Mathematical Modelling of Cylindrical Forming Di-block Co-polymers confined in circular annular pores

Inayatullah Soomro[1], Israr Ahmed[1], Syed Baqer Shah[1], Abdul Majid[1], Raza Muhammad[1], Abdul Hameed[1], Ghulam Abas[1], Andrie V. Zvelindovsky[2], Marco Pinna[2], Waqar Ahmed[2]

Department of Mathematics, Shah Abdul Latif University, Khairpur, Pakistan[1]
University of Lincoln, Lincolnshire, UK[2]

Abstract
Soft materials receive increasing attention in research community as promising candidates for applications in nanotechnology. These applications include separation membranes with nano-pores, templates for nano-electronics, innovative catalyst, and drug delivery particles depend on the shape, size and the surface properties of the structures. From a computational a point of view different methods have been used to study soft materials in bulk and in confinement. Cell dynamic simulation (CDS) method has proved to be one of the effective methods to study and analyse the morphological behaviour of soft materials. In this contribution, the cylindrical morphological behaviour have been investigated by confining material into the circular annular pores. The study and investigation of nano-materials have been conducted by the mathematical and computational model developed by using polar mesh system.

Key words:
Block copolymers, Cell dynamic simulations (CDS), Polar coordinates, Cylindrical forming diblock copolymer system.

1. Introduction

Investigations of morphological behaviour of diblock copolymers in the melt have been extensively carried out in the last few decades [1]. Block copolymers is one of the classes of soft materials which comprise of different polymer blocks covalently connected to each other, this class of materials is important due to its self-assemble property and the length scale of these ordered structures is at nano-meter scale (10-100 nm) [2-4]. Diblock copolymers are simplest linear block copolymers systems which are obtained by grafting covalently two distinct homo-polymers [5, 6]. Due to phase separation driven by chemical incompatibilities between the different blocks they can spontaneously forms various patterns of nanostructures depending on block-block interactions, block composition, architecture of blocks, molecular characteristics and furthermore, external conditions such as geometry of confinement [5-7]. Bulk phase diagram of diblock copolymers has been studied and well understood on basis of experiments and theoretical studies. A number of ordered micro domain structures have been explored in diblock copolymer melt such as lamellae, hexagonally packed cylinders, body-centred array of spheres and complex structure such as bicontinuous network structure gyroid [4, 6, 9, 15-17]. More complex block copolymers and various morphologies can be obtained by placing block copolymers under geometrical confinements [3, 6]. Block copolymers under geometrical confinement forms many fascinating structures that are not formed in the bulk. Spatial confinement provide powerful tool to break the symmetry of an ordered structure [20] and paves the way for fabricating novel morphologies [2]. Under confinements, interfacial interactions, symmetry breaking, structural frustrations and confinement-induced entropy can play vital roles in structural control of soft materials [6, 21]. The pore is most reasonable geometry to be considered and its effects on morphology formation are important for nanotechnology applications and biology [18]. The curvature and interfacial interaction influence micro domains to change their orientation [4]. To avoid the difficulty associated with irregular boundaries or arbitrary shaped boundaries, entire physical problem can be transformed into boundary fitted curvilinear coordinate system such as polar, spherical and cylindrical coordinates [19]. Cylindrical geometry provide high degree of curvature imposed on the surface of nanoparticles causes a frustration of chain packing at the interface which eventually consequences change in the morphology [20]. Previous studies were done on one dimensional (thin film) and two dimensional cylindrical pores confined systems and under three dimensional confinements (spherical and elliptical) pores [23]. To the best of our knowledge no one has studied diblock copolymers under geometric confinement using CDS method applied in polar mesh system. However, it is our aim and desire to fill this gape by providing a complete understanding for applying CDS method using polar grid system.

