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## LETTER TO THE EDITOR

## Pattern formation in microphase-separating copolymer gels

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### Abstract

Microphase separation in crosslinked diblock copolymers is investigated with a time-dependent Ginzburg–Landau model. Upon separation, polymers originally crosslinked in the homogeneous phase elongate parallel to the composition gradient. We take into account this elastic coupling as well as the random stress caused by the disordered network structure. The phase ordering process is numerically simulated to study the domain morphology. The random stress destroys the long-range orientational order of lamellae and creates jagged interfaces, which give rise to an asymmetric peak in the structure factor.

Polymer gels can exhibit ordered mesophases via microphase separation, which occurs in several ways. For instance, crosslinking a blend of A and B polymers in the homogeneous state causes an effective attraction between the two components, which is similar to the one in block copolymer melts [1]. The interplay between the entropic attraction and the chemical incompatibility leads to microphase separation upon cooling [2]. Copolymer gels [3, 4] and polyelectrolyte gels [5, 6] are among the other examples of microphase-segregating networks. In these materials attractive forces are present already in the uncrosslinked system.

While the onset of microphase separation has been studied extensively [7–16], much remains to be understood for the resulting domain morphology. The morphology is expected to differ from that of microphase-separating fluids such as diblock copolymer melts in two crucial aspects. Firstly, the random and non-equilibrium nature of crosslinking causes frozen internal stress in the network. For the lamellar phase, such random stress is predicted to destroy the long-range order of layer orientation [15]. In accord with this, recent experiments [3, 4] as well as a molecular simulation [16] found morphologies that significantly differ from periodic, globally-ordered patterns. Theoretical models of the highly heterogeneous morphology have been lacking so far [17]<sup>1</sup>. Secondly, upon segregation, polymers crosslinked in the homogeneous state spontaneously deform along the composition gradient, because of the incompatibility of the constituent monomers. For the lamellar phase, this means elongation perpendicular to the layer. If the layers are not uniformly aligned, their deformations interfere with each other and cannot be perpendicular to the layers everywhere. This is represented as an

<sup>1</sup> Phase behaviour of diblock copolymers in a random field has been analysed by Stepanow *et al* [17].

effective long-range interaction between orientationally correlated regions. Such non-local interaction would also affect domain morphology in the hexagonal phase, where the interface is curved and the spontaneous deformation is necessarily non-uniform. Thus, crosslinked binary polymers present an example of systems in which shear deformation is coupled to phase transition. Other materials showing this type of transition are liquid crystal elastomers [18] and martensitic alloys [21]. However, these systems do not involve long-range interactions that cause microphase separation, and in this sense the present system is unique.

In this letter, we address the domain morphology of microphase-separating gels with a phenomenological Ginzburg–Landau model, incorporating both the random disorder and strain-orientation coupling. We may point out that previous theories have treated elasticity only partially, through an effective polarization term [1], through the smectic Hamiltonian [15], or as a fixed random field [12]. By taking the elastic displacement to be independent of the compositional order parameter  $\psi$ , we can describe highly heterogeneous morphologies and their response to external strain. To be explicit, we assume a network of AB diblock copolymers crosslinked in the disordered phase and then quenched into either the lamellar or the hexagonal phase. The transition-induced deformation can be described by a coupling between the strain and the composition gradient tensor  $Q_{ij} = (\partial_i \psi)(\partial_j \psi) - (\delta_{ij}/d)(\nabla \psi)^2$  ( $d$  is the space dimension). The tensor is related to the interface normal  $\mathbf{n} = \nabla \psi / |\nabla \psi|$  just as the nematic order parameter tensor is related to the director in liquid crystals. We incorporate the random stress within the framework of linear elasticity [22, 23]<sup>2</sup>. We shall study the domain morphology by a two-dimensional numerical simulation of the phase ordering kinetics.

