Hierarchical Manipulation of Block Copolymer Patterns via Multiple External and Internal Fields

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Block copolymers: thin film behavior

- Internal fields:
  - $\chi$–parameter, $\chi_N$
  - Film thickness (surface fields)
  - Temperature
  - Solvent concentration

- External fields:
  - Patterned substrates
  - Shear, Electric field
  - Gradient fields: solvent evaporation rate, solvent crystallization, zone annealing, etc

- Processing (time –effectiveness):
  - Chain mobility: temperature annealing, solvent vapor annealing (SVA)
  - Non-equilibrium states (frozen by spin-coating conformations)
  - Structure identification

- Challenges:
  - Interdependence of parameters:
  - Guided optimization of patterns through understanding

- Solvent vapor annealing as a processing step
- Interplay between external and internal fields under processing conditions
Controlled swelling of polymer films

➢ Solvent vapor annealing as a processing step

Flow control & Thermo control:

\[ T_1 - \text{sample} \;; \; T_2 - \text{vapore} \]

Total flow = const

Elbs, Krausch, Polymer 2004, 45, 7935.
Knoll et al, JCP 2004, 120, 1105.

Partial vapor pressure of the solvent, %

\[ \frac{p}{p_0} = \frac{\text{Ch}_{\text{Solvent}}}{\text{Ch I} + \text{Ch II}_{N_2}} \]

University of Bayreuth, Germany
Krausch group
Controlled swelling of polymer films

✓ Method to determine the $\chi$ parameters in swollen polymer films (*Polymer* 2004, 45, 7935)


Thickness-dependent morphological behavior
Controlled swelling of polymer films

polystyrene-\textit{b}-polybutadiene (\(\varphi_{ps} = 24.5\) v%) 

✓ Scaling of microdomain spacings (Knoll et al. \textit{Nano Letters} 2007, 7, 843-846.)

Thickness dependent cylinder spacings

\[ T_1 \]
\[ T_2 \]
\[ T_3 \]
Controlled swelling of polymer films

- Film thickness-dependent and morphology-dependent swelling of block copolymer films (Gensel et al., Soft Matter 2009, 5, 2534)

- Oder-disorder transition and nonhomogeneous swelling of the films on the micrometer scale (Zettl et al. Langmuir 2010, 26, 6610)

\[ \phi = 0.57 \quad \phi = 0.63 \quad \phi = 0.64 \]

\( \phi \) - polymer volume fraction
Controlled swelling of polymer films

polystyrene-\textit{b}-polybutadiene ($\varphi_{ps} = 24.5 \text{ v\%}$)

- $M_w \approx 100 \text{ kg/mol}$
  - 100% partial vapor pressure
- $M_w \approx 50 \text{ kg/mol}$
  - 80% partial vapor pressure

Zettl, Knoll, Tsarkova, \textit{Langmuir} \textbf{2010}, 26, 6610
Tsarkova \textit{Macromolecules} \textbf{2012}, 26, 6610
Combining graphoepitaxy and EF

polystyrene-\textit{b}-poly(dimethylsiloxane)
($\varphi_{\text{PDMS}} = 30 \text{ v}\%$)
$a_0 = 35 \text{ nm}$

- graphoepitaxy – is limited to the gratings width $x < 1.5 \, \mu\text{m}$

Swelling ratio of 2.0-2.1 in the vapors of 2:1 toluene-heptane mixture

Combining graphoepitaxy and EF

polystyrene-\textit{b}-poly(dimethylsiloxane)
($\varphi_{\text{PDMS}} = 30 \text{ v\%}$)
$a_0 = 35 \text{ nm}$

Swelling ratio of 2.0-2.1 in the vapors of 2:1 toluene-heptane mixture
EF strength of 12.5 V/µm

Combining graphoepitaxy and EF

- What is the max separation between the fins x when EF and graphoepitaxy are combined (α = 0)?

- What if α > 0 (15, 30, 45, 90)?

