Programmable helical twisting in oriented humidity-responsive bilayer films generated by spray-coating of a chiral nematic liquid crystal

Citation for published version (APA):

Verpaalen, R. C. P., Debijs, M. G., Bastiaansen, C. W. M., Halilović, H., Engels, T. A. P., & Schenning, A. P. H. J. (2018). Programmable helical twisting in oriented humidity-responsive bilayer films generated by spray-coating of a chiral nematic liquid crystal. *Journal of Materials Chemistry A*, 6(36), 17724-17729. <https://doi.org/10.1039/C8TA06984K>

DOI:

[10.1039/C8TA06984K](https://doi.org/10.1039/C8TA06984K)

Document status and date:

Published: 28/09/2018

Document Version:

Typeset version in publisher's lay-out, without final page, issue and volume numbers

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

PAPER

Programmable helical twisting in oriented
humidity-responsive bilayer films generated by
spray-coating of a chiral nematic liquid crystal†Rob C. P. Verpaalen,^a Michael G. Debije,^a Cees W. M. Bastiaansen,^{ab} Haris Halilović,^c
Tom A. P. Engels^c and Albertus P. H. J. Schenning ^{*a}

Cite this: DOI: 10.1039/c8ta06984k

Received 19th July 2018
Accepted 28th August 2018

DOI: 10.1039/c8ta06984k

rsc.li/materials-a

A facile method is presented that generates humidity-driven helical twisting in thin, oriented polyamide 6 (PA6) films by spray-coating of a chiral nematic liquid crystal network (LCN). The LCN is self-aligned by the PA6 substrate, and the internal twist angle of the LCN provides the direction and extent of twisting for the expanding PA6 substrates. The handedness and extent of helical twisting in the bilayer film can be finely programmed by the degree of twist in the thin topping LCN layer. This straightforward spray-coating process and self-alignment of the liquid crystals (LCs) is compatible with high-throughput industrial manufacturing processes and is applicable to other stretched commodity polymers.

Introduction

Synthetic and natural commodity polymer materials are extensively used in an ever-expanding range of applications and are often considered mature from a processing, properties and applications point of view.¹ With the increasing interest in stimuli-responsive, smart actuators, for example as adaptive smart textiles and soft robotics, researchers are exploring new paths to introduce new functionalities to traditional commodity polymers.^{2,3} The fabrication of these novel, high-end products is appealing as it will extend their range of applications and makes new fields of interest accessible. Commonly, these new functionalities are introduced into commodity polymers *via* material blending or by applying a smart coating. From a processing point-of-view these techniques have a minimum impact on existing industrial infrastructures and are performed at low cost.

Stimuli-responsive, shape changing polymers are currently receiving a lot of attention. Such polymers typically respond to (environmental) stimuli such as light, heat or humidity. When anisotropic polymers are used such soft actuators demonstrate anisotropic expansion/contraction. Typically, bilayer actuators are fabricated to obtain a bending deformation as a result of the mismatch in expansion coefficients between both layers.^{4–6} In

humidity responsive bilayer actuators that bend, a hydrogel layer is often ab- and desorbing moisture. Swelling and shrinkage of a hydrogel layer frequently account for (large) macroscopic actuation, but provide limited mechanical strength.^{7,8} Appealing future applications, such as smart textiles and soft robotics, require more robust materials and preferably other deformations than simple bending. Macroscopic helical twisting motion, for example, is known to substantially reduce the length due to winding of the bilayer strip and is frequently generated by cutting oriented (sometimes bilayer) films at an angle to the alignment direction.^{9–12} To control this helical twisting, one needs to cut bilayer films at different angles. Therefore, it would be appealing to develop a more practical, straightforward method compatible with high-throughput industrial manufacturing processes.

