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Antifogging surface facilitated by nanoscale coatings with controllable hydrophobicity and cross-linking density[1]

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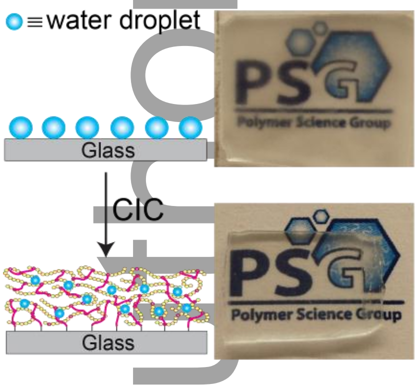
[1] **Supporting Information** is available online from the Wiley Online Library or from the author.

Antifogging and frost-resistant coatings can be used in a wide range of applications and enable high light transmission through substrates even under changes in environmental conditions. In this study, surface confined and cross-linked antifogging thin films are fabricated on glass slides *via* catalyst induced cross-linking (CIC), which has been recently introduced as an easy and efficient cross-linking methodology. Four different PEG-based polymers with different hydrophilicity were synthesized and used to prepare films via CIC. Films prepared from the most hydrophilic PEG-based polymers displayed the best antifogging performances when exposed to a temperature change from -20 to 22 °C. Furthermore, several parameters including, cross-linking density, surface roughness, hydrophobicity and exposure time were also evaluated in terms of film transparency. Through these measurements, it was determined that, more loosely cross-linked films retain antifogging ability for longer time periods due to higher film swellability as compared to, more highly cross-linked films. This study signifies the crucial role of the film cross-linking density and hydrophilicity on the antifogging function.



1. Introduction

The development of optical devices and sensors for use in extreme or rapidly changing environmental conditions has been accompanied by the necessity to develop surface coatings that ensure optimal and consistent optical performance.[1-10] In particular, antifogging surfaces that ensure adequate light transmission under extreme temperature changes are of importance in many applications, including spectacles,[11] goggles,[12, 13] mirrors,[14] windows,[15] analytical and medical devices, and optical sensor arrays. The phenomenon of fogging primarily occurs as a result of a change in environmental conditions such as temperature or humidity; whereby water vapor in the air condenses onto the surface, generating large discrete water droplets that give rise to light scattering.[16] The two most common techniques used to reduce fog generation involve: (i) increasing the surface energy by rendering the surface (super)hydrophilic,[4, 6, 17-24] or; (ii) developing superhydrophobic surfaces with highly ordered surface chemistries. The former enables water droplets to rapidly spread across the surface, reducing light scattering and thereby maintaining visual clarity, whereas superhydrophobic surfaces can induce a low adherence force to water droplets, resulting in water-repellent and self-cleaning abilities. However, both techniques are not without drawbacks. For example, hydrophilic coatings are easy to produce[18-21, 23, 24] but their ability to perform under more aggressive environments (i.e., freezing-fogging induced ice build-up) may be limited. Furthermore, superhydrophilic surface textures with water contact angles smaller than 5° often require relatively complicated procedures to fabricate.[4, 17, 25, 26] Similarly, superhydrophobic coatings with highly ordered surface features are not trivial to produce.[27]

Recently, it has been demonstrated that by judiciously combining hydrophobic and hydrophilic segments in a coating, antifogging characteristics can also be observed.[3, 8, 16] The proposed mechanism was attributed to the rapid absorption of water molecules into the hydrophilic segments of the coating preventing the formation of micro droplets on the surface. Furthermore, it has been suggested that once the water molecules are inside the coating they exist in a non-freezing state due to strong polymer-water hydrogen bonding. Such antifogging coatings have been fabricated by combining perfluoroalkyl groups with poly(ethylene glycol) (PEG) segments[16] or zwitterionic polymers.[3]

Antifogging coatings have been fabricated using a wide range of polymers with varying composition and properties, as well as different techniques, including layer-by-layer (LbL) assembly[3-5, 7, 22, 28] and grafting approaches.[29] Besides film composition, cross-linking of hydrophilic films is also an important feature to prevent the films from over-swelling and enhancing the film adhesion onto the substrate, thus ensuring coating stability. To date, many cross-linking methods have been explored and primarily involve a post cross-linking procedure wherein pre-deposited films (*via* spray, dip, or spin-coating) are exposed to ultraviolet (UV) light,[19, 21, 24] heat,[3, 28, 30] or solutions containing cross-linker[4, 19, 21] to induce film cross-linking. For example, Zhang *et al.* reported a one-pot approach towards the construction of antifogging thin films on the basis of partly cross-linked poly(vinyl alcohol)(PVA) and poly(acrylic acid)(PAA) by thermal cross-linking[30] and 2016, Ming and co-workers reported a novel dual-functional antifogging and antimicrobial polymer coatings, where the coating was UV cured using photoinitiator for 45 min.[31]

Herein, we report the facile synthesis of cross-linked, surface-confined antifogging coatings with high tuneability *via* a recently developed technique referred to as catalyst induced cross-linking (CIC), mediated by ring-opening metathesis polymerization (ROMP).[32] This technique occurs under mild reaction conditions (i.e., at room temperature and in the presence of air) and does not require the use of heat or UV light to induce cross-linking. The CIC approach involves the deposition of pre-functionalized polymers with pendent polymerizable norbornene groups (defined as macrocross-linkers) onto allyl modified-substrates, followed by exposure of the substrate to a solution consisting of Grubbs' catalyst dissolved in diethyl ether (a poor solvent for the polymer film) to induce cross-linking of the polymer film (**Scheme 1**).[32] Film cross-linking proceeds *via* ROMP of the pendent norbornene groups, while the film remains confined to the substrate surface due to the low compatibility between the polymer film and the solvent. Through the selection of appropriate macrocross-linkers (i.e., polymers pre-functionalized with pendent polymerizable groups), the hydrophilic/hydrophobicity ratio of the films can be tailored. Furthermore, the film's cross-linking density and swellability can also be precisely controlled by varying the catalyst concentration and reaction time. Using the CIC approach, a series of highly stable cross-linked anti-fogging films with high swellability and low light scattering can be fabricated.