2. Materials and Methods

Continuous physical space discretization into a uniform orthogonal computational space is the basic requirement for finite difference schemes. Furthermore, for accuracy, grid points will be clustered in space of large gradients, whereas for computational economy, grid points must be

spread out in space of small gradients. For these requirements Cartesian coordinate system is incompatible [27], however curvilinear coordinates are viable. In a CDS computation order parameter, $\psi(t,i)$ is evaluated at time step t and in cell i of a discrete lattice. The compositional order parameter in terms of local and global volume fractions is defined by the following relation:

$$\psi(i) = \phi_A(i) - \phi_B(i) + (1-2f) \qquad (2.1)$$

where ϕ_A, ϕ_B are the local volume fraction of monomers A and B respectively and f is global volume fraction of polymer system. The volume fraction of a monomer A is represented by, $f_A = N_A/(N_A + N_B)$, where N_A and N_B are the chain lengths of block A and block B respectively. The change with respect to time of order parameter is given by partial differential equation called Cahn-Hilliard-cook (CHC) equation [9]

$$\frac{\partial \psi}{\partial t} = M\nabla^2 \left(\frac{\delta F[\psi]}{\delta \psi} \right) \qquad (2.2)$$

where M is phenomenological mobility constant and can be taken as unit for correspondingly setting the time scale for diffusive process. In the equation (2.2) $F[\psi]$ is a free energy functional, which can be written as below:

$$F[\psi(r)] = \int dr [H(\psi) + \frac{D}{2}|\nabla \psi|^2]$$
$$+ \frac{B}{2}\int dr \int dr' G(r-r')\psi(r)\psi(r') \qquad (2.3)$$

In equation (2.3) the first term on the right hand side represents the short range interactions whereas the second term represents the long-range interactions, D is the diffusion constant, and B represents the chain length dependence to the free energy. The free energy function is given by:

$$H(\psi) = [-\frac{\tau}{2} + \frac{A}{2}(1-2f)^2]\psi^2 + \frac{v}{3}(1-2f)\psi^3$$
$$+ \frac{u}{4}\psi^4 \qquad (2.4)$$

where τ representing temperature constant and A, v, u are phenomenological constants. We can say all these parameters are related with molecular characteristics of diblock copolymer system [9]. Ohta and Kawasaki explained that τ, D and B are related with degree of polarization N, chain length b and the Flory-Huggins

parameter χ in the following mathematical relations are given by [28]:

$$\tau = -A(1-2f)^2 - \frac{1}{2N}\left(N_\chi - \frac{s(f)}{4f^2(1-f)^2} \right)$$
$$D\frac{b^2}{48f(1-f)}$$
$$\text{,and } B = \frac{9}{4N^2b^2f^2(1-f)^2} \qquad (2.5)$$

The Flory-Huggins parameter is inversely proportional to the temperature, if it is positive then it measures the strength of repulsion between incompatible blocks, if it has negative value it reflects the free energy which stimulates blocks towards mixing. In equations (2.5), s(f) is empirical fitting function of order 1. For simplicity we adopted the notation D and B by replacing the $\tilde{D}$ and $\tilde{B}$ respectively in equation (2.5). The parameters u and v can be calculated by the vertex function which is given by Leibler [29]. For simplicity these very complex functions are replace by approximate constant because the phenomena under consideration is quite general so that it is permissible for choosing the parameters for equations (2.2)-(2.4) as phenomenological constants [30]. Numerical evolution of CDS equation (2.2) by finite difference scheme for order parameter is given below:

$$\psi(i,t+1) = \psi(i,t) - \Delta t \{\langle\langle \Gamma(i,t) \rangle\rangle - \Gamma(i,t)\} \qquad (2.6)$$

Where $\langle\langle \Gamma(i,t) \rangle\rangle - \Gamma(i,t)$ represents isotropized discrete Laplacian in polar or cylindrical coordinates for free energy functional $\Gamma(i,t)$, where $i = (i_r, i_\theta, i_z)$ represents polar or cylindrical coordinates, and Δt is time steps for order parameter. Finite difference scheme for free energy functional is given by:

$$\Gamma(i,t) = g(\psi(i,t)) - \psi(i,t) + D[\langle\langle \psi(i,t) \rangle\rangle$$
$$-\psi(i,t)] + B\psi(i,t) \qquad (2.7)$$