Previously, we reported on a bilayer actuator comprising of oriented polyamide 6 (PA6) and an aligned nematic liquid crystalline coating that bends due to the ab- and desorption of moisture.¹³ PA6 is humidity responsive: typically, humidity sensitive polymer films expand in all directions as moisture is absorbed, though several researchers have designed bilayer actuators that directed the macroscopic response to humidity.^{14–16} We now present a facile, one step method to obtain humidity responsive helical twisting bilayer actuators comprised of oriented PA6 substrates topped by a chiral nematic liquid crystal network (LCN). A simple spray gun is employed to apply a twist-aligned LCN ($0 < \theta < 90^\circ$) coating that directs the humidity driven expansion of the bilayer into a helical curl. This technique allows access to a range of 3-dimensional deformations. The humidity responsive PA6 films are potentially interesting for fabricating smart textiles and generate a toolbox to functionalize conventional fabrics, for example.¹⁷

^aLaboratory of Stimuli-responsive Functional Materials and Devices, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

^bSchool of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, UK

^cDepartment of Mechanical Engineering, Materials Technology Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ta06984k

Experimental

Materials

LCNs were obtained *via* the copolymerization of 4-(3-(acryloyloxy)propoxy)benzoic acid (3OBA, Synthon), 4-((5-(acryloyloxy)pentyl)oxy)benzoic acid (5OBA, Synthon), and 4-((6-(acryloyloxy)hexyl)oxy)benzoic acid (6OBA, Synthon) with 1,4-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (C6M, Merck). The three nOBA monomers differ in methylene spacer length ($n = 3, 5$ or 6). The LC mixture consists of 86 wt% nOBA (1 : 1 : 1 ratio by weight), 12 wt% C6M and 2 wt% of the photoinitiator Irgacure 819 (Merck). A right-handed chiral dopant 1,4:3,6-dianhydro-D-glucitol bis[4-[[4-[[4-[(1-oxo-2-propenyl)oxy]butoxy]carbonyl]oxy]benzoyl]oxy]benzoate (LC756, BASF) is used in trace amounts to rotate the LC monomers in-plane. Oriented 15 μm thick polyamide (PA6) substrates, acquired from Goodfellow, UK, serve as the alignment layer for the LCs. All reagents were used as received.

Methods

Freestanding LCN films. Freestanding LCN films were prepared in cells. $30 \times 30 \text{ mm}^2$ glass slides were coated with planar polyimide (JSR Optmer AL1051), rubbed with a velvet cloth and glued anti-parallel to each other. Monomer mixtures were applied at the cell gap edge which filled through capillary action to form 20 μm planar poly(nOBA/C6M) films. An Omni-Cure S2000 UV-curing system (20 mW cm^{-2} for 600 seconds in a nitrogen atmosphere) is employed to fix the film in the nematic phase at 80 $^\circ\text{C}$. Internal stresses were relieved by a thermal post-cure step at 130 $^\circ\text{C}$ for 20 minutes.

LCN/PA6 bilayers. A thin LCN coating was spray-applied onto PA6 to prepare humidity-sensitive bilayer actuators. The LC monomers were dissolved in xylene (Sigma Aldrich) in a 1 : 5 weight ratio. Oriented PA6 substrates were dried with nitrogen gas to desorb moisture. An AMI 200 spray gun was employed to spray-apply $\sim 4 \mu\text{m}$ LC coatings using N_2 as a carrier gas at 1 bar. Self-aligned LC monomers were photopolymerized under the same conditions as for the freestanding LC films. The helical twisting power (HTP) of the chiral dopant was determined to be $\sim 50 \mu\text{m}^{-1}$ in the nOBA/C6M mixture (Fig. S1†). By varying the chiral dopant concentration, one can configure the in-plane alignment of the LCs (see eqn (1)):

$$\theta = d \times \text{HTP} \times c \times 360 \quad (1)$$

where d is the LCN layer thickness (in μm), c is the concentration of chiral dopant and θ is the resultant rotation (in $^\circ$) of the top layer of LCs with respect to the director of the base layer.¹⁸

Humidity response. Humidity-driven deformations of $20 \times 3 \times 0.019 \text{ mm}^3$ bilayer strips were investigated in a DataPhysics HGC 30 temperature-controlled humidity chamber into which dry or humid nitrogen was fed. The humidity level and temperature were monitored using a Vaisala HM42 probe. Photographs were taken with a smartphone camera. All images were analyzed using ImageJ open access software.