2. Results and Discussion

The applicability of the CIC approach[32] to generate antifogging coatings were explored and several fabrication parameters were studied using a series of PEG-based macrocross-linkers with pendant norbornene (NB) functionalities that act as both cross-linking points and to impart hydrophobic domains. The polyethylene glycol (PEG)-based macrocross-linker **P1** was synthesized according to the literature,[33] and contained *ca.* 5 mol% NB functionalities as determined by ^{1}H NMR spectroscopic analysis (**Figure 1**). The other PEG-based copolymers **P2**-**P4** containing 9, 20 and 35 mol% pendant NB groups (as determined by ^{1}H NMR spectroscopic analysis) were synthesized *via* radical copolymerization of oligo(ethylene glycol) methacrylate (OEGMA) and a norbornene methacrylate derivative in monomer feed ratios of 90:10, 80:20 and 65:35, respectively. The pendant NB groups of **P1**-**P4** (**Scheme 1**; highlighted in pink) are the hydrophobic groups responsible for cross-linking the thin films *via* ROMP.

The CIC approach mediated by ROMP was used to fabricate cross-linked antifogging films using PEG-based macrocross-linkers, **P1-P4** (**Scheme 1**). Briefly, cleaned glass slides were immersed in a solution of allyl-modified poly(ethylene imine) (allyl-PEI) for 30 min, resulting in a physically absorbed ultrathin allyl-PEI monolayer (thickness ≤ 3 nm as determined by AFM analysis). It should be noted that this allyl-PEI layer acts not only as an adhesive layer, but also, a cross-linking point where the macrocross-linkers can be cross-linked to the surface *via* the norbornene groups. Individually, copolymer **P1**-**P4** solutions (30 mg.mL^{-1} in $CHCl_3$) were spin-coated (2000 rpm, 35 s) onto the allyl-PEI functionalized substrates, and the spin-coated films were subsequently submerged into a solution of 2nd generation Grubbs catalyst (0.5 mg.mL^{-1} in diethyl ether) for 30 min. This allowed for film cross-linking *via* ROMP of the pendant norbornene groups. The substrates were then washed thoroughly with dichloromethane and chloroform to remove any non-cross-linked polymer prior to analysis.

The obtained film thicknesses following cross-linking were determined to be 290 ± 10 nm *via* atomic force microscopy (AFM) scratch analysis (Supporting Information (SI), **Figure S1**). The film thicknesses before and after ROMP-mediated cross-linking were approximately constant, as confirmed by AFM analysis, implying an almost quantitative cross-linking process and hence complete retention of the polymeric materials on the substrate. The surface roughness (as indicated by the root mean square (rms)) of the cross-linked dry films were relatively smooth, ranging from 6.7 nm for **P1** films to 1-2 nm for **P2**-**P4** films (**Figure S2**). The slight differences in surface roughness may be explained from the different arrangements of the deposited films influenced by the different polymer architecture, crystallinity and interaction between functional groups and the solvent.[32]

The antifogging performance of the **P1**-**P4** functionalized substrates and a positive control (unfunctionalized glass slide) were studied by measuring the UV-Vis transmission (λ = 350-750 nm) of the substrates as prepared, and after storage at -20 °C for 1 h followed by exposure to ambient lab conditions (temperature: 22 °C, relative humidity: 20 %). The transmittance of the as prepared substrates (**P1**-**P4** films) and control glass were very similar, with values between 80 to 90 % (**Figure 1a**). This indicates that the cross-linking process did not inhibit light transmittance nor contribute to light scattering. Subsequently, the substrates were cooled to -20 °C for 1 h and the transmittance was re-measured after exposure to ambient conditions for 5 s (**Figure 1b)**. Complimentary photographic images of the coated substrates versus the un-coated glass control was also taken upon re-exposure to ambient conditions. As expected, the control glass with no polymer film was very foggy and displayed a significant decrease in transmittance (20 %, **Figure 1b** and **c**, red trace and control, respectively). This phenomenon is attributed to water droplet condensation on the surface. In comparison, **P1**, **P2** and **P3** coated substrates displayed high transmittance (~ 85-90 %) comparable to the as prepared substrates demonstrating that indeed the PEG based films impart antifogging properties (**Figure 1b** and **a**, respectively). From the photographic images taken upon re-exposure to ambient conditions, **P1** and **P2** (5 and 9 mol% NB groups, respectively) coated substrates maintained superior clarity even after one minute, which is in good agreement with the UV-vis transmittance measurements (**Figure 1c** and **b**, respectively). Initially, the **P3** (20 mol% NB groups) coated substrate was also relatively clear compared to the control glass but, after 0.5 min slight fogging was observed. Together with UV-vis transmission data and these optical observations, it can be seen that the antifogging performance is time dependent, as well as being influenced by the polymer film cross-linking density and hydrophobicity. This notion was further observed with the **P4** (35 mol% NB) coated substrate where the transmittance decreased to ~ 60 % (**Figure 1b**) after re-exposure to ambient conditions. This was also observed from the photographic images (**Figure 1c**). From the results obtained, it can be suggested that either a high cross-linking density or increased hydrophobicity plays an important role in affecting antifogging performance.

To further determine if surface hydrophobicity or cross-linking density plays a more dominant role in antifogging performance, water contact angle measurements of **P1-P4** coated substrates were measured as this provides an indication of surface hydrophobicity. Briefly, 3 µL of water was dropped onto vacuum dried, **P1-P4** coated glass and the corresponding contact angles were measured on a tensiometer. Expectedly, films consisting of lower amounts of NB groups (i.e., 5 (**P1**) and 9 (**P2**) mol% NB, respectively) exhibited the lowest contact angles (*ca.* 19° and 23°, respectively,

Figure 2a) as they are the most hydrophilic. In contrast, the contact angle of the more hydrophobic **P3** and **P4** coated substates were significanly higher (*ca.* 50° and 51°, respectively, **Figure 2a**). It should be noted that although, **P3** and **P4** coated films displayed similar surface hydrophobicities, their antifogging performance was signifcantly different wherein **P3** based films were 20% (**Figure 1b**) more transmitent then **P4** based films after re-exposure to ambient conditions after cooling at -20°C for 1h. This result suggests that the cross-linking density plays a more signficant factor in affecteing antifogging performance than surface hydrophobicity. =. It should be noted that in these types of coatings, the effect of hydrophobicity (i.e., when hydrophobic domains are ≤ 30%) has little effect on antifogging performance.[8] However, when films are ≥ 30% hydrophobic (e.g., perfluoroalkyl films), severe fog production is observed. This is attributed to the water droplets coalescing resulting in light scattering.[8] This same trend was observed in these experiments where **P4** based films (35 mol% NB) exhibited *ca.* 30% reduction in transmission after 5 s at ambient conditions after being stored at -20°C for 1 h (**Figure 1b**).

