Polymerization-Induced Phase Separation near Patterned Surface

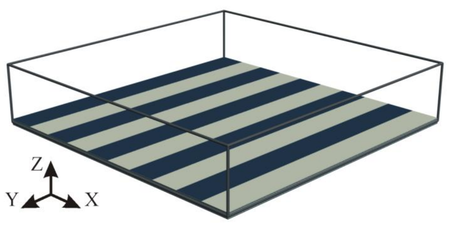
Alexey A. Gavrilov, Elena N.Govorun, Alexander V. Chertovich
Physics Department, Moscow State University, Leninskie Gory, Moscow 119991, Russia
E-mail: chertov@polly.phys.msu.ru

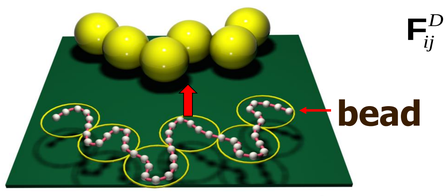
Systems and methods

•Polymerization-induced microphase separation (PIPS) in thin films
•Initially homogeneous blend of two types (A and B) of monomers at $0<\chi<2$
•Long blocks formed during copolymerisation segregate from each other
•The reaction probabilities $p_{AA} = p_{BB}$ and $p_{AB} = p_{BA}$ are the model parameters

Method of simulations: dissipative particle dynamics

Groot R.D. and Warren P.B. J. Chem. Phys. ***107*** *(1997) 4423*





$$\mathbf{F}_{ij} = \mathbf{F}_{ij}^{Cons} + \mathbf{F}_{ij}^{Diss} + \mathbf{F}_{ij}^{Random}$$

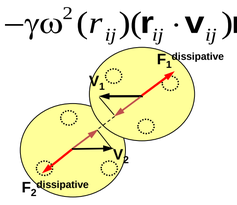
$$\mathbf{F}_{ij}^{C} = a_{ij}\omega(r_{ij})\mathbf{r}_{ij}$$

$$\omega(r_{ij}) = \begin{cases} 1 - r_{ij}/r_{cut} & r_{ij} \le r_{cut} \\ 0 & r_{ij} > r_{cut} \end{cases}$$

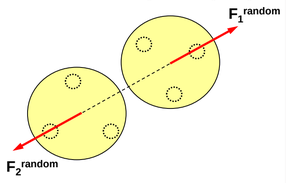
$$a_{ij} = f(\chi_{FH}; \delta_{solv}; \kappa)$$

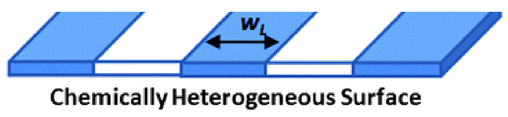
$$\left\langle \mathbf{F}_{i\alpha}^{R}(t)\mathbf{F}_{j\beta}^{R}(t') \right\rangle = 2k_B T\gamma\delta_{ij}\delta_{\alpha\beta}\delta(t-t')$$

$$\mathbf{F}_{ij}^{D} = -\gamma\omega^2(r_{ij})(\mathbf{r}_{ij}\cdot\mathbf{v}_{ij})\mathbf{r}_{ij}$$