The basic variables of our Ginzburg–Landau model are the compositional order parameter  $\psi = \psi(\mathbf{r})$  and the elastic displacement  $\mathbf{u} = \mathbf{u}(\mathbf{r})$ . The former is proportional to the difference between the volume fractions of the two constituent monomers, say A and B, as

$$\psi \propto \phi_A - \phi_B. \quad (1)$$

The latter defines the linear strain tensor

$$E_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right). \quad (2)$$

For weakly crosslinked rubbers and gels, the bulk elastic modulus is much larger than the shear modulus (except in the neighbourhood of the spinodal for the volume phase transition). Therefore, we neglect volume change and impose the incompressibility condition

$$\nabla \cdot \mathbf{u} = 0. \quad (3)$$

The model free energy is composed of three parts as  $F = F_\psi + F_{\text{int}} + F_{\text{nd}}$ . The first part  $F_\psi$  is equivalent to the free energy for block copolymer melts in the weak segregation regime, given by

$$F_\psi = \int d\mathbf{r} \left[ \frac{A}{2} \psi^2 + \frac{C}{4} \psi^4 + \frac{L_0}{2} (\nabla \psi)^2 + \frac{L_1}{2} (\nabla \psi)^4 - \frac{M}{2} \psi \frac{1}{\nabla^2} \psi \right]. \quad (4)$$

The inverse operator  $1/\nabla^2$  is defined as  $(1/\nabla^2)\psi(\mathbf{r}) = -\int d\mathbf{r}' G(\mathbf{r} - \mathbf{r}')\psi(\mathbf{r}')$  using the Green function  $G(\mathbf{r})$  for the Laplace equation:  $\nabla^2 G(\mathbf{r}) = -\delta(\mathbf{r})$ . Note that the long-range interaction ( $\propto M$ ) is formally equivalent to de Gennes' elastic free energy for crosslinked homopolymer blends [1]. There the term arises solely due to crosslinking. For copolymer gels,  $M$  has contributions both from copolymerization and from crosslinking. The quartic gradient term is not essential and is added only to enhance the numerical stability of the simulation scheme. We note that, if  $L_1$  is too large, the term will induce an unusual 2D square

<sup>2</sup> A general formulation of the random stress is given in [22].

phase instead of the hexagonal one [24]. We do not take such a possibility into account and keep  $L_1$  sufficiently small.

The second part of the free energy,  $F_{\text{int}}$ , describes the coupling between strain and concentration gradient. Upon phase transition of the gel, each part of the system tends to elongate spontaneously and along the concentration gradient, as discussed above. The locally most favourable strain  $E_{ij}^0$  can be expanded in terms of  $Q_{ij}$ . Assuming small deformation, we retain only the linear term as

$$E_{ij}^{(0)}(\mathbf{r}) = \alpha Q_{ij}(\mathbf{r}), \quad (5)$$

where  $\alpha$  is the anisotropy parameter. The elastic free energy for this deformation is already incorporated in  $F_\psi$  as the de Gennes' polarization term [1]. When the internal strain deviates from the optimal value  $E_{ij}^{(0)}$ , we have an additional ('mismatch') contribution to the elastic energy, which we write as

$$F_{\text{int}} = \mu \int d\mathbf{r} (E_{ij} - \alpha Q_{ij})^2, \quad (6)$$

where  $\mu$  is the shear modulus.

Finally, we incorporate the frozen heterogeneity of the polymer network through the random stress  $R_{ij} = R_{ij}(\mathbf{r})$ , which adds the term

$$F_{\text{rnd}} = \int d\mathbf{r} R_{ij} E_{ij} \quad (7)$$

to the free energy. Because of the assumption of incompressibility,  $R_{ij}$  has only the shear component. We also assume it to have a Gaussian distribution with

$$\langle R_{ij}(\mathbf{r}) R_{kl}(\mathbf{r}') \rangle = R^2 \delta(\mathbf{r} - \mathbf{r}') \left( \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} - \frac{2}{d} \delta_{ij} \delta_{kl} \right), \quad (8)$$

where  $R$  is the disorder strength.

