Electric Field-Induced Nano-Scale Surface Patterning in Mexylaminotriazine-Functionalized Molecular Glass Derivatives

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ABSTRACT: Nano-scale surface patterns were observed in thin films of mexylaminotriazine-functionalized glasses containing polar groups upon the application of an electric field at temperatures over their glass transition temperatures (T_g). This phenomenon occurred due to the surface deformation process initiated by external electric field instabilities on the films. The minimal surface deformation temperature (T_{dewet}) relative to T_g was found to increase as a function of the polarity of the substituents and the surface pattern roughness was observed to increase linearly with temperature for a fixed electric field and exposure time. Reversal of the electrical field polarity and the use of both hydrophilic and hydrophobic substrates didn't significantly change the surface deformation behavior of the films, which is due to the deposition of charges at the free interface. The application of a mask between the electric field electrodes allowed to selectively pattern areas that are exposed. Furthermore, it was observed that this surface deformation behavior was reversible, since heating the films to a temperature above T_g in the absence of an electric field caused the erasure of all surface patterns.

Introduction

For applications involving the use of thin films, it is crucial to achieve control over the morphology of those films, as the organization within the film at the molecular level directly impacts several of its macroscopic properties. The presence of nano-scale surface patterns on thin films can dramatically alter their properties, including surface area, surface tension, permeability, adhesion and optical response. The patterning of thin films at the nano-scale is useful in a number of applications ranging from enhanced absorption in solar cells^{1,2} and Raman spectroscopy³ to bionanotechnology⁴.

Many techniques exist for the nano-scale surface patterning of thin films. Some of these techniques involve post-deposition processing, such as photolithography, focused ion beam engraving⁵ and nanoimprint lithography⁶, while in other methods, surface patterns can form spontaneously as a result of dewetting-related phenomena^{7,8}, which are caused by instabilities at the free surface or at the film-substrate interface

caused by Van der Waals interactions, or due to phase segregation of different components (e.g. in the spinodal dewetting of block copolymers^{9,10}). Dewetting can occur directly during film deposition in some systems^{11,12}. In other cases, dewetting can be induced by instabilities exerted on the film, including mechanical¹³, thermal^{14,15}, selective e-beam exposure¹⁶, electrohydrodynamic force¹⁷⁻¹⁹ or external electric fields. In particular, applying electric fields to cause surface patterning is appealing because the size of the surface features can be controlled by the strength of the electric field. This phenomenon has been previously studied through simulations^{20,21}, and it has been experimentally accomplished on viscous and elastic thin film bilayers²², PMMA-Polystyrene bilayers²³⁻²⁵ and trilayers²⁶, as well as on thin films of polyaniline conducting polymers²⁷. While this behavior has been reported for single polymers, the large majority of reports on electric field-induced surface deformation are on polymer materials in multilayer configurations. Moreover, no instances of electric field-induced surface deformation on

small molecules, thereafter also referenced to as dewetting for simplicity purposes, have been reported so far.

Azobenzene chromophores are known both for their photomechanical²⁸ and non-linear optical properties²⁹. Materials incorporating azo moieties can undergo various light-induced deformations, the most common being the formation of surface relief gratings (SRG) by interfering laser beams. On the other hand, in the processing of these materials for non-linear optical applications, the molecules are typically oriented using a corona poling process involving an electric field. However, various groups have reported that under certain poling conditions, a degradation of the optical quality of the film occurs, though the underlying molecular phenomenon behind this macroscopic alteration has not yet been probed in depth, and was dismissed as undesirable³⁰⁻³². As these processing conditions are similar to the ones used for the electric field-induced dewetting of polymers, it is likely that surface deformation of nonlinear optical chromophores, including azobenzene derivatives, could occur during this process under appropriate conditions, and be responsible for the loss of optical quality observed. If this is the case, this phenomenon, while initially dismissed as parasitic, would provide a tool that allows for the formation of surface patterns in selected areas with shapes of various sizes and of various degrees of regularity. These randomly formed nanostructures would complement the formation of SRG, in which the grooves are typically homogeneous in size, direction and periodicity.