Aside from characterizing the antifogging performance of the coated films when going from freezing to ambient conditions, the **P2** coated substrate and the glass control were exposed to a humid atmosphere chamber (temperature: 35 °C, relative humidity: 85 %) for 5 min and photographed from different angles to explore their antifogging properties (**Figure S3a** and **b**, respectively). Whereas the **P2** coated substrate displayed good clarity, there was a significant build-up of water droplets on the control glass. These results highlight the ability of the **P2** polymer film to mitigate the formation of water droplets that cause light diffusion and scattering even in humid atmospheres, demonstrating the versatility of these antifogging films for application in various environments.

From the UV-vis transmittance measurements and visual observations, it is evident that the antifogging performance of the **P1**-**P4** films correlates with the NB content (hydrophobic content) in the polymers. Higher percentages of NB groups (**P3** and **P4**, 20 and 35 mol% NB, respectively) were shown to display significantly reduced antifogging function when compared to substrates coated with lower percentages of NB groups (**P1** and **P2**, 5 and 9 mol% NB, respectively). Thus, it can be suggested that increased hydrophobicity restricts the uniform dispersion of water leading to the formation of water droplets on the surface of the films which consequently lead to light diffusion and scattering. In contrast, hydrophilic polymer films such as **P1** and **P2** with less hydrophobicity (5 and 9 mol% NB groups, respectively) allow the water to be uniformly dispersed across the surface. The results indicate that the hydrophilic PEG content needs to be high enough to ensure that water molecules disperse uniformly throughout the polymer film. Nevertheless, to generate robust surface coatings a certain degree of cross-linking is required to prevent film detachment from the surface, over-swollen, and fragile.[8] From these results using the CIC approach the minimum required amount of cross-linkable pendant NB group is 5 mol%. Materials for antifogging function need to be as highly hydrophilic as possible while certain hydrophobicity is required for film stability and cross-linking process.

It is noteworthy that the polymers containing more NB content will result in more highly cross-linking films with lower swellability. The swellability of the films also has a major influence on antifogging performance as this correlates to how much water can be absorbed from the surface into the films. It is expected that the **P1**-**P4** based films would exhibit different cross-linking densities; where films fabricated with lower amounts of NB (**P1** and **P2**, 5 and 9 mol%, respectively) would be less cross-linked and hence more swellable than those fabricated with higher amounts of

NB (**P3** and **P4**, 20 and 35 mol%, respectively). The swellability of **P3** based films was subject to earlier work where the cross-linking time and catalyst concentration were shown to affect the overall film swellability in water. Expectedly, increasing the cross-linking time from 3 min to 30 min significantly decreased the film swellability by *ca.* 84-95%.[31] Additionally, by increasing the catalyst concentration the film cross-linking density could also be increased. With these results, it is expected that **P3** based films would swell more than **P4** based films since **P4** has a higher mol% of NB groups.[31] In terms of antifogging performance, the higher swellability of the **P3** films would allow for a greater absorption of water droplets into the film and thus, superior antifogging performance than **P4** based coatings. This idea was further suggested in the UV-vis transmission results where indeed **P3** based films observed greater transparency than **P4** based coatings (**Figure 1b** and **c**). When comparing the performance of **P3** coatings versus **P1** and **P2** based coatings, the **P3** coatings were inferior to **P1** and **P2**.

The surface roughness of the as-prepared cross-linked **P1**-**P4** based films *via* CIC was determined by measuring their respective root mean square (RMS) values *via* AFM analysis. In general, all of these films were relatively smooth with the RMS values of < 2 nm except, **P1** based films (RMS = 6.7 nm) **(Figure S2)**. Thus, although **P2**-**P4** films display similar surface roughness their antifogging properties were significantly different with **P2** films observing superior antifogging properties when compared to **P3** and **P4** based films. This performance is suggestively attributed to the low crosslinking density and increased hydrophilicity of **P2** films when compared to **P3** and **P4** films. Previously, we reported that the surface roughness and cross-linking density of the films can be altered by varying catalyst concentration using the CIC approach.[31] These studies revealed increasing the cross-linking time and catalyst concentration increased the cross-linking density while, an increase in cross-linking time and a decrease in catalyst concentration increased the overall surface roughness of the films.[31]

