Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Polymer Networks with Bi-continuous Gradient Morphologies Resulting from the Competition between Phase Separation and Photopolymerization

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1) Chemical structure of polymers used in this study :

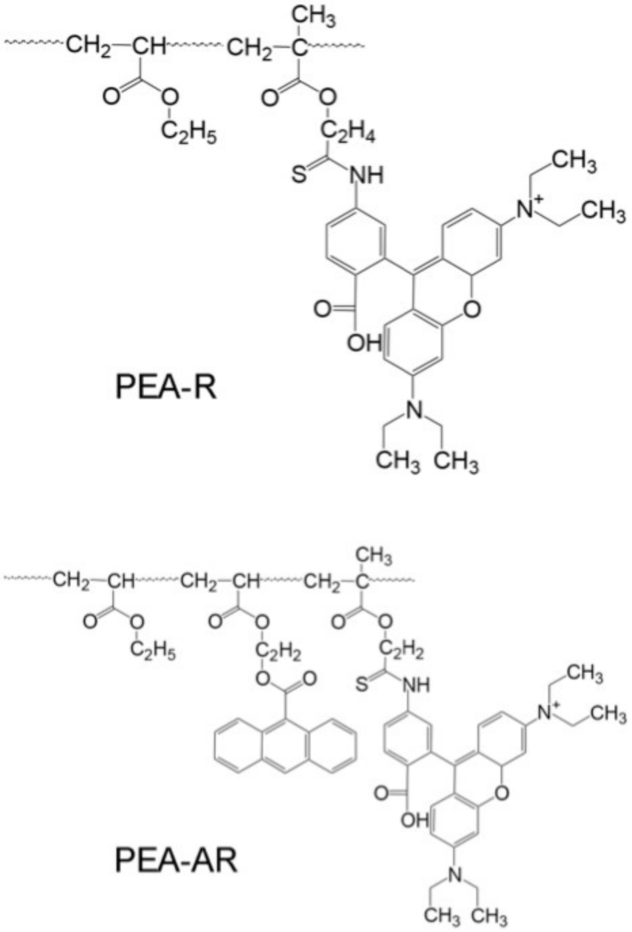

Figure S1. Rhodamine B-labeled poly(ethyl acrylate) [PEA-R] and doubly labelled with anthracene and rhodamine B [PEA-AR].

2) **Analysis of the Uni-axially Gradient Morphology: the Correlation**

Function Method.

Broadening of the 2D-FFT intensity distribution by the gradient bi-continuous morphology.

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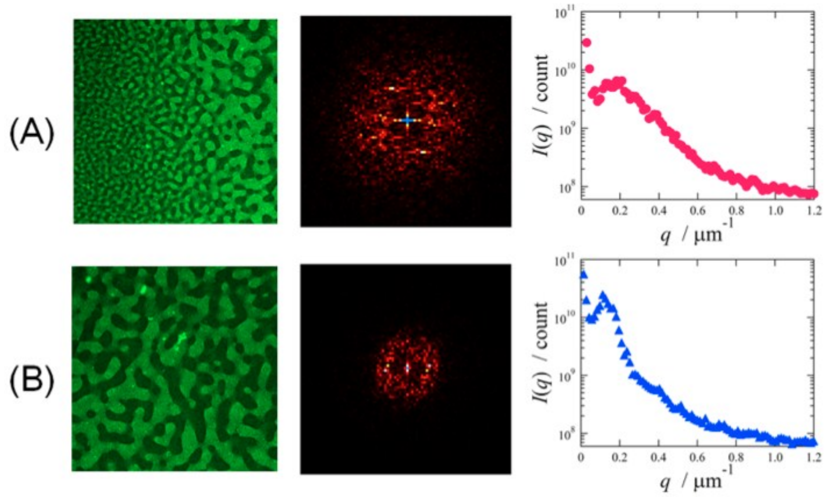

Figure S2. Analysis by using 2D-FFT for (A): a *gradient* bi-continuous morphology and for (B): a *uniform* bi-continuous morphology. Compared to the case of spatially uniform structure, the 2D-FFT power spectra were greatly broadened in the presence of a structural gradient (A).

The Correlation Function (CF) Method.

Since the morphology with a gradient of characteristic length scales along the Z-direction is spatially uniform within the XY plane for a given Z-coordinate, the 2D-FFT (fast Fourier transform) techniques would be appropriate for quantitative analysis of the morphology as previously reported.[S1)] However, for the uni-axially graded morphology exclusively in the XY plane observed at a given depth (Z-axis) of the sample, the 2D-FFT technique combined with the circular averaging cannot provide a correct analysis of the gradient morphology. The circular average of the 2D-power spectra would average out the distribution of the characteristic length scale ξ along the gradient, resulting in the broadened 1D Fourier power spectra illustrated, as an example, in **Figure S2 (A)**. Therefore, averaging of these 2D Fourier power spectra results in a distortion of the 1D-FFT results. We have accordingly developed the so-called correlation function (**CF**) techniques to analyze the uni-axially graded co-continuous morphology in the XY plane. In brief, the correlation function of the density $\rho(y)$ obtained for the fluorescent component in the morphology can be defined as:

$$g(x,\Delta y) = \frac{<\rho(x,y)\cdot\rho^*(x,y+\Delta y)>}{<\rho(y)\cdot\rho^*(y)>} \qquad (1)$$

