $J = 8$ Hz, 4H), 7.63−7.55 (m, 4H), 7.51−7.43 (m, 4H), 4.69 (s, 4H). LRMS (FAB$^+$): 479.4 m/z (M+H) (experimental) 479.1 (calculated).

Preparation of Films. Polymer films were prepared on Si wafers (Wafer World) by spin-coating toluene solutions containing varying amounts of **1** and PS. Typically, films were spun at 3000 rpm for 1 min. For the PS film on PMMA, PS was dissolved in cyclohexane and directly spin-coated onto a PMMA film. Some groups avoid direct spin-coating of one film on top of another because of potential modification of the interface. For our studies, it was important to
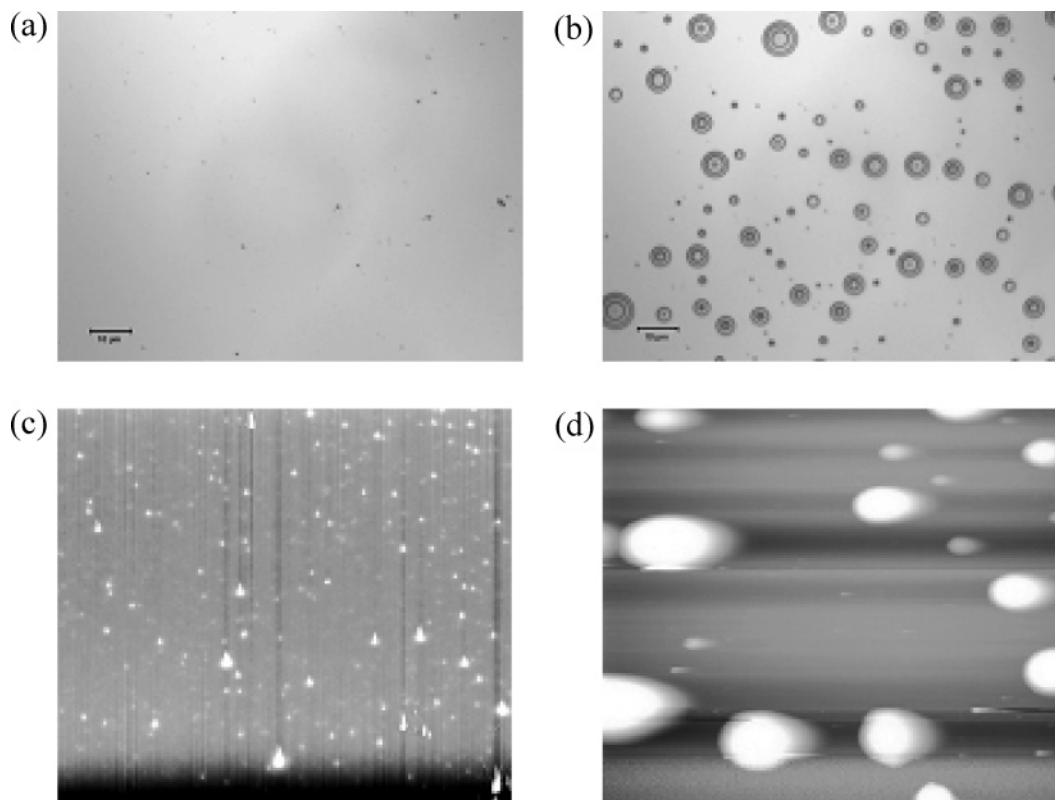
Figure 8. Optical microscope images of PS films on PMMA films after annealing at 170°C overnight: (a) irradiated PS film containing a ratio of **1** to PS of 17:1 (b) PS film without **1**. AFM images: (c) irradiated PS film containing a ratio of **1** to PS of 17:1 and (d) PS film without **1**.

find systems in which dewetting can be easily observed. Direct spinning of one film on top of another provided a convenient method to prepare films that clearly undergo dewetting as shown in a number of previous investigations. Si wafers were cleaned by boiling in "piranha" solution (7:3 sulfuric acid/H_2O_2) for 1 h followed by an extensive rinse with H_2O and methanol. Caution: "Piranha" is a very strong oxidant and reacts violently with many organic materials. Substrates were dried with a stream of argon and placed in a UV/ozone cleaner for 20 min prior to casting the film. For GPC measurements 2.6K PS (Mn measured by GPC) (Polymer Laboratories) was used. For all other experiments, 30K PS (Polymer Laboratories) was used.

Photochemical Cross-Linking of PS Films with 1. Films were placed in sealed glass vials and purged with argon for 10 min. For dewetting studies, films were irradiated for 1 h with a Rayonet Photochemical Reactor equipped with lamps that emit at 350 nm. For GPC studies, films were irradiated for 90 min. Extended irradiation times (>5 h) were found to produce insoluble material that cannot be analyzed by GPC.

Instrumental Measurements. Infrared spectra were obtained with a Thermo Nicolet Nexus 870 FT-IR spectrometer. The sample was prepared by spin-coating a 1 mL toluene solution containing 0.0053 g of 30K PS (Polymer Laboratories) and 0.0084 g of **1** at 750 rpm for 30 s on a KBr disk. Gel permeation chromatography measurements were performed on a Knauer GPC system with a Knauer K-2301 refractive index detector. Three 5 μm particle size columns (one 100 A and two MIXED-D pore types) placed in series were employed for the chromatography. The system was calibrated against linear polystyrene standards ranging in molecular weight from 580 to 377 400 Da. Experiments were performed at room temperature in THF eluant with a flow rate of 1.0 mL/min. Films for GPC studies were prepared by spin-coating concentrated solutions of **1** and PS in toluene at 500 rpm for 50 s on a glass microscope slide. After irradiation, the films were removed from the slide with HPLC grade THF and transferred to GPC vials. Film thicknesses were measured with a Beaglehole ellipsometer in variable angle

mode. A refractive index of 1.5 was used for all samples. Measurements were performed three times in different locations on the surface and averaged.

Dewetting Studies. Dewetting was induced either by heating the films in a vacuum oven at 170° overnight or by hanging the films in a flask saturated with toluene vapor for 30 min. Dewetting morphologies were imaged using AFM and OM. AFM images were obtained with a ThermoProbes Autoscope CP Research System. Surfaces were imaged in noncontact mode. The average roughness and average height values were calculated for at least three random images from each surface and averaged. OM images were obtained with a Nikon Eclipse optical microscope equipped with an INSIGHT digital camera.

Supporting Information Available: Supplementary figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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