Combining graphoepitaxy and EF

- Flow field
  - thickness gradient from mesas to trenches
  - domain orientation perpendicular to the sidewalls of the topographic features at $1.5 \mu m < x < 6 \mu m$
  - above $6 \mu m$ – multigrain pattern with random orientations
  - the flow induced orientation is not stable (dynamic field) and vanishes with increasing the time of annealing

![Graph showing orientation distribution](image1)

![Graph showing orientation distribution](image2)
Combining graphoepitaxy and EF

- EF stabilizes flow-field induced orientation (perpendicular to the direction of the graphoepitaxy field)

- Graphoepitaxy field dominates over the EF, but the quality of the resulting pattern is improved by the combined approach.

The correlation length of up to 20 µm was an order of magnitude greater than that produced by either graphoepitaxy or electric field alignment alone, and was achieved at reduced annealing times.

Hard mask (HM) supported block copolymer films

HM8006-8 from JSR Micro, spin coated and cured on a hot plate 50 nm thick coating

Partial vapor pressure of the solvent, %

\[ \frac{p}{p_0} = \frac{\text{Ch 1}_{\text{Solvent}}}{\text{Ch 1} + \text{Ch 2}_{\text{N}_2}} \]
Enhanced ordering on HM support

Polystyrene-\(b\)-poly(2vinylpyridin) ~ 100 kg/mol (SV), lamella-forming

Chloroform – nearly non selective solvent

\[ \frac{p}{p_0} = 20\% \]

Dry thickness ~50 nm (~\(L_0\))

1 hour of annealing

A. Stenbock-Fermor et al., *Macromolecules* 2014, 47, 3059-3067
Kinetics of lamella reorientation

Polystyrene-\(b\)-poly(2vinylpyridin) \(\sim 100\) kg/mol

\[ h_{sw}\!<\!1.5\ L_0 \quad h_{sw}\!\sim\!1.5\ L_0\!\sim\!75\ nm \]

\[ \frac{p}{p_0}\!\approx\!80\%,\;30\;\text{min} \]

Einstein relation
\[ a = (Dt)^{1/2} \]
with \(a\!\sim\!L_0\!\sim\!50\;\text{nm},\;t_{Si}\!\sim\!9\;\text{h}\;\text{and}\;t_{HM}\!\sim\!0.5\;\text{h}\]

\[ \frac{D_{HM}}{D_{Si}}\!\sim\!10 \]

Larger solvent up-take by block copolymer film supported by HM?
Ellipsometric thickness measurements

$p/p_0 = 20\%$
Ellipsometric thickness measurements

Polymer film does not swell more on HM-support as compared to that on silica wafer-support
UV-VIS ellipsometry W.Ogieglo (DWI Aachen)

A. Stenbock-Fermor et al., in preparation
Segregation power in swollen films

Polystyrene-block-polybutadiene diblock copolymer

\[ M_w = 47 \text{ kg/mol (26 \%PS)} \]
\[ a_0 = 32 \text{ nm (SAXS)} \]

\[ p/p_0 = 55\%, 1 \text{ hour} \]

*Macromolecules* 2012, 45, 5185.
Langmuir 2010, 26, 6610.
Segregation power in swollen films

Polystyrene-block-polybutadiene
diblock copolymer

$M_w = 47 \text{ kg/mol (26 \%PS)}$

$a_o = 32 \text{ nm (SAXS)}$;

Reduced interactions between block copolymer films and swollen HM-support are decisive in accelerating block copolymer chain dynamics at small degrees of swelling.

$p/p_0 = 55\%, \ 1\ \text{hour}$

$p/p_0 = 60\%, \ 10\ \text{min}$

Macromolecules 2012, 45, 5185.
Langmuir 2010, 26, 6610.
ACS Nano 2008, 2, 1143.
L.T. in Nanostructured Soft Matter
Enhanced chain dynamics

Reduced interactions between block copolymer films and swollen HM-support should facilitate dewetting

Supression of dewetting on HM support

A. Stenbock-Fermor et al., in preparation
Conclusions

- Up to 20 µm correlation length of ordered domains by combining graphoepitaxy and electric field at a reduced annealing times.

- Enhanced chain dynamics of HM supported films at low degrees of swelling

- Suppressed dewetting of polymer films HM substrates
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