Here, $\rho(y)$ represents the concentration of the fluorescent polymer component at the position of observation, and $\rho^*(y+\Delta y)$ is the conjugate part of $\rho(y)$ observed at the location $(y+\Delta y)$ in the morphology. In practice, $\rho(y)$ would be proportional to the fluorescence intensity measured at the location y by the laser-scanning confocal microscope (LSCM). As an example for the analysis using this correlation function (**CF**) method, a bi-continuous morphology obtained for a uni-axially gradient structure exclusively along the X-axis illustrated in **Figures S3(a) and S3(b)** was analyzed using this **CF** method. For this purpose, the line profiles of the fluorescence intensity at three positions A, B and C *perpendicular* to the gradient were measured and are shown in **Figure S3(c)**. Due to the low S/N ratio, all the line profiles taken at three positions A, B and C did not clearly exhibit a spatially periodicity with respect to Y. The spatial

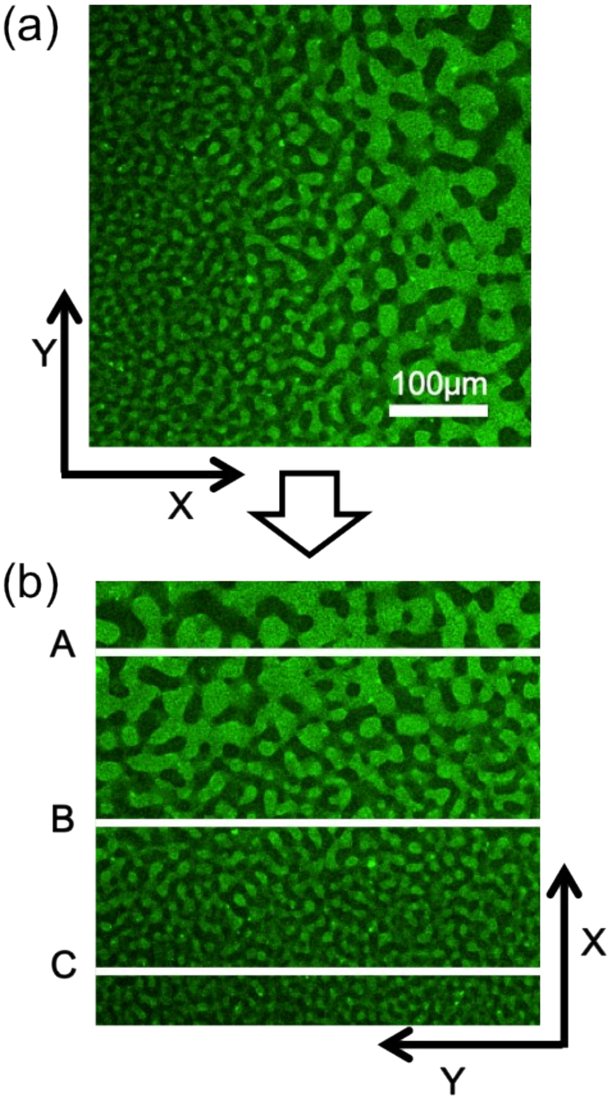

Figure S3. (a) : Typical *uni-axially* graded co-continuous morphology in the micrometer scales; (b) the same gradient co-continuous structure with three positions A, B and C subjected to the analysis using the correlation function (CF) method.

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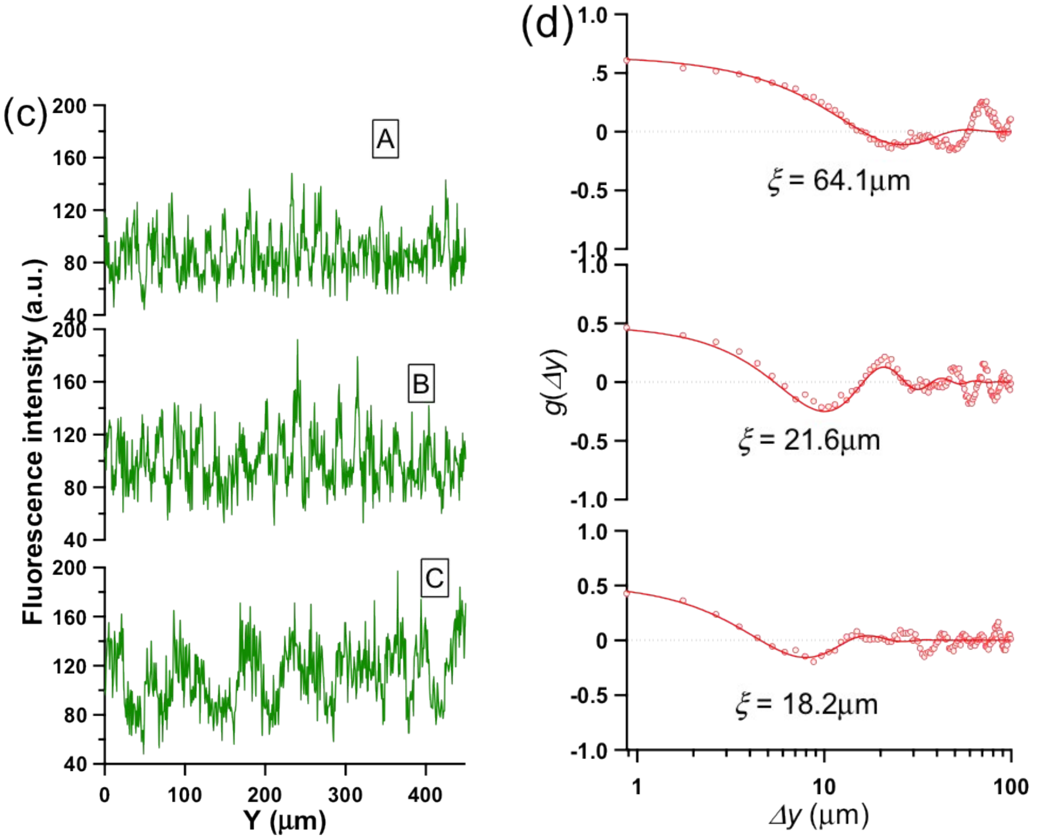