Thus, to further investigate the effect of surface roughness on antifogging performance four different **P2** films with varying cross-linking densities were prepared (**A-D**). The least cross-linked film **A** was fabricated by immersing **P2** spin-coated film in catalyst solution (0.5 mg.mL^{-1} in diethyl ether) for 3 min. While films **B**, **C** and **D**, were produced by the submersion of **P2** spin-coated films in different catalyst concentrations (0.05, 0.25, 0.5 mg.mL^{-1} in diethyl ether, for **B**, **C** and **D**, respectively) for 30 min. Once fabricated, the cross-linked films were fully swollen in water and AFM analysis was conducted to measure their respective RMS values and surface topologies (**Figure 3c** and **d**, respectively). An increase in surface roughness of the swollen films could be observed upon increasing the cross-linking time (i.e., from 3 min to 30 min), however increasing the catalyst concentration had no substantial effect on RMS values (**Figure 3c**). Furthermore, based on previous work the cross-linking density of four **P2** films was expected to follow the order **A** < **B** < **C** < **D**. The polymer coated films **A**-**D** and control glass **E** were stored at -20 °C for 1 h before being exposed to ambient conditions (22 °C, 20 %). The antifogging performance of these films was monitored visually over 5 min. Immediately after exposure (5 s) to ambient conditions all of the polymer films **A**-**D** showed good antifogging performance (**Figure 3a**). However, after 2 min at ambient conditions, the most densely cross-linked film **D,** started to become foggy whereas films **A**-**C** maintained good clarity (**Figure 3b**). After 3.5 min, the second most densely cross-linked film **C** became lightly foggy, while the more loosely cross-linked films **A** and **B** still maintained good antifogging performance. These results support the hypothesis that the cross-linking density (i.e., swellability) of the film contribute significantly towards antifogging performance, while, the surface roughness does not seem to have any any significant correlation with antifogging performance. As a result of a higher cross-linking density, film **D** was only able to swell slightly with water vapor, and once saturated, larger water droplets formed on the surface leading to light diffusion and scattering. The slightly lower cross-linking density of film **C** prolonged the formation of water droplets to 3.5 min, whereas films **A** and **B** with the lowest cross-linking density were able to mitigate fogging of the surface completely. As expected, the control glass **E** presented the worst clarity for the entire 5 min time frame of the experiment. Therefore, the expected time for sustaining antifogging function of the films based on cross-linking density (**A** < **B** < **C** < **D**) agrees well with the results obtained (**A** ≈ **B** > **C** > **D**). This experiment demonstrates that the cross-linking density and swellability of the film plays a major role in the antifogging performance, independent of the film hydrophobicity, although for many systems these factors are likely to be interrelated.

3. Conclusions

In conclusion, we have successfully applied the CIC approach to prepare cross-linked PEG-based antifogging films on glass substrates with various hydrophilicities and cross-linking densities. The technique used in this study is facile, rapid, effective, and occurs under mild conditions. Several polymers with different hydrophilicities were used to assess antifogging performance. The most hydrophilic polymer films with water contact angles of ~ 20 ° displayed the best antifogging function, as evidenced from high UV-vis transmittance measurements and visually when the substrates were exposed to abrupt temperature changes (-20 °C to 22 °C). Furthermore, films prepared from the same polymer (constant hydrophobicity) but with different cross-linking densities were used to independently investigate the effect of film cross-linking on antifogging performance. The most densely cross-linked films resulted in the shortest antifogging performance, while the loosely cross-linked films remained fog free. From these results it was concluded that a balance of hydrophilicity and cross-linking density (swellability) plays a crucial role in antifogging performance, whereby antifogging films needs to have enough water vapor absorption and swelling, whilst still being cross-linked enough to maintain film stability.

4. Experimental Section

Film assembly via CIC

A glass slide (~ 2 × 2 cm) was added to a 28 mL vial containing 2 mL of allyl-PEI solution (1 mg·mL^{-1} in 0.5 M NaCl, passed through a 0.45 µm filter). The glass slide was allowed to stand for 1 h at room temperature, removed and washed with water (1 × 20 mL), THF (2 × 20 mL) and DCM (3 × 20 mL). The obtained allylated glass substrate was then ready for the next step of the process.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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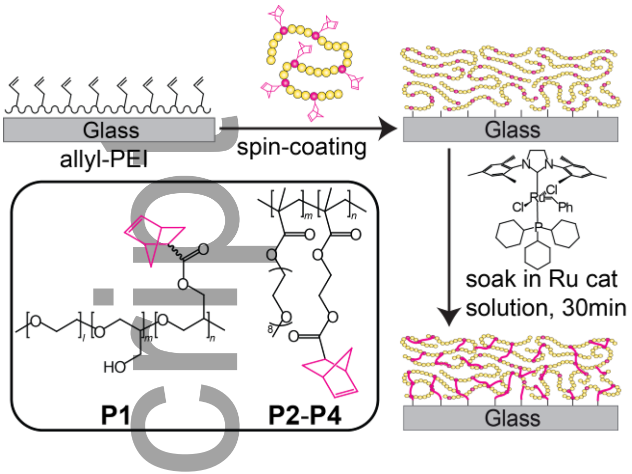

Scheme 1. Schematic of the CIC process for manufacturing antifogging films with structure of macrocross-linkers **P1** PEO-*g*-NB with 5 mol% NB groups, and **P2**-**P4** POEGMA-*g*-NB with 9, 20 and 35 mol% NB groups, respectively.

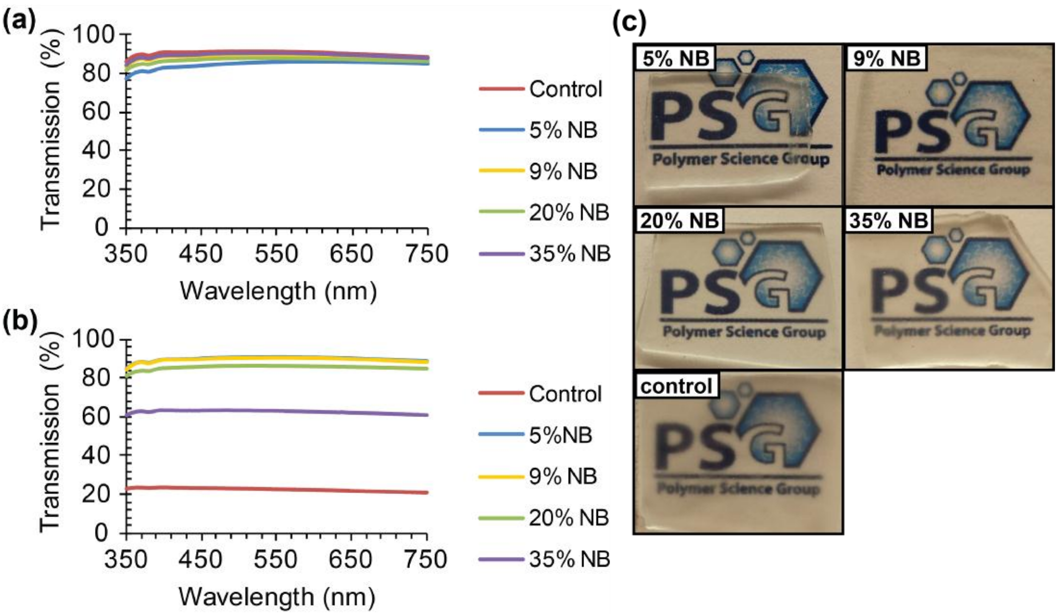

Figure 1(a). as-prepared and (b) after 5 s at ambient conditions after being stored at -20°C for 1 h light transmittance at normal incident angle for the control glass slide and **P1**-**P4.** (c) Photographic images of the glass control and **P1**-**P4** coated substrates upon re-exposure after being stored at -20°C for 1 h.