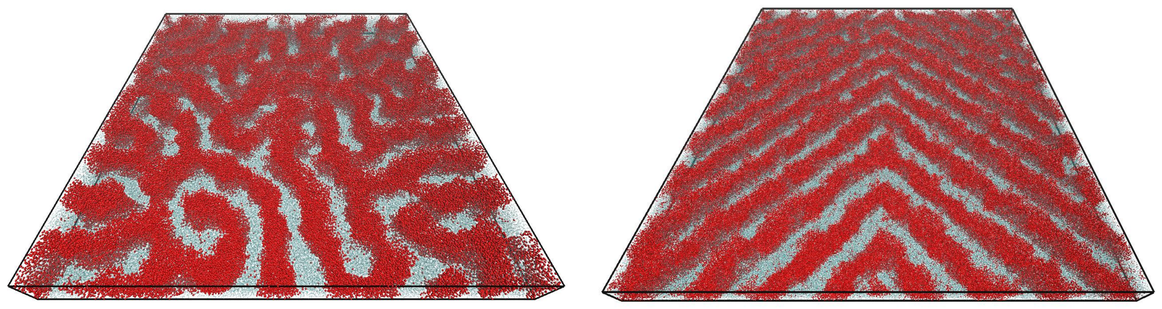


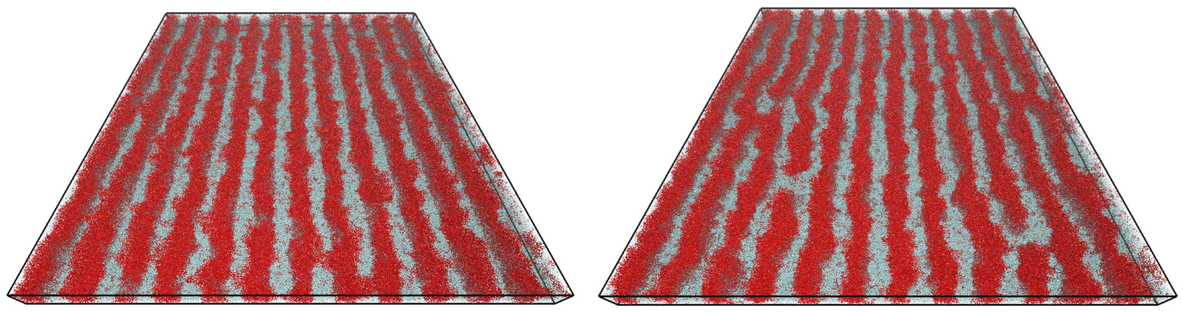
$$\mathbf{F}_{ij}^{R} = \sqrt{2k_B T\gamma}\,\xi_{ij}\omega(r_{ij})\mathbf{r}_{ij}$$



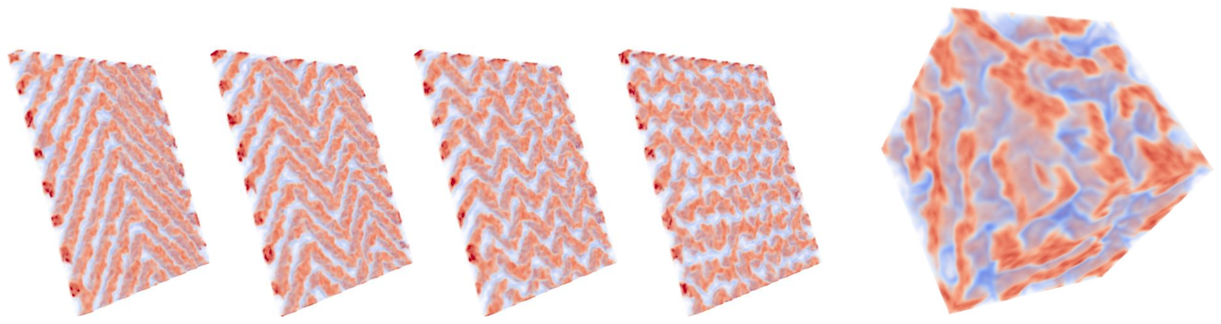


RESULTS



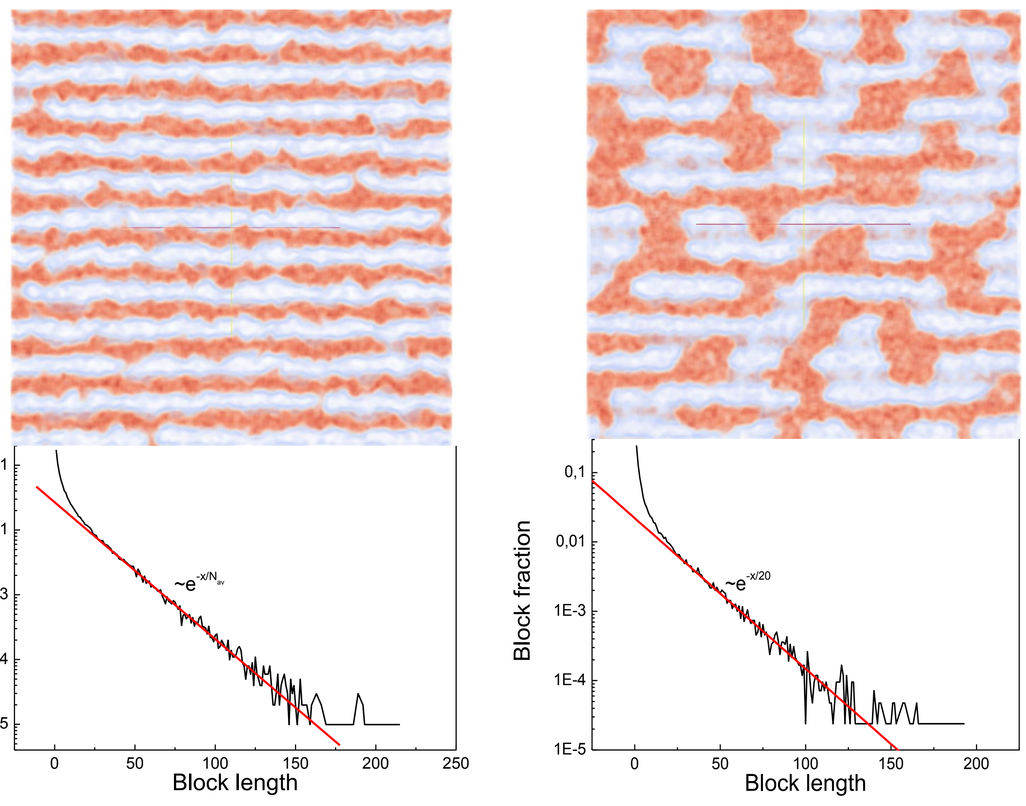


•The pattern facilitates the formation of structures with long-range order, which are stable after the removal of the pattern