In orientationally heterogeneous states, the elastic strain mediates non-local effective interaction between orientationally correlated regions. To see this, we eliminate the strain from the free energy by assuming the mechanical equilibrium condition

$$\frac{\delta}{\delta \mathbf{u}} (F_{\text{int}} + F_{\text{rnd}}) = 0 \quad (9)$$

under a given average strain  $\overline{E_{ij}}$  and the local incompressibility (3). In doing this we borrow the results for nematic gels [19]. They elongate along the director upon the isotropic–nematic transition, which is described by a linear coupling between the nematic order parameter  $Q_{ij}$  and strain. Here we concentrate on the case  $\overline{E_{ij}} = 0$ : the gel is clamped in a rigid box and cannot deform as a whole. We can rewrite the elastic part of the free energy as  $F_{\text{int}} + F_{\text{rnd}} = \mu \int d\mathbf{r} (E_{ij}^2 + P_{ij} E_{ij} + \alpha^2 Q_{ij}^2)$ , where  $P_{ij} = -2\alpha Q_{ij} + \mu^{-1} R_{ij}$ . The equilibrium displacement is given by [19, 20]

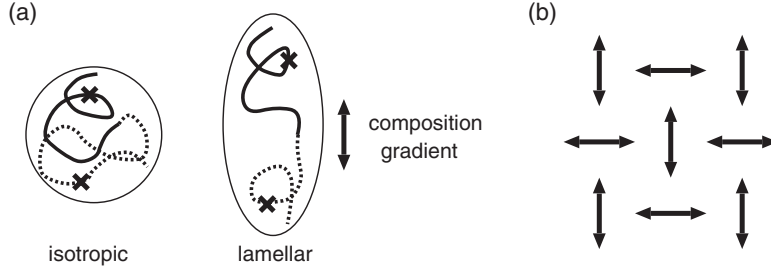
$$\mathbf{u}(\mathbf{q}) = \frac{i}{2\mu|\mathbf{q}|} (\mathbf{1} - \hat{\mathbf{q}}\hat{\mathbf{q}}) \cdot (\hat{\mathbf{q}} \cdot \mathbf{P}(\mathbf{q})), \quad (10)$$

where  $\hat{\mathbf{q}} = \mathbf{q}/|\mathbf{q}|$  is the normalized wavevector and  $\mathbf{1}$  is the unit tensor. The effective free energy is then obtained as

$$F_{\text{int}} + F_{\text{rnd}} = -\mu \int_q \left[ \frac{1}{2} |(\mathbf{1} - \hat{\mathbf{q}}\hat{\mathbf{q}}) \cdot (\hat{\mathbf{q}} \cdot \mathbf{P}(\mathbf{q}))|^2 - \alpha^2 |\mathbf{Q}(\mathbf{q})|^2 \right], \quad (11)$$

where  $\int_q = \int d\mathbf{q}/(2\pi)^d$ , or, in real space,

$$F_{\text{int}} + F_{\text{rnd}} = -\mu \int d\mathbf{r} \left[ \frac{1}{2} \mathbf{P} : \left( \frac{\nabla \nabla \nabla \nabla}{\nabla^2 \nabla^2} - \frac{\nabla \nabla}{\nabla^2} \right) : \mathbf{P} - \alpha^2 \mathbf{Q}^2 \right]. \quad (12)$$



**Figure 1.** (a) Conformations of a copolymer chain with crosslinks (marked by  $\times$ ). Microphase separation induces elastic strain parallel to the composition gradient. We depict the gradient as an apolar vector since its reversal does not change the induced strain. (b) Schematic picture of orientational correlation favoured by the Q–Q interaction (12). The composition gradient in the centre (shown by a vertical arrow) is better correlated in the oblique directions than in the other directions.

The first term in the integrand contains Q–Q and Q–R interactions that are highly anisotropic and long-ranged: in a given direction, they decay as the  $(-d)$ th power of the distance. The Q–Q interaction is an  $O((\nabla\psi)^4)$  quantity and does not shift the spinodal point. Its anisotropy can be interpreted in the following way [19, 20]. In an inhomogeneous state, each part of the gel tends to elongate along the local concentration gradient, which causes conflict between layers with different orientations. The conflict is resolved by the correlation pattern shown in figure 1(b), which minimizes the effective elastic energy. Orientational correlation is enhanced in the directions parallel or perpendicular to the composition gradient, and is enhanced in oblique directions.