Characterization. The alignment of PA6, LCN and bilayer films were examined with polarized optical microscopy (Leica

DM2700 M). Dynamic mechanical analysis (DMA) was performed on $10 \times 5.3 \text{ mm}^2$ ribbons cut from the larger LCN films with a DMA Q800 apparatus (TA instruments) equipped with a humidity chamber. In a controlled environment the anisotropic mechanical properties were determined at 20 $^\circ\text{C}$. Elastic moduli (E'_{xx} , E'_{yy}) and damping characteristics ($\tan \delta$ -values) were measured at a 1 Hz frequency and a 10 μm amplitude. In constant stress mode dimensional changes (α_x , α_y) were measured as a function of the relative humidity (RH). Cold-fractured bilayer films were sputter coated with Pt (JEOL, JFD-2300HR) and cross-sectional scanning electron micrographs were recorded under vacuum with a JSM-IT100 (JEOL).

Results and discussion

For the preparation of the humidity responsive actuators that show reversible helical twisting, a chiral nematic LC mixture was spray-applied onto oriented PA6 using xylene as a solvent for the LC monomers (Scheme 1A and B). Xylene was selected because it is a non-solvent for the PA6 substrate. The LCs subsequently self-aligned using the stretched PA6 as the alignment layer. The LCs were then photopolymerized to obtain bilayer actuators. Polarized optical micrographs revealed that the LCNs containing no chiral dopant align at the PA6 interface. While the film is oriented planar at the PA6-interface, the LC tends to reduce surface free energy by gradually rotating through the film depth to attain homeotropic alignment (that is, out-of-plane) at the air interface, and therefore can be considered as a splay alignment.¹⁹ A homogeneous black state appears between crossed polarizers as the PA6 orientation direction was aligned with one of the polarizers while in-plane sample rotation of the sample results in a bright state, indicating alignment (see Fig. S2†). For practical reasons, 4 μm LCN coatings were used. The helical twisting of the bilayer is controlled by the precise but small amount of a right-handed chiral dopant added from a xylene stock solution to the LC mixture concentration, the dopant HTP and thickness of the LCN layer. The LCN of the prepared bilayer actuators had in-plane rotation angles between 0 and 135 $^\circ$. Scanning electron micrographs of the cryogenically fractured bilayers verified a total cross-sectional thickness of 19 μm (Fig. S3†). Ribbons of $20 \times 3 \times 0.019 \text{ mm}^3$ along the PA6 orientation direction were exposed to various humidity levels. The anisotropic LCN/PA6 bilayer actuators will be referred to as BA. θ , with θ specifying the in-plane LC twist between the base and surface layers. As the humidity level increases, PA6 is expected to expand, and, directed by the twisted LCN layer, develops curvature with the LCN on the inside of the curvature (Scheme 1C).

The humidity response of a LCN/PA6 bilayer with a 45 $^\circ$ twist (BA.45) was examined first (see Fig. 1A). From a stock solution, 0.06 wt% of the chiral dopant was added to the nematic LC mixture. The right-handed chiral dopant added to the LC mixture rotates the LC director 45 $^\circ$ counter-clockwise in-plane. The UV-cured bilayer ribbon was mounted in the humidity chamber at room temperature and the humidity level was changed step-wise. We describe macroscopic deformations in these humidity-driven systems in terms of changes in the

Scheme 1 The preparation procedure of the bilayer actuators based on commercially available oriented PA6 films. (A) The chemical structures of the liquid crystal molecules in the LCN mixture. (B) PA6 is taped to a glass slide, a liquid crystal coating is spray-applied and subsequently photopolymerized in the nematic phase. (C) Schematic illustrations that highlight the step-wise 3D deformation into a helix as the humidity level rises.

inverse diameter and pitch, which is the inverse length to make a 360° twist, as a function of the relative humidity. At higher humidity (80%), the inverse pitch is extracted from the well-defined helical shape. The inverse pitch at low humidity levels is determined by extrapolation (in Fig. 1B and C). It was anticipated that significant swelling of the oriented PA6 substrate, predominantly along the stretching direction, was directed by the counter-clockwise LC coating orientation to form a right-

handed helix (see Scheme 1C). In Fig. 1, this 3-dimensional deformation was observed as more moisture is fed into the humidity chamber and the helix gradually forms and tightens.