For the case when polymers are being placing between two confining circular walls then the above equation for free energy functional can be modified as following:

$$\Gamma(i,t) = g(\psi(i,t)) - \psi(i,t) + D[\langle\langle \psi(i,t) \rangle\rangle$$
$$-\psi(i,t)] - s_i(r) \qquad (2.8)$$

where $s_i(r) = h_i \times \phi_i \times \delta_{n_r=1 \, or \, n_r=N_r}$, i denoting the attracting block (either A or B) of block copolymer system,

h_i is the strength of interaction between walls and the blocks and $\delta_{a=b}$ is Kronecker delta [31]. Periodic boundary condition used in angular direction whereas the reflective boundary conditions are used in radial and height direction. The discretisation of free energy function $g(\psi)$ is given by:

$$g(\psi)=[1+\tau-A(1-2f)^2]\psi-\upsilon(1-2f)\psi^2$$
$$-u\psi^3 \qquad (2.9)$$

The discretisation of Laplacian in polar and cylindrical coordinates mandatory for computation of equations (2.8) and (2.9). In the following sections isotropized discrete Laplacian in polar and cylindrical coordinates will be derived.

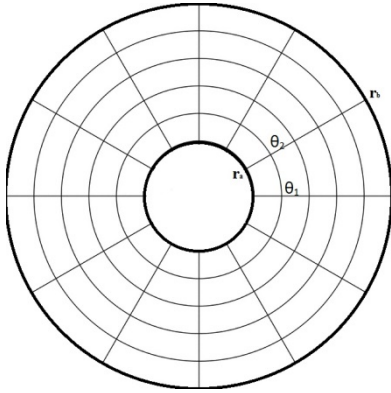## 2.1 Isotropic finite difference scheme of Laplacian in polar coordinate.

Fig. 1 Polar mesh diagram

The conservative form of Laplacian in polar coordinates is given by:

$$\nabla^2\psi=\left(\frac{1}{r}(r\psi_r)_r+\frac{1}{r^2}\psi_{\theta\theta}\right) \qquad (2.10)$$

With $r_a \leq r \leq r_b$ and $0 \leq \theta \leq 2\pi$

Finite difference scheme for the above Laplacian is given below:

$$\nabla^2\psi=\frac{1}{r_i(\Delta r)^2}\left[r_{i+\frac{1}{2}}(\psi_{i+1,j}-\psi_{i,j})-r_{i-\frac{1}{2}}(\psi_{i,j}-\psi_{i-1,j})\right]$$
$$+\frac{1}{r_i^2(\Delta\theta)^2}\left[\psi_{i,j+1}-2\psi_{i,j}+\psi_{i,j-1}\right] \qquad (2.11)$$

Here domain is a circular mesh contained between two circles of radius r_a and r_b, $r_i = r_a + i\Delta r$ and $\theta_j = j\Delta\theta$ for $i = 1,2,...,N_r$, $j = 1,2,...,N_\theta$

The Laplacian stencil relation is given by:

$$\nabla^2 = S + O_1(h_1^n) + O_2(h_2^n) \qquad (2.12)$$

where S denotes a stencil in polar coordinate system and the terms $O_1(h_1^n) + O_2(h_2^n)$ are the truncation errors of the order n due to finite mesh sizes h_1, h_2. The stencil must satisfy the following condition.