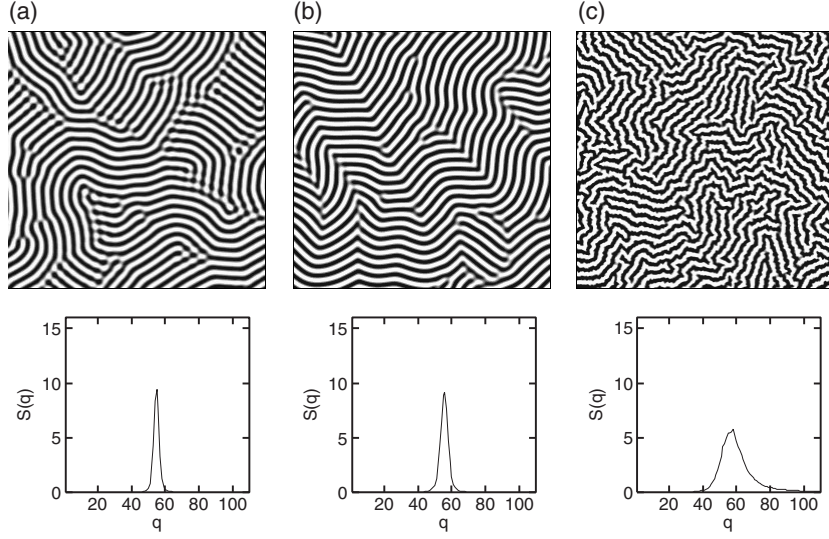
For the dynamics of the composition field, we employ the simplest kinetic equation for a conserved system,

$$\frac{\partial\psi}{\partial t} = \Gamma \nabla^2 \frac{\delta F}{\delta\psi}. \quad (13)$$

We assume that the elastic displacement relaxes much faster than the composition, and that the mechanical equilibrium condition (9) holds every moment. By solving these equations numerically, we simulated the process of microphase separation following a quench from the isotropic phase. A typical choice of the parameters was  $A = -1$ ,  $C = 1$ ,  $L_0 = 0.5$ ,  $L_1 = 0.5$ ,  $M = 0.8$ ,  $\mu = 2$ , and  $\alpha = 4$ , with the grid size set to unity. We varied the random stress  $R$  and the composition  $\bar{\psi}$ . We imposed periodic boundary conditions on a  $512 \times 512$  lattice and integrated equation (13) using the Euler scheme with time increment  $\Delta t = 0.05$ . To minimize artefacts of lattice anisotropy, spatial gradients are discretized using next-nearest neighbours. The displacement field was renewed by solving equation (10) every 10–20 time steps, using a fast Fourier transform. Correlation functions and structure factors are obtained from the statistics of 20 independent runs.

In figure 2 we show the domain morphologies in the late stage of microphase separation for symmetric composition  $\overline{\psi(\mathbf{r})} = 0$ . For uncrosslinked and crosslinked systems without random stress, we obtained regularly ordered lamellar patterns. The lamellae in the latter have sharper bends than in the former, which reflects the enhancement of  $\nabla\psi$  (and hence of  $\psi$ ) by Q–Q elastic interaction. The average internal strain  $\sqrt{\overline{E_{ij}^2}}$  was 0.11, or 8% in local elongation ratio. Random stress of modest strength freezes the layer ordering dynamics in its early stage, and creates jagged interfaces. In the same figure we show the structure factor

$$S(q) = \langle |\psi(q)|^2 \rangle. \quad (14)$$



**Figure 2.** Snapshots of  $\psi(r)$  and the structure factor  $S(q) = \langle |\psi(q)|^2 \rangle$ . Shown are the data at  $t = 6400$  of (a) an uncrosslinked system  $(\mu, \alpha) = (0, 0)$ , (b) clean gel  $(\mu, \alpha, R) = (2, 4, 0)$ , and (c) disordered gel  $(\mu, \alpha, R) = (2, 4, 0.3)$ , each for symmetric composition ( $\bar{\psi} = 0$ ).