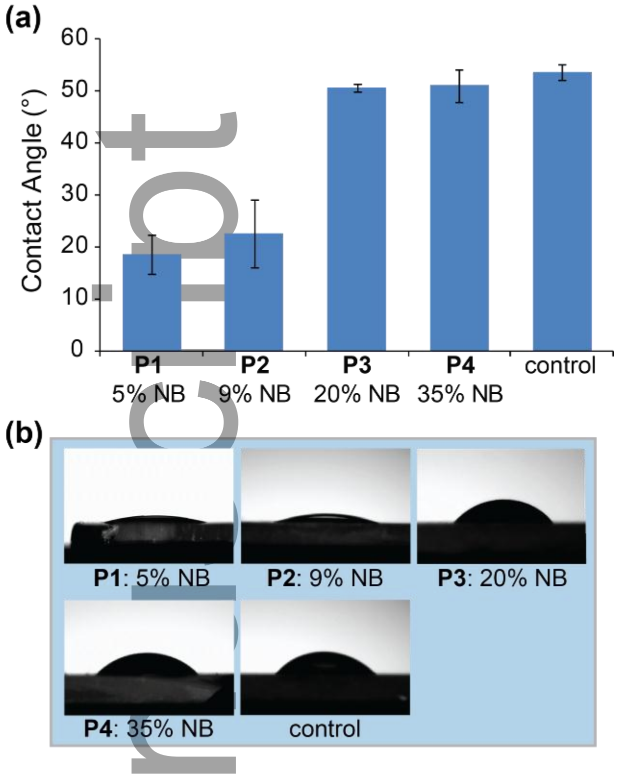

Figure 2. (a) Contact angle and (b) photographs of water droplets on **P1**-**P4** coated substrates and the control glass.

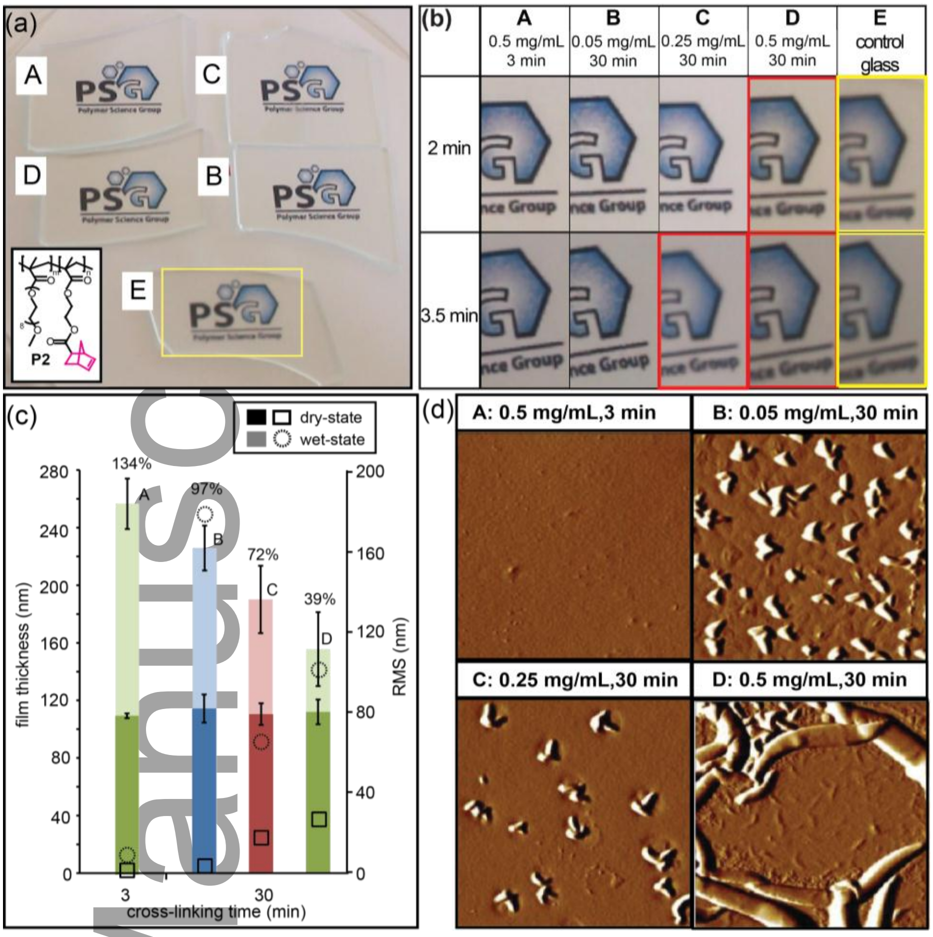

Figure 3. (a) Photograph of coated glass slides (**A**-**D**) and uncoated control (**E**) immediately after exposure (5 s) to ambient conditions from being stored at -20 °C for 1h; film **A** (prepared using a catalyst concentration of 0.5 mg.mL^{-1} and reaction time of 3 min), film **B** (0.05 mg.mL^{-1}, 30 min), film **C** (0.25 mg.mL^{-1}, 30 min), film **D** (0.5 mg.mL^{-1}, 30 min), film **E** (control glass). (b) Magnified images of coated glass slides (**A**-**D**) and control (**E**) after 2 min (top) and 3.5 min (bottom) exposure to ambient conditions from being stored at -20 °C for 1h. (c) Film thickness and Surface roughness values of the films (**A**-**D**) in dry and wet states, as determined by AFM analysis. (d) 20 × 20 µm AFM amplitude retrace images of swollen **P2** films (**A**-**D**) in water for 21 h. Note (c) and (d) is adapted from Ref. [32]

Surface confined and cross-linked poly(ethylene glycol) (PEG)-based films with great antifogging function are fabricated *via* catalyst induced cross-linking (CIC), which is an efficient methodology to produce films with controllable properties including thickness, cross-linking density and swellability. Using the produced films under changes in environmental conditions, the crucial role of film cross-linking density and hydrophilicity on the antifogging function was demonstrated.