Azo chromophores have been mostly incorporated in polymers, such as PMMA, but they also could be incorporated in small molecules that can be processed into amorphous films. Those materials are called molecular glasses, and can readily form glassy phases, while benefitting from the advantages associated with small molecules, such as easy purification, characterization and processing, and a more reproducible behavior as a result of their monodisperse nature. While several groups have reported molecular glasses containing azobenzene moieties, our group introduced a family of molecular glasses based on a mexylaminotriazine core to which other compounds can be bonded in a covalent fashion, including various azo chromophores^{33,34}. These procedures are simple and high-yielding, and the resulting adducts form glasses that are very stable towards crystallization and form high-quality thin films. Furthermore, films of some of these mexylaminotriazine derivatives have been demonstrated to exhibit surface patterning upon deposition by spin-coating and dewetting upon heating, making them ideal candidates for dewetting under external triggers³⁵.

In the present work, the macroscopic alterations occurring during the electric field corona poling of thin films of mexylaminotriazine

molecular glasses bearing various polar functional groups, including a series of six closely related azobenzene chromophores for comparison purposes, was studied. It was found that these materials exhibit surface deformation, behavior upon the application of an electric field above their glass transition temperatures (T_g), which is not limited to the presence of an azobenzene group. Similar behavior was also observed in PMMA functionalized with azo chromophore Disperse Red 1 (DR1-PMMA). The dewetting temperature was found to be slightly above T_g in most cases, and to increase in the presence of additional groups that can participate in hydrogen bonding, or with azothiazole chromophores that exhibit slow cis-trans isomerisation due to their high polarity. Though it is unclear what is the exact contribution of these effects, it is believed that both lead to a decreased molecular mobility in the material. This dewetting behavior is independent on the direction of the electric field, and the substrate was not found to play a major role in this process, as both hydrophilic and hydrophobic substrates yielded similar results, with only minor differences in dewetting temperatures. The rate of growth of surface patterns was correlated with the strength of the electric field, temperature, and time, and the surface patterns disappeared upon heating in the absence of an electric field, thereby allowing for reversible patterning.

Herein, not only did the source of the optical damage occurring in thin films of azo materials during electric-field corona poling been elucidated, but the underlying surface deformation phenomenon was found to constitute an appealing approach for the surface patterning of molecular glasses in general and azo materials in particular, that can be easily controlled to reversibly generate specific patterns on selected areas. As the patterns generated by this method can adopt irregular shapes, this process constitutes an alternative to photomechanical patterning methods, with the additional incidental benefit of orienting the dipoles of the molecules as a result of the electric field, which is central to nonlinear optical applications.

Experimental Section

Thin Film Deposition

Solutions of compounds **1** to **6** were prepared at a concentration of 4 wt% in CH_2Cl_2 , while compounds **7** and **8** were prepared at a concentration of 3 wt% in tetrahydrofuran. They were mechanically shaken for 1 hour and then filtered through a 0.45-micron syringe filter. A Headway Research spin-coater was used for the deposition of thin films. Approximately 0.2 mL of solution was deposited on a 3 x 3 cm² BK7 glass slide, followed by spinning at a rate of 1000 rpm for 20 seconds. After deposition, all films were dried in a Yamato ADP-21 oven at 95 °C for 30

minutes. This procedure yielded uniform films having an average thickness around 400 nm as measured using a Sloan Dektak II D profilometer (model 139961).

Electric Field Poling

A custom-built corona poling apparatus was fabricated in our lab: A Cole-Parmer Digi-Sense temperature controller was used to heat, up to 110 °C, a round aluminum hot plate, having a diameter of 5 cm. After each heat cycle, the hot plate was cooled using a fan in order to return it to room temperature. The hot plate temperature was monitored using a calibrated P-N junction temperature sensor that was directly connected to the temperature controller. During the poling process, the BK7 glass slides, with the various compounds spin-coated on them, were placed directly on the hot plate. The hot plate aluminum surface was used as one of the poling electrodes, while the other electrode consisted of a thin metallic wire suspended horizontally at 0.9 cm above the sample, using a hollow 7.5-cm round aluminum tube. The corona discharge voltage was supplied using a Hippotronics High-Voltage DC power supply.

Atomic Force Microscopy (AFM)

An Ambios Q-Scope Atomic Force Microscope was used in the tapping mode with a 40 N m⁻¹ force constant Quesant Premounted cantilever probe to record the surface topography of the thin films. Root mean square roughness and surface area were calculated using the Gwyddion software³⁶.