The peak intensity is not much affected by the Q–Q interaction while it is lowered by the Q–R interaction. For quantitative characterization of the patterns it is useful to define the orientational correlation function

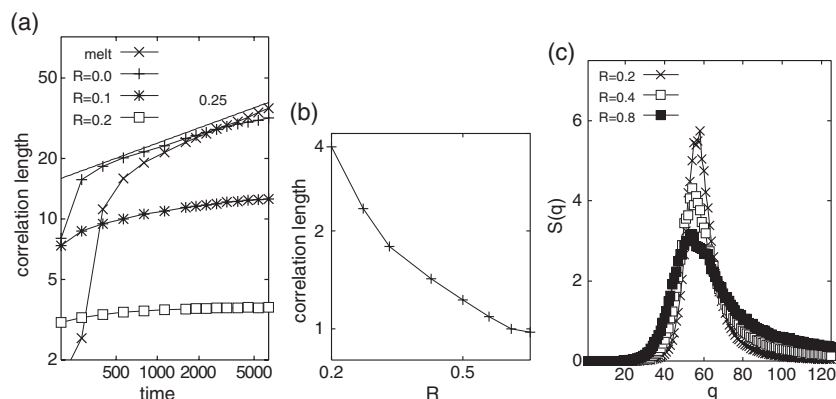
$$G(|\mathbf{r} - \mathbf{r}'|) = \langle \widehat{\mathbf{Q}}(\mathbf{r}) : \widehat{\mathbf{Q}}(\mathbf{r}') \rangle, \quad (15)$$

where  $\widehat{\mathbf{Q}}$  is the ‘hardened’ nematic order parameter defined as  $\widehat{\mathbf{Q}} = \mathbf{n}\mathbf{n} - \mathbf{1}/d$ , where  $\mathbf{n} = \nabla\psi/|\nabla\psi|$ . By using  $\widehat{\mathbf{Q}}$  instead of  $\mathbf{Q}$ , we can smooth out the oscillation in the correlation function of  $\mathbf{Q}$ , which reflects the underlying layer structure [25]. We define the orientational correlation length  $\xi$  by the equation  $G(\xi) = (1/e)G(0)$ . It is known that block copolymer melts in the weak-segregation regime and obeys the diffusive kinetic equation (13) showing a power-law-type coarsening,