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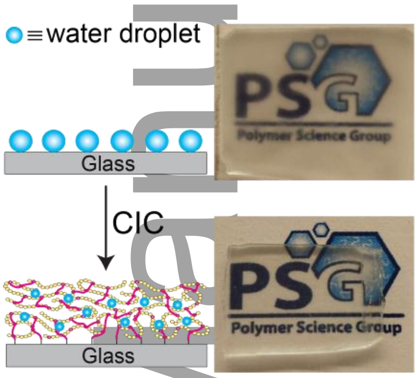
Antifogging surface facilitated by nanoscale coatings with controllable hydrophobicity and cross-linking density



Supporting Information

for *Macromol. Mater. Eng.*, DOI: 10.1002/mame.2016#####

Antifogging surface facilitated by nanoscale coatings with controllable hydrophobicity and cross-linking density

Eunhyung Nam, Edgar H. H. Wong, Shereen Tan, Qiang Fu, Anton Blencowe, Greg G. Qiao*

Materials

Azobis(2-methyl-propionitrile) (AIBN) was purchased from Acros Organics. Allyl bromide (99%), calcium hydride (CaH_2), diethyl ether (DEE, anhydrous), 1,4-dioxane (≥ 99%), 2-hydroxyethyl methacrylate (97%), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (EDCI, ≥ 98%), 4-(dimethylamino)pyridine (DMAP, ≥ 99%), ethyl vinyl ether (EVE, 99%), Grubbs catalyst (2nd generation), 5-norbornene-2-carboxylic acid (mixture of *endo* and *exo*, 98%) and poly(ethylene imine) (PEI) (M_w ~ 25 kDa) were obtained from Aldrich and used without further purification. Oligo(ethylene glycol) methyl ether methacrylate (M_n ~ 500 Da) was obtained from Aldrich and passed through basic alumina prior to use. Alumina (basic), ethanol, isopropanol, magnesium sulfate ($MgSO_4$, anhydrous), *n*-hexane and toluene were obtained from Merck and used directly. Diethyl ether (DEE), *N*,*N*-dimethylformamide (DMF), chloroform ($CHCl_3$), sodium bicarbonate ($NaHCO_3$) and sodium hydroxide (NaOH) were obtained from Chem-Supply and used directly. Anhydrous, deoxygenated dichloromethane (DCM) and tetrahydrofuran (THF) were obtained by distillation under argon from CaH_2 and sodium benzophenone ketyl, respectively. Deuterated chloroform ($CDCl_3$) was obtained from Cambridge Isotope Laboratories. High-purity water with a resistivity greater than 18 MΩ·cm was obtained from an in-line Millipore RiOs/Origin water purification system.

Characterization methods

Polymer molecular weight characterization was carried out via gel permeation chromatography (GPC) using DMF as the mobile phase on a Shimadzu liquid chromatography system equipped with a PostNova PN3621 MALS detector (λ = 532 nm), Shimadzu RID-10 refractometer (λ = 633 nm) and Shimadzu SPD-20A UV-Vis detector, using three Phenomenex Phenogel columns in series (500, 10^4 and 10^6 Å porosity, 5 µm-diameter bead size) operating at 75 °C. DMF with 0.05 $mol\cdot L^{-1}$ LiBr (> 99%, Aldrich) was employed as the mobile phase at a flow rate of 1 $mL\cdot min^{-1}$. NovaMALS software (PostNova Analytics) was used to determine the molecular weight characteristics using calculated d*n*/d*c* values.

^{1}H nuclear magnetic resonance (NMR) spectroscopy was conducted on a Varian Unity 400 MHz spectrometer at 400 MHz using deuterated solvent ($CDCl_3$) as reference and at a sample concentration of ~ 20 $mg\cdot mL^{-1}$.

Atomic force microscopy (AFM) images of air-dried films on glass slides were acquired with an MFP-3D Asylum Research instrument. Typical scans were conducted in AC mode with ultrasharp SiN gold-coated cantilevers (MikroMasch, Bulgaria). Image processing and surface roughness analysis were performed using the Nanoscope and Igor Pro software programs, respectively. Film thicknesses were estimated by film scratching (mechanical removal) and by tracing a profile along the film and the scratched zone. The thickness measurements reported represent mean values over 3 different analysis sites per substrate.

Transmittance measurements between 350 and 750 nm were recorded using a Shimadzu UV-Vis Scanning Spectrophotometer (UV-2010 PC).

Water contact angle measurements were recorded with a Data Physics OCA 20 Tensiometer. Measurements were recorded with OCA software, using a sessile drop profile. Water droplets of 3 µL were dropped carefully onto the sample surfaces.

Experimental Methods

1. Monomer and polymer preparation

*1.1 Synthesis of **P1***

The synthesis of norbornene functionalised P(EO-*co*-Gly) was adapted from the literature,[1] and involved three steps: (i) the copolymerization of ethylene oxide (EO) and 2,3-epoxypropyl-1-ethoxyethyl ether protected glycidol (EEGE) to prepare the copolymer P(EO-*co*-EEGE); (ii) hydrolysis of the copolymer to form poly(ethylene oxide-*co*-glycidol) (P(EO-*co*-Gly)) and (iii) the partial esterification of P(EO-*co*-Gly) with norbornene carboxylic acid.