$$\sum_{k=1}^{3}\sum_{l=1}^{3}S_{k,l}=0. \qquad (2.13)$$

After mathematical manipulations, the isotropized discrete five point Laplacian in polar coordinates can be written in the following form:

$$\langle\langle\psi\rangle\rangle-\psi=\alpha\sum_{i=1}^{N_r}\sum_{j=1}^{N_\theta}\left[\frac{1}{r_i(\Delta r)^2}\left\{(r_{i+\frac{1}{2}})\psi_{i+1,j}+(r_{i-\frac{1}{2}})\psi_{i-1,j}\right\}\right.$$
$$\left.+\frac{1}{r_i^2(\Delta\theta)^2}(\psi_{i,j+1}+\psi_{i,j-1})\right]$$
$$-\sum_{i=1}^{N_r}\sum_{j=1}^{N_\theta}\psi_{i,j}, \qquad (2.14)$$

Where $\alpha=\dfrac{r_i^2(\Delta\theta)^2}{r_i(r_{i-\frac{1}{2}}+r_{i+\frac{1}{2}})+2}$ is the weighting factor for the nearest neighbourhood points.

3. Simulation Results

Diblock copolymer system is investigated in annular circular pore using polar grid system. In the first section, Mathematical and computational model have been examined using binary fluid simulations. In the second section, using CDS method we carry out study on diblock copolymer cylindrical forming system with various pore sizes in two dimensions. In the next section, diblock copolymers cylindrical forming system will be investigated in hollow cylindrical pore. Cylindrical morphology in cylindrical pore will be explored with various dimensions of cylinder. Polymer system will be examined with geometrical one dimensional and two confinements by placing preferential attractive walls with one of the blocks of polymer system.

3.1 Simulations of Binary Fluid

To test the method and developed CDS code, simulations of a binary fluid were carried out in the annular circular pore system. The simulation results for the binary mixture were obtained by using CDS parameter systems for lamella forming system except (B = 0). In this case, instead of microphase separation, a macrophase separation occurred in the pore system. This simulation setup is useful to investigate the behaviour of the mixture in the pore system. The simulation results were obtained on one million time steps to get the minimum energy level of the system.
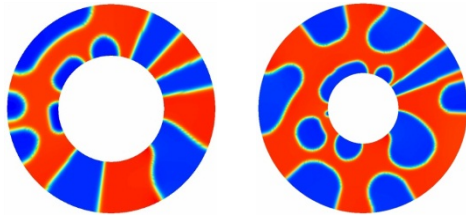

Fig. 3.1 Phase separation for binary fluid were obtained on 1 million time steps, in a pore system with the interior radius of the pore system was fixed at r_a = 3.0 and the grid sizes are (a) 30x360 (b) 60x360

The simulation result shows that domain clearly divide into two rich subdomains. In the pore system shown in Figure 3.1, domain divided into two rich subdomains, where A-rich subdomain is blue having its minimum $\psi^+ = 0.9090243$ and B-rich subdomain having its minimum $\psi^- = -1.077136$. The pore system shown in Figure 3.4(b) also divided into two subdomains, where A-rich subdomain has its minimum $\psi^+ = 0.908395$ and B-rich domain has its minimum $\psi^- = -1.083791$.

3.2 Cylindrical forming system in circular annulus nano pore

In this section, morphology of cylindrical diblock copolymer system in circular annular nanopores will be investigated. Cylindrical forming system can be achieved by using parameters, volume fraction f=40 and temperature parameter τ =20. The CDS system parameters used in the computations are given in table 1.