Films of azo glasses **1-6** with thicknesses of around 400 nm were prepared by spin-coating from CH₂Cl₂ solution, and were poled under 8 kV corona voltage at various temperatures for 30 min. At temperatures over the glass transition temperatures (*T_g*) of the materials, the films developed a cloudy appearance. Closer investigation of the surface of the films by atomic force microscopy (AFM) revealed the presence of nanostructures ranging from spherical to more irregularly-shaped grains with diameters and heights varying from 200 nm to over 1 μm. The formation of these nanostructures is accompanied by an increase in the surface area of the films that can reach up to 27 % (as calculated by the Gwyddion software). AFM images of Disperse Red 1 glass **4** before and after electric-field poling at 80 °C are shown in Figure 1, along with a selected profile, while images of other compounds are shown in Figure S1 (Supporting Information). The observed phenomenon is likely the result of dewetting induced by the application of the electric field, thereby causing surface instability, and leading to the formation of nanostructures. It is to be noted that dewetted films were confirmed by XRD to remain completely amorphous (Figure S2),

Results and Discussion

therefore the changes observed in surface topology are not the result of crystallization or another phase transition. While dewetting only occurs at temperatures over T_g , owing to the higher mobility of the materials, the minimum

Table 1. Glass transition temperatures (T_g) and minimal dewetting temperatures (T_{dewet}) for compounds 1-8 and DR1-PMMA.

Compound	T _g (°C)	T _{dewet} (°C)
1	63	70
2	68	70
3	64	70
4	71	75
5	72	100
6	73	110
7	95	105
8	82	85
DR1-PMMA	91	90

To confirm whether this dewetting phenomenon was attributable to the azo chromophore or to the mexylaminotriazine unit, films of model mexylaminotriazine glasses **7** and **8**, substituted with an hydroxy and a nitro group, respectively, and Disperse Red 1-substituted PMMA (DR1-PMMA), were subjected to electric-field poling under similar conditions. Compounds **7** and **8** were selected because they contain highly polar groups, and as a result are more likely to interact with the

electric field in a fashion similar to compounds **1-6**. In all cases, the films showed similar dewetting behavior. The presence of an azobenzene moiety is therefore not necessary for dewetting to occur. AFM images are shown in Figure S1, while T_{dewet} values are listed in Table 1. Again, the T_{dewet} value of hydroxy-substituted glass **7** relative to its T_g is higher than for nitro-substituted derivatives **8** and DR1-PMMA, possibly a consequence of the -OH group. It is not yet clearly understood why compounds **5-7** dewet at higher temperatures relative to T_g than compounds **1-4**, **8** and DR1-PMMA, but it is believed to be associated to a lower molecular mobility at temperatures above T_g . As compounds **5-7** all contain additional groups that can participate in hydrogen bonding (the thiazole nitrogen atoms of compounds **5-6** and the -OH group of compound **7**), the molecules are more likely to be held together more strongly, even above T_g ,³⁷ thereby decreasing mobility in the material, which is required for dewetting. Additionally, the azothiazole chromophores in compounds **5** and **6** are known for showing very slow cis-trans isomerisation, as a consequence of their highly dipolar nature (push-pull effect).³⁴ This increased rigidity would also act to limit molecular mobility in the solid. As dewetting occurs with both materials containing azobenzene chromophores and mexylaminotriazine units, this behavior is likely due to the presence of aromatic moieties, as is the case with most reported instances of polymers that can undergo electric field-induced dewetting, including polystyrene and polyaniline.²²⁻²⁷ It is also likely that similar behavior is shared with other classes of polar glass-forming organic compounds, but similar experiments have not been previously reported with other small-molecule materials.

Figure 2. AFM scans of thin films of Disperse Red 1 glass **4** (a) after poling under 8 kV corona voltage at 80 °C for 30 minutes, and (b) after thermal annealing of a poled film at 100 °C for 10 minutes.

As previous studies³⁵ on mexylaminotriazine glasses had shown that dewetting could occur upon thermal annealing of the films over T_g in certain cases depending on the respective polarities of the material and the substrate, it is crucial to determine if the observed behavior is caused by the electric field, or if it is only due to heating. Heating the films of compounds **1-8** in the absence of an electric field did not result in any perturbation in the morphology of the films. Furthermore, annealing dewetted films at temperatures above T_g resulted in a complete erasure of the surface features, as is shown in Figure 2 with an AFM scan of a dewetted sample of Disperse Red 1 derivative **4** after being subjected to thermal annealing in the absence of an electric field. In the current study, all compounds selected contain highly polar groups, therefore the dewetting behavior observed is triggered by the application of an electric field at temperatures where the glass is malleable enough to allow sufficient molecular mobility, rather than simply the result of an instability between the material and the substrate. To gain a better understanding of how