1.1.1 Synthesis of copolymer P(EO-co-EEGE)

Copolymerization was conducted according to the literature under the help of A. Prof. Wang (Fudan University, China).[1] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H 1.20-1.15 (*m*, 3H, $\mathrm{C}\mathit{H_3}\mathrm{CH_2O}$), 1.30-1.22 (*m*, 3H, $\mathrm{O(C}\mathit{H_3}\mathrm{)CHO}$), 3.79-3.41 (*m*, 4H, $\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H_2}\mathrm{O}$), 4.74-4.62 (*s*, 1H, $\mathrm{O(CH_3)C}\mathbf{H}\mathrm{O}$-) ppm; GPC-MALLS (DMF): M_n = 22.7 kDa, M_w/M_n = 1.08.

1.1.2 Synthesis of copolymer poly(ethylene oxide-co-glycidol) [P(EO-co-Gly)]

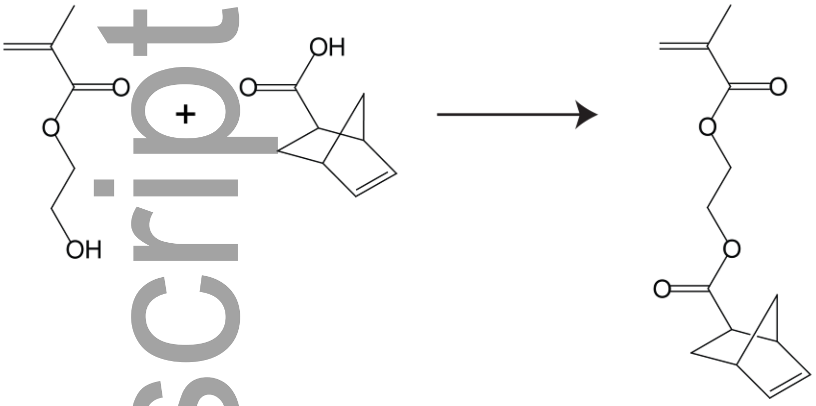
Deprotection of P(EO-*co*-EEGE) was conducted according to the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H 3.79-3.41 (*m*, 4H, $\mathrm{C}\mathbf{H_2}\mathrm{C}\mathbf{H_2}\mathrm{O}$) ppm; GPC-MALLS (DMF): M_n = 21.1 kDa, M_w/M_n = 1.10.

*1.1.3 Synthesis of copolymer P(EO-co-NB) **P1***

P(EO-*co*-Gly) (500 mg, 0.03 mmol, 1 equiv.), norbornene-2-carboxylic acid (69.1 mg, 0.5 mmol, 20 equiv.), EDCI (95.9 mg, 0.5 mmol, 20 equiv.) and DMAP (6.11 mg, 0.05 mmol, 2 equiv.) were dissolved in DCM (10 mL) and stirred at 30 °C for 18 h. The crude reaction mixture was then concentrated *in vacuo* (1 mbar, 30 °C), redissolved in MeOH (2 mL) and dialyzed (MWCO = 3500 $g\cdot mol^{-1}$) against H_2O and subsequently methanol for 2 days. The solution was then concentrated *in vacuo* (1 mbar, 50 °C), and the residue was re-dissolved into DCM (2 mL) and precipitated into DEE (20 mL). The product was collected by centrifugation and dried *in vacuo* (1 mbar, 30 °C) to afford **P1** as a white powder, 307 mg (62 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H 1.54-1.26 (*m*, 4H, $\mathrm{C}\mathbf{H_2}\mathrm{CHC}\mathbf{H_2}$), 3.04-2.89 (*m*, 3H,$\mathrm{C}\mathbf{H}\mathrm{C}\mathbf{H}\mathrm{CH_2C}\mathbf{H}$), 4.32-3.94 (*m*, 2H, $\mathrm{OC}\mathbf{H_2}\mathrm{CH}$), 6.19-5.91 (*m*, 2H, $\mathrm{C}\mathbf{H}\mathrm{=C}\mathbf{H}$) ppm; GPC-MALLS (DMF): M_n = 20.6 kDa, M_w/M_n = 1.81.

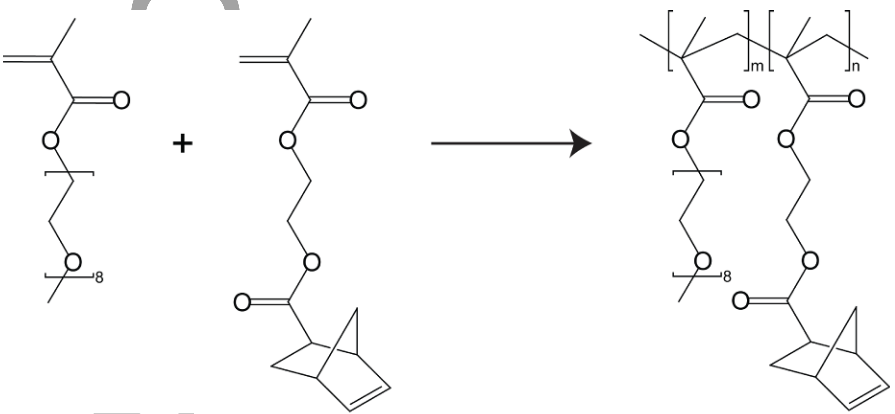
1.2 Synthesis of ***P2-P4***

1.2.1 Synthesis of 2-(methacryloyloxy)ethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate



To a solution of 2-hydroxyethyl methacrylate (1.30 g, 10.0 mmol) and 5-norbornene-2-carboxylic acid (1.45 g, 10.5 mmol) dissolved in anhydrous DCM (50 mL), was added EDCI (2.30 g, 12.0 mmol) and DMAP (146 mg, 1.2 mmol). The reaction mixture was stirred at 25 °C for 4 h, followed by sequential washing with saturated $NaHCO_3$ (2 x 30 mL), 0.5 M HCl solution (2 x 30 mL), brine (30 mL), and water (30 mL). The organic phase was then dried over $MgSO_4$ and concentrated *in vacuo* to afford the monomer as a light yellow oil, 2.22 g (81 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H 6.15-6.05 & 5.86-5.83 (*m*, 2H, C**H**=C**H**), 6.08 & 5.55 (*s*, 2H, C$\mathbf{H_2}$=CCH_3), 4.34-4.16 (*m*, 4H, C$\mathbf{H_2}$OC(=O)), 3.15 (*s*, 1H, C**H**), 2.90 (*m*, 1H, C**H**), 2.85 (*m*, 1H, C**H**), 2.21-2.17 & 1.86-1.82 (*m*, 1H, C**H**H), 1.90 (*s*, 3H, C$\mathbf{H_3}$), 1.46-1.44 & 1.38-1.34 (*m*, 1H, C**H**H), 1.36-1.34 (*m*, 1H, C**H**H), 1.31-1.29 & 1.23-1.21 (*m*, 1H, C**H**H) ppm.