To see if the helical twisting in the PA6 film can be programmed by the LCN coating, the chiral dopant concentration was adjusted to vary the in-plane twist angle through the LCN film. Fig. 2A demonstrates that both bending and helical twisting motions are accessible by altering the in-plane LCN

Fig. 1 The evolution of 3D shape morphing in the LCN/PA6 bilayer actuator BA.45. (A) At low humidity the $20 \times 3 \times 0.019$ mm³ strip is pre-bent towards the LCN side. The in-plane director rotation in the LCN coating winds the bilayer as the humidity level is gradually increased and PA6 absorbs moisture. At 80% RH a right-handed helix has formed. The scale bar equals 3 mm. (B) Humidity-driven deformations change the diameter of the sample. The inverse diameter (in mm⁻¹) is plotted as a function of relative humidity. (C) The inverse pitch, the inverse distance needed to rotate 360° , versus relative humidity in BA.45 samples.

Fig. 2 LCN/PA6 bilayer actuators macroscopically deform as the surrounding humidity level changes. The in-plane twist angle θ is a key parameter to enable the formation of helices. (A) Bilayer actuators bend or curl in response to humidity changes. The recorded images are taken at different humidity levels and highlight bending or helical motion as θ varies. (B) The inverse pitch, an inverse length needed for the bilayer to rotate 360° at 60% RH (red diamonds) and at 80% RH (black diamonds), is plotted *versus* the in-plane twist angle θ . The grey areas indicate the bending bilayers, where the inverse pitch approaches infinity.

director rotation. At low humidity, all bilayer actuators are nearly straight. In more humid environments the bilayers begin to macroscopically deform within seconds and reach maximum twist within minutes (for example, a film moving from 5 to 60%

RH completes deformation within 2 minutes, see Movie S1†). Over a three-day period, it was observed that bilayer films only lost minor curvature when maintained at constant, elevated humidity levels. The inverse pitch at 60 and 80% RH are plotted

in Fig. 2B as a function of director rotation. The samples BA.0 and BA.90 both bent as PA6 swells predominantly along its orientation direction and follows the path of least resistance. The grey regions in the figure correspond to bent bilayers in which the inverse pitch goes to infinity. In contrast, at twist angles of $0 < \theta < 90^\circ$, helical deformation was observed. The largest macroscopic deformation was found in samples with a 45° in-plane twist, (BA.45).^{15,20,21} Moreover, for twist angles greater than 90° , it is expected that the deformations become smaller because the average in-plane modulus increases as twist angles become larger, resulting in increased resistance to deformation at high twists.

To understand the programmed helical twisting in more detail, the humidity induced shape and mechanical changes of both PA6 and LCN films were studied with dynamic mechanical analysis (DMA). In Fig. S4A–C† the impact of moisture absorption on the mechanical properties of oriented PA6 and LCN films, measured parallel (x-direction) and perpendicular (y-direction) to the alignment direction, are shown. PA6 absorbs moisture from the environment, which forms H-bonds with the amide moieties in the backbone. As most of the binding sites are occupied, available free volume is filled with water molecules, resulting in plasticization.²² This plasticizing has a dramatic effect on mechanical properties: in dry conditions, the storage modulus E'_{xx} equals ~ 4 GPa drops to ~ 0.7 GPa at 80% RH, for example. In Fig. S4B† a maximum $\tan \delta$ -value is found at 55% RH, defining a humidity induced glass transition temperature at 20°C . In contrast, the bare LCN films did not show softening at higher humidity. Fig. S4C† illustrates how moisture accumulation affects the length of the two films. The LCN swells minimally, reaching isotropic strain-values of only 0.15% at 80% RH. In contrast, PA6 elongates up to 2.8% along the orientation direction, and 1.3% in the transverse direction.²³ Based on this data it can be concluded that changes in environmental humidity result in the uptake or loss of water from only PA6, resulting in elongation or shortening of the length of the PA6 film, respectively, forcing the combined LCN/PA6 bilayer to bend or curl.