experimental parameters, notably electric field, temperature and time, influence the rate of growth of dewetted nanostructures, a more in-depth study was performed on Disperse Red 1 glass **4** where all three parameters were varied separately, and the roughness of the films was calculated from the AFM scans using the Gwyddion software. Graphs of root mean square roughness as a function of electric field, temperature and time for compound **4** are shown in Figure 3. The corona voltage was varied between 6 kV and 8 kV, while keeping the temperature constant at 80 °C and the exposure time at 30 min (Figure 3a). Below 6 kV, corona discharge could not be achieved, while voltages over 8 kV resulted in arcing between the poling station electrodes. The effect of temperature on dewetting was observed at temperatures ranging from 75 to 100 °C upon poling for 30 min with 8 kV corona voltage (Figure 3b), while the nanostructure growth as a function of time was monitored after exposure times of 5, 10, 20, 30 and 60 minutes under 8 kV at 80 °C (Figure 3c).

Figure 3. Graphs of root mean square (RMS) roughness of thin films of Disperse Red 1 glass **4**: (a) as a function of corona voltage with constant temperature (80 °C) and time (30 min), (b) as a function of temperature with constant voltage (8 kV) and time (30 min), (c) as a function of time with constant voltage (8 kV) and temperature (80 °C).

As it can be observed from Figure 3a, the strength of the electric field has little impact on the growth rate of the surface patterns, with

slightly larger grains obtained with a lower voltage of 6 kV. Temperature, on the other hand, had a very pronounced effect on average grain size, which increased in a nearly linear fashion with temperature (Figure 3b). It is to be noted that while the structures observed at lower temperatures are spherical, the structures observed at higher temperatures (90-100 °C) are irregular grains with elongated shapes that appear to result from the coalescence of several spherical structures. Finally, dewetting as a function of exposure time showed a rapid initial growth period to eventually reach a plateau after 20-30 min, as shown in Figure 3c. Thus, temperature seems to have the most impact on dewetting and aggregate size. These observations appear in contradiction with the model proposed by Shaffer et al. for polymers, where a direct correlation was observed between the electric field and grain size.¹⁸ In the case of mexylaminotriazine molecular glasses, temperature, which is correlated with viscosity and with diffusion rate, is the most impactful factor in determining grain size, while the impact of electric field is negligible. The difference in behavior observed with respect to polymers could be due to the absence of chain entanglement, as well as the presence of hydrogen bonds between molecules, even at temperatures above T_g , that result in differences in diffusion rates under different environments. For example, it has been demonstrated that the degree of hydrogen bonding in mexylaminotriazine glasses decreases as a function of temperature,³⁷ while the chain entanglement of polymers is only weakly dependent on temperature.

The effect of the direction of the electric field on the dewetting phenomenon was studied to determine if the nanostructures are affected by the build-up of negative or positive charges at the substrate-film interface and if the molecular dipoles, aligning in the direction of the field, have an influence on the nanostructure shapes and height. As observed in Figure 4, AFM scans of films of compound **3** poled under +8 kV or -8 kV voltage under otherwise similar conditions gave films with similar grain sizes and topologies. Therefore, the direction of the molecular dipoles has no effect on the resulting surface patterns.

Figure 4. AFM scans of films of compound **3** poled at 70 °C for 30 minutes under of (a) +8 kV, and (b) -8 kV.

Likewise, to determine if the observed dewetting arises from an instability at the substrate-film interface or at the film-air interface, films of compounds **1-6** that were deposited on glass slides that have been rendered hydrophobic by silanization with phenyltrichlorosilane were poled under 8 kV at various temperatures. Previously reported³⁵ thermal annealing of molecular glasses had been found to yield different results depending on the polarity of the substrate, with untreated glass favoring dewetting for mexylaminotriazine derivatives with alkyl substituents, while silanized glass favored dewetting for analogues with highly polar substituents. T_{dewet} values on films deposited on hydrophobic substrates are listed in Table 2. In all cases, dewetting still occurred upon heating over T_g under an electric field, independently of the substrate. However, the T_{dewet} values for compounds **2-3** were slightly higher than with an untreated substrate, while that of highly polar azothiazole derivatives **5** and **6** were lower with a hydrophobic substrate. It is thus likely that a higher substrate-film interfacial energy promotes dewetting more easily, but the interfacial energy values between the materials and both substrates are close enough that similar behavior is observed in both cases with only slight differences.