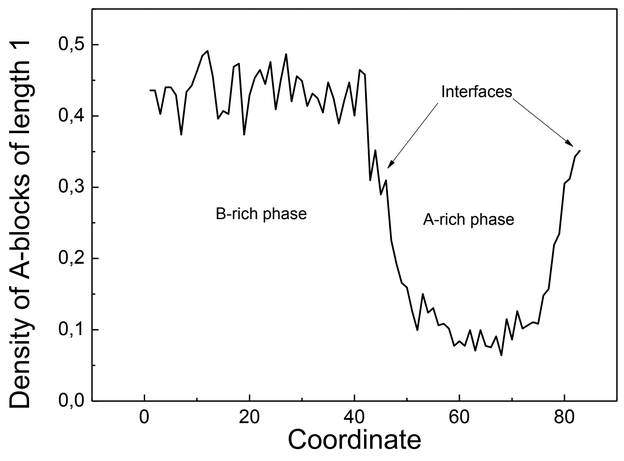


•More complex patterns like bends can be reproduced
•Bulk copolymerization gives no long-range structure

Reaction Parameters



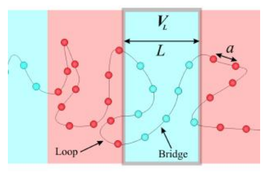
•If the reaction probabilities are too low, the resulting structures are very different even though the block-length distributions are the same
•In the course of reaction too large aggregates are formed, which probably leads to different distributions of blocks along the polymer chains – the long blocks are segregated from the short ones

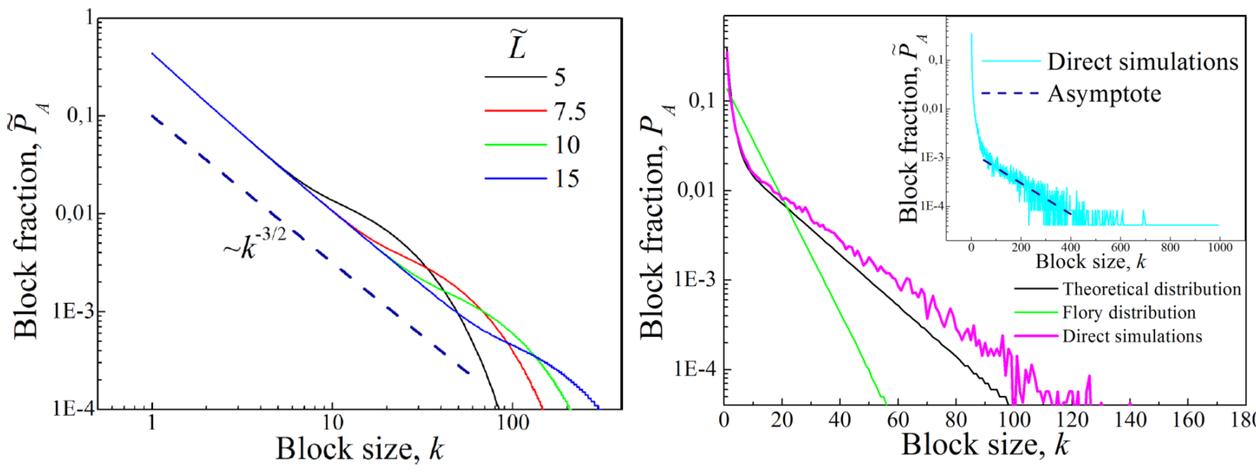


•Short blocks are located in the opposite domains, which decreases the roughness

Some theory

$$P_A(k) \cong \begin{cases} k^{-3/2}, & 1 << k << (L/a)^2 \\ \left(\frac{a}{L}\right)^3 \exp\left(-\frac{\pi^2 a^2}{6L^2}k\right), & k >> (L/a)^2 \end{cases}$$





Conclusions

• The presence of a pattern facilitates the formation of long-range order in melts of copolymers obtained during PIPS.
• Complex patterns can be reproduced
• Similar block-length distributions obtained under different reaction conditions can lead to very different structures due to different block sequences

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