Essentially, the samples can be viewed as laminates consisting of discrete layers that rotate LC orientation in-plane and the angular dependency and anisotropy within the bilayers can be simulated with FEM (more details on the numerical model can be found in the ESI†). By using the measured values of the LCN and PA6 elastic moduli (E'_{xx} , E'_{yy}) and coefficients of hygroscopic expansion (α_x , α_y) as inputs to the FEM model, a fitting procedure was carried on the PA6 α_x -value to visually match the actuation state at 40% RH, resulting in the actuation

Fig. 3 The humidity-sensitive material properties were employed in a finite element method (FEM) to describe the deformation in LCN/PA6 bilayer actuators. The macroscopic deformations of samples with an in-plane twist angle θ of 45° are depicted at increasing humidity levels to demonstrate helical twisting motion.

Fig. 4 In nature, humidity levels are always coupled to temperature. In terms of actuation, a bilayer actuator with an in-plane twist angle of 67.5° (BA.67.5) was exposed to various temperature levels at constant humidity. The scale bar equals 3 mm.

states depicted in Fig. 3. These calculations, however, somewhat underestimate the deformations presented in Fig. 1B.

To study the influence of the temperature on the humidity response, the BA.67.5 film was maintained at a constant 50% RH while the temperature was varied (Fig. 4). Upon increasing the temperature, the bilayer unwinds and the thermal deformation was found to be reversible, although with some hysteresis. Straightening of the strip can be assigned to several causes: PA6 has a negative thermal expansion coefficient above its T_g , and therefore contracts along its orientation direction.²⁴ Likely, the moisture-capacity of PA6 also decreases (*i.e.* moisture desorption) at higher temperatures.^{25,26} Moreover, the LCN coating expands out-of-plane.²⁷ In dry conditions, the LCN has a $T_g \sim 100^\circ\text{C}$ and therefore little thermal expansion is expected below 100°C .²⁸

Conclusions

An elegant spraying procedure was employed to program helical twisting in conventional PA6 films. In this method, the humidity-sensitive PA6 underlayer self-aligned the liquid crystal mixture, in which the handedness and in-plane twist angle was controlled by the addition of chiral molecules. Shape morphing was found to be programmable by varying the director twist angle in the LCN coating *via* the concentration of chiral dopant. At low humidity, bilayer strips were nearly straight and macroscopically deformed as moisture was fed into the system. Reversible humidity-driven helical motion occurred at twist angles $0 < \theta < 90^\circ$ and angles unequal to multiples of 90° . In-plane director rotations of 0 and 90° led to bending motion in bilayer actuators. Moreover, at a fixed humidity level, 50% RH, helical bilayers reversibly unwind as the temperature increased. These bilayer actuators may potentially find application in smart textiles, to dynamically change the packing density, or soft robotics to manipulate material positions.

Our procedure is not restricted to oriented PA6, but also other stretched polymers, such as poly(ethylene terephthalate), can be used (see Fig. S5†).²⁹ The elegance of this system is further found in the self-organized coating: in principle, any chiral nematic LC mixture can be used to access helical twisting and its response to different stimuli can be tailored by changing the chemistry (Fig. S6†). A combination of humidity-sensitivity and in-plane LC director control resulted in humidity-driven helical motion. The application method is believed to be compatible with typical high-throughput polymer manufacturing processes and access a range of macroscopic motions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors would like to thank Celestina Collura, Kai Claesens, Maarten Vlaswinkel and Frits Verheggen for valuable discussions related to this work. This work was supported by The Netherlands Organization for Scientific Research (NWO) under project No. 731.015.502.