Table 1: CDS parameter system for cylindrical forming system

τ	f	u	v	B	D	A
0.30	0.40	0.50	1.50	0.02	0.50	1.50

The computational results for diblock copolymer Cylinder forming system in circular annulus nanopores are obtained by expanding pore size using exterior radius of pore for various values of pore radius. Simulation results are obtained on 1 Million time steps and in all simulation processes results got equilibrium state very well before one million time step. The simulations were started by initial random values for disordered state of order parameter in the range of $\Psi = \pm 0.5$, where Ψ represents order parameter. The simulation results were obtained in a pore system which is contained by concentric circles of radius r_a and r_b, where r_a represents interior radius of the pore system and r_b represents the exterior radius of the pore system. The interior radius of pore systems were fixed at r_a = 3.0 and the pore systems were extended by increasing the exterior radius of pore systems as r_b = 4, 5, 6, 7, 9. The size of the pore system is represented here by d = r_b - r_a . The simulation results were obtained with various pore sizes are shown in figure 3.2.
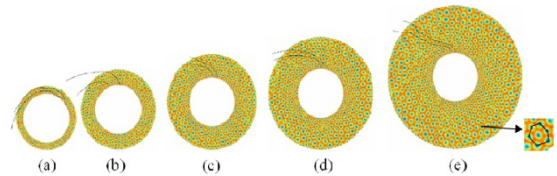

Fig 3.2. Simulation results of diblock copolymer system obtained in various disk sizes. The Cylindrical system in the pore geometry with pore sizes (a) d = 1 (b) d = 2 (c) d = 3 (e) d = 4 (f) d = 6

Cylindrical system in the pore geometry shows that microdomains make alignment on the logarithmic spiral lines in the pore system. Microdomains also show the hexagonal packing arrangements in the pore geometry. In Figure 3.2(a) the system is shown with pore size d = 1 cylinders lie on the logarithmic spiral lines where spiral line are shown by dashed lines. In this system spiral rays are narrowed or spiral lines have short distances from the origin. The pore system with size d = 2 also shows that the cylinders are aligned on the logarithmic spiral lines where spiral lines are shown by the dashed lines as shown in Figure 3.2(b). In this system spiral rays are bit wider or have a more distance from the centre of the pore system as compared to previous sized pore system. The pore system having pore size d = 3 as in Figure 3.2(c) shows micro domains lie on the spiral lines having almost same spiral rays distance from the origin of the pore system. However, the pore system with size of the pore d = 4 shows cylinders on the spiral lines having spiral rays wider due the size effect of the pore geometry. Furthermore, pore system with size d = 6 shows micro domains on the spiral lines with spiral rays very much wider due the size effect

of the pore geometry as shown in Figure 3.2(d). The cylinders in the pore system are also hexagonally packed as shown in Figure 3.2(d) along with zoomed snapshot of the image. This shows that in the pore geometry cylinders align on the spiral rays and spiral arms becomes wider with respect to increase in the pore size of the system. The experimental study shows that the frustration caused by the confinement distorts the natural packing of hexagonal arrangements of the microdomains [32, 33].

The pore system is also expended by the increasing interior radius of the pore system at two fixed values $r_a = 5$ and $r_a = 7$ and the exterior radius of the pore system was increased at different values to expand the pore system. In both pore systems we obtained similar patterns of the cylindrical forming system in the pore geometry. The cylindrical forming systems were observed packed along the spiral lines in the pore geometry due to curvature influence. Hexagonal packing of the micro domains was also observed inside the pore geometry.

Diblock copolymer cylindrical forming system was studied in circular annulus pore system using preferential attractive circular walls having interaction strength $\alpha = 0.2$ between the walls and one of the segments of the polymer system. In one dimensional confinement attractive circular wall interaction with one of the segments of the polymer system applied in radial r direction in annular pore system. The simulation results were obtained in a pore system by keeping fixed the interior radius of the pore system $r_a = 3$ and pore size was expanded by increasing exterior radius r_b of the pore system. The parameter $d = r_b - r_a$ represents the pore size of the pore geometry. In the first case, attractive wall for interaction with monomer **A** was applied in one dimension in the pore system.

them in the concentric circles in the pore geometry. However, there are still micro domains packed on the rough spiral lines inside the pore system. Micro domains which had been distorted from both spiral and circular packing were due to the packing frustration caused by interplay of both curvature and confinement effects. In pore system having pore size d = 2 as shown in Figure 3.3(a) the cylinders were packed in three concentric circles in the pore system. The pore system with size of the pore d = 3, micro domains were packed in four concentric circle in the pore geometry. The pore size d = 4, contains cylinders packed in six concentric circles in the pore system. In this sized system micro domains are not well packed in the in circular lines due the size effect. The pore size d = 6, contains eight circular lines of the micro domains in the pore system. In this sized system micro domains are also not well packed in the circular lines due to the size effect.