1.2.2 Synthesis of ***P2-P4***



A solution of oligo(ethylene glycol) methyl ether methacrylate (0.576 g, 1.2 mmol), 2-(methacryloyloxy)ethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (0.075 g, 0.3 mmol) and AIBN (0.005

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g, 0.03 mmol) in 1,4-dioxane (4 mL) was degassed with nitrogen for 20 min at room temperature and the reaction mixture was heated to 100 °C for 2 h under nitrogen. The reaction mixture was cooled to room temperature, and precipitated into DEE:hexane (7:2) solution (45 mL). The precipitate was isolated by centrifugation, re-dissolved in THF (3 mL), then re-precipitated into DEE:hexane (7:2) solution (45 mL). The precipitate was isolated by centrifugation, and dried *in vacuo* (20 mbar, 25 °C) for 24 h to yield [POEGA-*co*-NB] **P3** as a white viscous liquid; GPC-RI (THF): M_n = 31.6 kDa, M_w/M_n = 1.8; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H 6.19-6.14 & 5.91 (*m*, 2H, C**H**=C**H**), 4.20-4.00 (*m*, 2H, C**H₂**OC(=O), ester groups), 3.63 (*m*, 4H, C**H₂**C**H₂**O, ethylene glycol groups), 3.05-2.90 (*m*, 3H, C**H** + C**H** + C**H**), 2.22 (*m*, 1H, C**H**H), 2.13 (*m*, 3H, C**H₃**), 1.92-1.76 (*m*, 1H, C**H**HCH₃), 1.51-1.29 (*m*, 3H, C**H**H + C**H**H + C**H**H), 1.10-0.70 (*m*, 1H, C**H**HCH₃) ppm. **P2** and **P4** were synthesized by varying the monomer feed ratio between oligo(ethylene glycol) methyl ether methacrylate and 2-(methacryloyloxy)ethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (91:9 and 65:35, respectively). Pendant norbornene functionality of **P2**, **P3** and **P4** was 9, 20 and 35 %, respectively, as determined by ^{1}H NMR spectroscopic analysis.

2. Planar template preparation

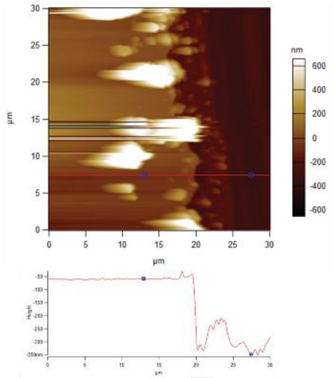
2.1 Allyl functionalization of glass slide by deposition of allyl-PEI

A glass slide (~ 2 × 2 cm) was added to a 28 mL vial containing 2 mL of allyl-PEI solution (1 mg·mL^{-1} in 0.5 M NaCl, passed through a 0.45 µm filter). The glass slide was allowed to stand for 1 h at room temperature, removed and washed with water (1 × 20 mL), THF (2 × 20 mL) and DCM (3 × 20 mL). The obtained allylated glass substrate was then ready for the next step of the process.

2.2. Film assembly via CIC

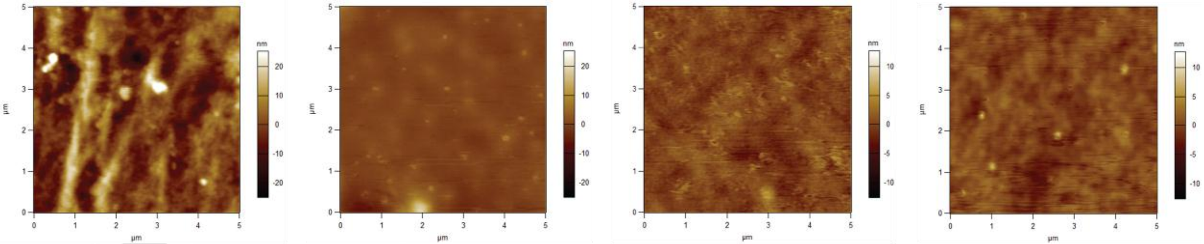
As a general example, the allyl functionalised glass slide (from method 2.1) was spin-coated with **P1** in $CHCl_3$ (200 µL, 30 mg·mL^{-1}, 2000 rpm, 35 s), then immersed in Ru catalyst solution (0.5 mg·mL^{-1} in dry diethyl ether) for 30 min. The glass slide was then washed with and soaked in DCM for 12 h to remove any non-cross-linked polymers, and dried *in vacuo* prior to analysis.

4. Supporting Figures



thickness: 290nm

Figure S1. The z-profile of the scratched zone (20 × 20 µm) of **P1** cross-linked films with different film thicknesses as determined by AFM analysis.



P1: 5 mol%
RMS: 6.74 nm

P2: 9 mol%
RMS: 1.68 nm

P3: 20 mol%
RMS: 1.15nm

P4: 35 mol%
RMS: 1.28 nm

Figure S2. Images (5 × 5 µm) of **P1**, **P2**, **P3** and **P4** cross-linked films as determined by AFM analysis.

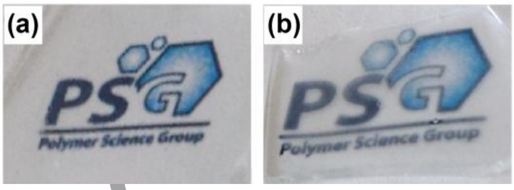


Figure S3. Photos of (f) **P2** and (g) the control glass exposed to a humid atmosphere (temperature: 35 °C, relative humidity: 85 %).

References

[1] P. Li, Z. Li, J. Huang, *Macromolecules* **2007**, *40*, 491.