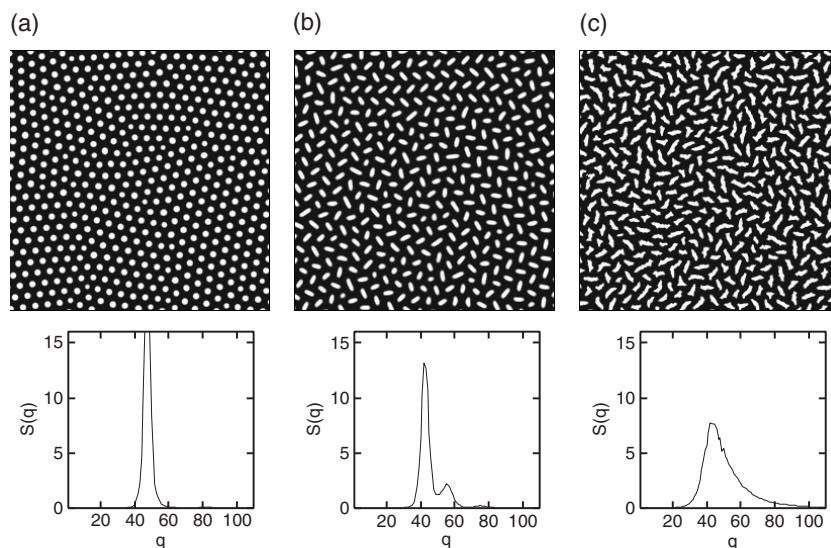
$$\xi \propto t^y, \quad (16)$$

with the exponent  $y = 1/4$  [25, 26]. In figure 3, we show the correlation length versus time. For an uncrosslinked system, the instantaneous growth exponent  $\tilde{y}(t) = d(\ln \xi)/d(\ln t)$  is slightly larger than  $1/4$  in the latest stage of our simulation. We confirmed that the deviation is due to the quartic gradient term in  $F_\psi$ . The Q–Q elastic interaction makes the growth slower. The exponent  $\tilde{y}(t)$  in the late stage is well fitted by the constants  $\tilde{y}_\infty = 0.21$  for  $\mu = 1$  and  $\tilde{y}_\infty = 0.18$  for  $\mu = 2$ . The random stress makes the growth much slower and monotonically decreases  $\tilde{y}(t)$  [27]<sup>3</sup>. For  $R \geq 0.2$ , the growth of  $\xi$  was virtually frozen by the end of the runs. The equilibrium correlation length  $\xi_{\text{eq}}$  for  $R \geq 0.2$  is plotted versus  $R$  in figure 3(b), which shows that  $\xi_{\text{eq}}(R)$  decays more weakly than a power law. This is in contrast with the 2D random-field  $XY$  model or nematic liquid crystal, which, in the strong disorder regime, show a nearly exponential decay of the orientational correlation length as a function of the random field strength [28–30]. The shape of the structure factor also varies with  $R$ , as shown in figure 3(c). For strong disorder, the peak has a broader tail on the large  $q$  side. It may be worth mentioning

<sup>3</sup> This is in contrast to thermal noise, which also causes a wavy layer morphology but accelerates the growth [27].



**Figure 3.** (a) The orientational correlation length  $\xi$  versus time (log–log plot). The line  $\xi \propto t^{1/4}$  is shown to guide the eye. (b) Equilibrium orientational correlation length  $\xi_{eq}$  versus disorder strength  $R$  (log–log plot). (c) The structure factor  $S(q)$ . The peak shape is asymmetric for strong disorder.



**Figure 4.** Snapshots of  $\psi(r)$  and the structure factor  $S(q) = \langle |\psi(q)|^2 \rangle$ . Shown are the data at  $t = 6400$  of (a) an uncrosslinked system  $(\mu, \alpha) = (0, 0)$ , (b) clean gel  $(\mu, \alpha, R) = (2, 4, 0)$ , and (c) disordered gel  $(\mu, \alpha, R) = (2, 4, 0.3)$ , each for asymmetric composition ( $\bar{\psi} = 0.3$ ).

that a similar asymmetric peak has been found in a recent Monte Carlo simulation [16]. The broad tail reflects the jagged interface, and the asymmetry of the peak shape becomes evident as the orientational correlation length becomes shorter than the interfacial thickness.

Finally we examine the case of asymmetric composition, by setting  $\bar{\psi} = 0.3$  in the initial condition. A cubic term in the free energy, as incorporated in a recent Ginzburg–Landau simulation of asymmetric diblock copolymers [31], is neglected as it does not significantly alter the morphology. In figure 4, we show the domain morphology of uncrosslinked and crosslinked systems with and without quenched disorder. The Q–Q elastic interaction causes elongated droplets that have a herring-bone-like correlation pattern. This configuration is



partially understood by the anisotropy of the Q–Q interaction (figure 1(b)): elongated droplets induce anisotropic strain around each, and tiling of such droplets lowers the elastic energy in comparison to the hexagonal pattern of circular droplets. The structure factor  $S(q)$  contains two peaks, corresponding to the separation between and the width of the droplets, respectively. Sufficiently strong random stress smears out the second peak, and the remaining peak is broader on the large  $q$  side as for the symmetric composition. The droplets get thinner and their length acquires a wider distribution for stronger disorder. For very strong disorder ( $R = 0.8$ ), the domains look like randomly bent strings with some branches (not shown).

To summarize, we set up a time-dependent Ginzburg–Landau model of microphase separation in block copolymer gels. Interplay between quenched disorder and transition-induced strain plays important roles in determining the domain morphology in the mesophases. The response to external strain is an interesting issue which will be discussed elsewhere. We hope that the present work stimulates further experimental and theoretical study of pattern formation in mesophasic gels.

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