The simulation results for diblock copolymer cylindrical system with preferential attractive circular wall with interaction between circular walls and monomer **B** were obtained in circular annular pore system. Interaction strength $\alpha = 0.6$ applied between the circular walls of the pore system and **B** segment of the polymer system in the pore geometry. Similarly, the simulation results were obtained in a pore system whose interior radius $r_a = 3$ of the pore system was fixed and the pore size was extended by exterior radius r_b of the pore system, where d defined the pore size of the pore system.
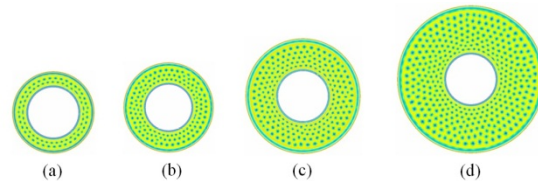
Fig. 3.4 Cylindrical systems with interfacial affinity to B block and the pore size of the systems are (a) d = 2 (b) d = 3 (c) d = 4 (d) d = 6.0.

The cylindrical forming system under geometric confinement with circular walls having affinity with **B** monomer shows similar patterns as was in the case when walls had affinity with **A** monomer in the pore geometry. Microdomains are packed along the concentric circles inside the pore system. The pore system of size d = 2 shows micro domains packed into two concentric circles in the pore geometry as shown in Figure 3.4(a). However, similar sized system pore walls having affinity with the **A** monomer showed micro domains are packed into three concentric circles in the pore system which is due to the incompatibility of segments of the polymer system. Incompatibility of both segments squeeze down the micro domains because the **A** segment remains outside of the
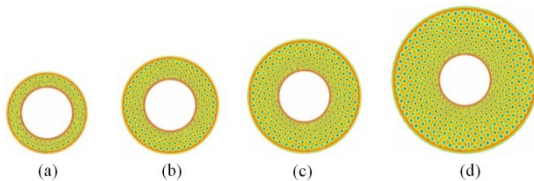

Fig. 3.3 Simulation results for diblock copolymer system obtained with preferential attractive walls having affinity to A block and the pore size of systems are (a) d = 2 (b) d = 3 (c) d = 4 (d) d = 6

The simulation results obtained in one dimensional circular confinement show that the surface preference influences the micro domains to form circular alignment in concentric circles around the centre of the pore system. Surface affinity to **A** segment of the polymer system distort the spiral alignment of the micro domains pack

micro domains and when the **B** segment was placed on the circular walls. The pore system d = 3 shows cylinders are packed in three concentric circles in the pore system as shown in Figure 3.4(b). Similarly the pore system d = 4 shows micro domains are aligned in five concentric circles in the pore geometry as shown in Figure 3.4(c). Finally the pore system d = 6 shows micro domains are packed in seven concentric circles in the pore system as shown in Figure 3.4(d). Simulation results show that the spiral packing of micro domains is influenced by the curvature effect whereas the micro domains packed into concentric circles due the confinement effect in the pore geometry.

4. Conclusion

The computation study have been carried out on diblock copolymer cylindrical forming system using CDS method applied in curvilinear coordinates. The computational results were obtained by confining nano particles in the circular annular domain using polar mesh system. Cylindrical forming system in the neutral circular annular pore system shows, the novel packing arrangements along the spiral lines. However, in the larger pore systems spiral packing arrangements alters and system regains in the classical hexagonal packing arrangements in the circular pore system. While, in the presence of interacting circular walls microdomains induces packing arrangements in the concentric circular rings in the pore geometry.

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