Notes and references

- 1 M. Lewin, *Handbook of fiber chemistry*, CRC/Taylor & Francis, 2006.
- 2 P. J. Lemstra and R. Kirschbaum, in *Polymer*, 1985, vol. 26, pp. 1372–1384.
- 3 T. Xiang, L. R. Wang, L. Ma, Z. Y. Han, R. Wang, C. Cheng, Y. Xia, H. Qin and C. S. Zhao, *Sci. Rep.*, 2014, **3**, 1–5.
- 4 M. Yamada, M. Kondo, J. I. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett and T. Ikeda, *Angew. Chem., Int. Ed.*, 2008, **47**, 4986–4988.
- 5 A. Agrawal, T. Yun, S. L. Pesek, W. G. Chapman and R. Verduzco, *Soft Matter*, 2014, **10**, 1411–1415.
- 6 Y. Haldorai and J. Shim, *New J. Chem.*, 2014, **38**, 2653.
- 7 L. Ionov, *Soft Matter*, 2011, **7**, 6786–6791.
- 8 S. J. Jeon, A. W. Hauser and R. C. Hayward, *Acc. Chem. Res.*, 2017, **50**, 161–169.
- 9 M. Wang, B. P. Lin and H. Yang, *Nat. Commun.*, 2016, **7**, 1–8.
- 10 Y. Sawa, F. Ye, K. Urayama, T. Takigawa, V. Gimenez-Pinto, R. L. B. Selinger and J. V. Selinger, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 6364–6368.
- 11 L. T. De Haan, J. M. N. Verjans, D. J. Broer, C. W. M. Bastiaansen and A. P. H. J. Schenning, 2014, 3–6.
- 12 S. Iamsaard, S. J. Afshoff, B. Matt, T. Kudernac, J. J. L. M. Cornelissen, S. P. Fletcher and N. Katsonis, *Nat. Chem.*, 2014, **6**, 229–235.
- 13 M. Dai, O. T. Picot, J. M. N. Verjans, L. T. De Haan, A. P. H. J. Schenning, T. Peijs and C. W. M. Bastiaansen, *ACS Appl. Mater. Interfaces*, 2013, **5**, 4945–4950.
- 14 K. Zhang, A. Geissler, M. Standhardt, S. Mehlhase, M. Gallei, L. Chen and C. M. Thiele, *Sci. Rep.*, 2015, **5**, 1–13.
- 15 M. Chen, J. Frueh, D. Wang, X. Lin, H. Xie and Q. He, *Sci. Rep.*, 2017, **7**, 769.
- 16 L. Ionov, *Langmuir*, 2015, **31**, 5015–5024.
- 17 J. Hu, H. Meng, G. Li and S. I. Ibekwe, *Smart Mater. Struct.*, 2012, **21**, 053001.
- 18 M. Mitov, *Adv. Mater.*, 2012, **24**, 6260–6276.
- 19 C. L. Van Oosten, C. W. M. Bastiaansen and D. J. Broer, *Nat. Mater.*, 2009, **8**, 677–682.
- 20 J. M. Boothby and T. H. Ware, *Soft Matter*, 2017, **13**, 4349–4356.
- 21 A. Ryabchun, F. Lancia, A.-D. Nguindjel and N. Katsonis, *Soft Matter*, 2017, **13**, 8070–8075.
- 22 N. J. W. Reuvers, H. P. Huinink, H. R. Fischer and O. C. G. Adan, *Macromolecules*, 2012, **45**, 1937–1945.
- 23 B. E. Trembl, R. N. McKenzie, P. Buskohl, D. Wang, M. Kuhn, L. S. Tan and R. A. Vaia, *Adv. Mater.*, 2018, **30**, 1–6.
- 24 C. L. Choy, W. P. Leung and E. L. Ong, *Polymer*, 1985, **26**, 884–888.
- 25 A. Koshimo and T. Tagawa, *J. Appl. Polym. Sci.*, 1965, **9**, 45–54.
- 26 T. Asada and S. Onogi, *J. Colloid Sci.*, 1963, **18**, 784–792.
- 27 D. J. Broer and G. N. Mol, *Polym. Eng. Sci.*, 1991, **31**, 625–631.
- 28 K. D. Harris, C. W. M. Bastiaansen and D. J. Broer, *J. Microelectromech. Syst.*, 2007, **16**, 480–488.
- 29 O. T. Picot, M. Dai, D. J. Broer, T. Peijs and C. W. M. Bastiaansen, *ACS Appl. Mater. Interfaces*, 2013, **5**, 7117–7121.