Figure S3. (c): Fluorescence intensity distribution of the morphology shown in Fig. 3(b); (d): the normalized correlation function of fluorescence intensity observed at three positions A, B and C with the fitting results using Eq. (2).

gradient of the morphology impedes the exact evaluation of the characteristic length scales because the gradient of characteristic length scales is averaged out by the procedure of analysis using 2D-FFT. Consequently, we have introduced an analysis method based on the spatial correlation function $g(x,\Delta y)$ defined in Eq. (1) to quantify the periodicity of the graded co-continuous (spinodal) structures. Taking advantages of this spatial modulation of the morphology, the characteristic length scale ξ of the structure was calculated by seeking the translational distance (Δy) of the composition profile $\rho(y)$ so that $\rho(y)$ becomes coincident with itself at $\rho^*(y+\Delta y)$ upon translation along the y-axis. The concept is sketched in **Figure S4**. Upon shifting the fluorescence intensity profile $\rho(y)$ and $\rho^*(y+\Delta y)$ along the Y-axis, there exist two cases:

1) The two concentration profiles are *in-phase:* the normalized correlation function takes its maximum $g(\Delta y) =$ (+1.0).

2) The two concentration profiles are *out-of-phase:* the normalized correlation function becomes minimum $g(\Delta y) =$ (-1.0).

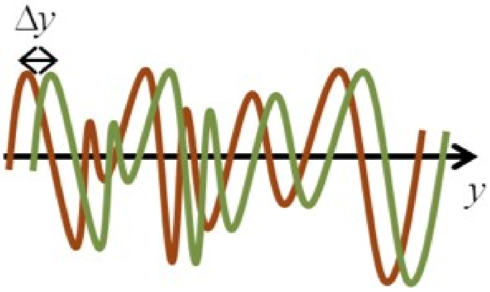

Figure S4. Schematic presentation of the shift △y between the two composition profiles.

Between these two limits, the normalized correlation function can take any value between (+1.0) and (-1.0) as illustrated in **Fig. S3(d)**. Therefore, the characteristic length scale ξ corresponding to a periodic concentration profile $g(x, \Delta y)$ can be calculated from the relation $\Delta y = (\xi)$ which is assured by the feature of periodic property of the spinodal morphology. However, because there exists a distribution of characteristic wavelengths in the spinodal structures, the deviation (fluctuations) of $(\Delta\xi)$ from the central wavelength of the spinodal structures needs to be considered. Assume that $g(x,\Delta y)$ decays exponentially with the distance (Δy), the characteristic length scale ξ was finally obtained by fitting the periodic function $g(x,\Delta y)$ to the following model equation proposed for the spatially graded bi-continuous morphology[S2]:

$$g(x,\Delta y) = \cos\left(\frac{2\pi\,\Delta y}{\xi(y)}\right)\,\exp\left[-\frac{2\pi\,\Delta y}{\Delta\xi(y)}\right] \qquad (2)$$

Shown in **Figure S3(d)** are the results of the analysis applying this correlation function method to analyze the spatially graded bi-continuous structure illustrated in Fig. S3(b). It was found that the calculation (solid curve) is well fitted to the experimental data (points) and the results of analysis are also consistent with the uni-axially graded morphology observed by a laser-scanning confocal microscope (LSCM) illustrated in Fig. S3 (b).

References

S1）H. Nakanishi, N. Namikawa, T. Norisuye and Q. Tran-Cong-Miyata, *Soft Matter* 2006, **2**, 149-156.

S2) M. Teubner and R. Strey, *J. Chem. Phys.* **87**, 3195 (1987). It is worth noting that the difference between Eq.(2) of this manuscript and Eq. (7) of Teuber-Strey in Ref. S2) is that the ***cosine*** function was used instead of ***sine*** function because the normalized correlation function defined by Eq. (1) should be unity at (delta y) = 0.