Table 2. Minimal dewetting temperatures (T_{dewet}) for films of compounds **1-6** deposited on hydrophobic substrates silanized with phenyltrichlorosilane.

Compound	T_{dewet} (°C)
1	70
2	75
3	75
4	75
5	90
6	100

From these observations, as well as previous observations on polymers, the origin of this dewetting phenomenon seems to arise not from an instability at the interface between the film and the substrate, as is the case for thermal dewetting, but rather from an instability at the free interface. It is due to the deposition of electric charges at the film's interface with air during the poling process. These charges cause the dipoles of the molecules to align in the direction of the electric field, and the molecules are then attracted towards the upper poling electrode. At temperatures above T_g , the molecules possess sufficient mobility to physically rise towards the upper electrode, which causes their agglomeration in grains as a result of material depletion near the substrate. Inverting the electric field polarity results in the inversion of molecular dipoles orientation, however, nearly identical nano-scale patterns were obtained. The pressure P exerted during poling on the grounded molecular thin film can be estimated from

electrostatics as $P = \epsilon_0 U^2 / 2L^2$ in which ϵ_0 is the permittivity of air, U is the corona poling voltage and L is film thickness. Under $U = 6000$ V, the pressure P exerted on an $L = 400$ nm-film is about 1 GPa. This is sufficient pressure to induce surface deformations in plastic materials, which justifies the observed behavior.

Thus far, it was shown that an electric field-induced dewetting process yields consistent behavior with various mexylaminotriazine derivatives. Moreover, certain applications require the dewetting process to be present selectively on only certain areas of a film. This was successfully achieved by placing a metallic mask, located at 1 mm above the sample and in between the two poling electrodes, as shown in Figure 5a (a picture of the experimental setup is shown in Figure S3). Exposing mexylaminotriazine samples through a mask under dewetting conditions has resulted in selective dewetting in the areas not obscured by the mask, as shown in Figure 5b, using a sample of compound **3**. The shape of the mask can be clearly identified on the

film as noted by the presence of the dewetted areas, which are visually cloudy. A profilometer was used to measure thickness changes on the dewetted and non-dewetted zones and it was found that there was a substantial increase in height of the dewetted areas versus the non-dewetted areas, with a difference comparable to the roughness values given in Figure 3b.

Figure 5. (a) Diagram of the experimental setup by incorporating a mask between the electrode and sample; (b) picture of a film of compound **3** poled at 80 °C for 30 min under 8 kV through a patterned mask.

Conclusions

In the present study, mexylaminotriazine glasses containing polar groups were found to dewet upon the application of an electric field at temperatures over their glass transition temperatures (T_g). The minimal dewetting temperature (T_{dewet}) relative to T_g was found to increase as a function of the polarity of the substituents. Nano-scale grainy topologies were obtained, with the size of the grains increasing almost linearly with temperature. Reversing the electrical field polarity and modifying the surface of the substrate did not result in any significant changes in the dewetting behavior, which is driven by the accumulation of charges at the free interface. The application of a mask allowed to selectively pattern areas that are exposed. Also, it was found that heating in the absence of an electric field could erase the dewetting surface patterns, thereby reverting to topologically planar films. The process described herein therefore represents a simple process to selectively and reversibly generate nano-scale surface patterns in thin films of mexylaminotriazine molecular glasses, including glasses bearing azobenzene chromophores. It is complementary to the photomechanical processes or solvent-driven patterning processes occurring in azobenzene derivatives.

ASSOCIATED CONTENT

Supporting Information. AFM images of dewetted films of compounds **1-8** and DR1-PMMA, XRD scans of compounds **1-8** before and after electric-field poling, and a picture of the poling experimental setup. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors.

Funding Sources

The research reported herein was funded by the Canadian Defense Academy Academic Research Program (OL) and the National Science Research Council of Canada Discovery Grants (RGPIN-2015-05743 for RGS and RGPIN-2015-05485 for JMN).

Notes

Marvin was used for drawing, displaying and characterizing chemical structures, substructures and reactions, Marvin 15.1.12, 2015, ChemAxon (<http://www.chemaxon.com>).

ACKNOWLEDGMENT

The authors would like to acknowledge the technical expertise and help of Mr. Bob Whitehead for the XRD scans, and Dr. Gabriela Aldea-Nunzi for the hydrophilic and hydrophobic glass slides.

ABBREVIATIONS

AFM, Atomic Force Microscopy; XRD, X-ray Diffraction; T_g , Glass Transition Temperature.

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