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尺寸標度競爭下 $A_m(B_2C)_n$ 共聚合物的自組裝行為(2/3) 期中進度報告(精簡版)

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計畫主持人：黃慶怡

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中文摘要

關鍵詞：共聚合物；自身聚集行為；耗散粒子動力學；等級結構；結構內有結構

本計畫主要想探討在尺寸標度的競爭下 ABC 共聚合物的自身聚集行為，如何受到分子結構 (molecular architecture)、成分間的不相容性、各成分的組成、以及聚合度的影響。一般來說，在傳統的 AB 塊狀共聚合物中，所形成的微結構通常只具有一個特徵尺寸大小(10-1000Å)，如果能夠在 B 塊狀中以非共價鍵或共價鍵的方式將第三種小分子 C 連接在 B 塊狀中，此時來自於單體 B 與 C 的不相容性所造成的微結構(B-rich、C-rich)尺寸等級，將會比來自於塊狀 A 與 B(C)之間的不相容性所造成的微結構(A-rich、B(C)-rich)尺寸來得小許多，因而造成了二種尺寸標度等級的微結構可能性。此等級結構的形成，目前發現與材料的光電性質有著特殊的變化，因而增加了共聚合物在光電材料上的應用發展。在第二年度中，我們已成功地將三種系統：A₂B miktoarm star、A-block-(B-graft-C)、以及 A₂-star-(B-alt-C)的結構模擬行為，投稿並刊登至三篇期刊中。

英文摘要

Keywords: **block copolymers; self-assembling behavior; dissipative particle dynamics; hierarchical structure; structure-within-structure**

We employ dissipative particle dynamics (DPD) to examine the self-assembling behavior of ABC copolymers which involve competing length scales. Hierarchical polymeric materials, with *structure-within-structure* morphologies, have attracted interest due to their potential as responsive materials. In this project, we systematically examine the effects of composition, degree of copolymerization, and the incompatibility between each pair of components, on the formation of microstructures with two different length scales in different architectures of copolymers including AB₂ miktoarm star, A-block-(B-graft-C), and A₂-star-(B-alt-C).

前言、目的與文獻探討

由於分子生物、物理、化學、材料科學等的蓬勃發展與應用，對於物質之分子或分子集團其結構的了解日益重要。尤其是塊狀共聚合物系統，由於化學鍵在兩個塊狀之間形成，因此來自於不同分子種類的不相容性，並不會促使巨觀相分離的產生，取而代之的是奈米級微結構的形成(10-1000Å)，這些型態具有新穎的材料特性和高價值的科技應用。一般來說，最簡單的 AB 塊狀共聚合物，其所形成的微結構通常只具有一個特徵尺寸大小，若能將其改進使之產生有二種特徵尺寸等級可能性的微結構，將更有助於尖端科技產業的發展[1]。例如：最近有學者在 PS-P4VP(polystyrene-b-poly(4-vinylpyridine))塊狀共聚合物中，將 P4VP 一端接上 PDP(pentadecylphenol)支鏈，而形成了 PS-(P4VP-comb-PDP)共聚合物系統，發現到在較高溫下，來自於 PS 與 P4VP(PDP)之間的不相容性，會導致微結構(PS-rich and P4VP(PDP)-rich)的形成；然而，隨著溫度的降低，另一較小尺寸的微結構(P4VP-rich and PDP-rich)會因為 P4VP 與 PDP 之間的不相容性而在其中產生，因而形成了二種尺寸等級的微結構可能性；此現象的產生因而導致了材料的光電性質有著特殊的變化，而增加了共聚合物在光電材料上的應用發展[2-5]。因此，最近相關於運用理論計算方法來探討高分子材

料系統形成等級結構(hierarchical structure)的研究，也就是相關於一較大結構中衍生另一較小結構(structure-within-structure)方面的研究，開始吸引學者的注意。

目前大部分理論計算的研究系統，主要集中在二種共聚合物混摻系統[6-10]以及 ABC 三團聯線性共聚合物系統[11]這二種，基本上，在這些系統中若能形成二種尺寸之等級結構，其尺寸均相差不大；因此，若要拉大尺寸等級的差異性，我們認為以下的共聚合物系統，例如：A-*block*-(B-*graft*-C)、以及 A-*block*-(B-*alt*-C)、•••等較適合。這是因為來自於單體 B 與 C 的不相容性所造成的微結構(B-rich、C-rich)尺寸等級，理所當然比來自於塊狀 A 與 B(C)之間的不相容性所造成的微結構(A-rich、B(C)-rich)尺寸來得小。就晚學所知，目前除了文獻中有一篇相關於 A-*block*-(B-*alt*-A)系統的自組裝行為分析[12]，尚無人針對此類系統作完整的相行為分析。另外，文獻中也有一些理論研究顯示了藉由改變分子間的建構方式(architecture)，例如：A-*block*-(B-*graft*-C) linear-comb [13]、AB_n 或 ABC 等 miktoarm 星形高分子[14-17]，共聚合物所展現的微結構型態與尺寸等級深受其影響。然而這些相關的研究目前仍屬少數、並不完整。

因此，為了能更深入了解尺寸標度競爭下共聚合物的自組裝行為，在本計畫中，我們選擇了以下三種系統 AB₂ miktoarm star、A-*block*-(B-*graft*-C)、以及 A₂-*star*-(B-*alt*-C)共聚合物 (如 Fig. 1 所示)，我們運用耗散粒子動力學(Dissipative Particle Dynamics, DPD)計算法，來模擬微結構衍變如何受到 architecture、成分間的不相容性、各成分的組成、以及聚合度的影響。二年下來，每一系統都有具體令人振奮的結果，且已整理三篇投稿並刊登至期刊中。

DPD Simulation Method

In the DPD simulation [18], the time evolution of motion for a set of interacting particles is solved by Newton's equation. For simplicity, we assume that the masses of all particles are equal to 1. The force acting on the i -th particle $\vec{f}_i$ contains three parts: a conservative force $\vec{F}_{ij}^C$, a

dissipative force $\vec{F}_{ij}^D$, and a random force $\vec{F}_{ij}^R$, i.e.,

$$\vec{f}_i = \sum_{i \neq j} \left(\vec{F}_{ij}^C + \vec{F}_{ij}^D + \vec{F}_{ij}^R \right) \quad (1)$$

where the sum is over all other particles within a certain cut-off radius r_c . As this short-range cut-off counts only local interactions, r_c is usually set to 1 so that all lengths are measured relative to the particle radius.

The conservative force $\vec{F}_{ij}^C$ is a soft repulsive force and given by

$$\vec{F}_{ij}^C = \begin{cases} a_{ij} \left(1 - \frac{r_{ij}}{r_c} \right) \vec{n}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases} \quad (2)$$

where a_{ij} is the repulsive interaction parameter between particles i and j , $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, $r_{ij} = |\vec{r}_{ij}|$,

and $\vec{n}_{ij} = \frac{\vec{r}_{ij}}{r_{ij}}$. The repulsion parameter a_{ij} is often related to the Flory-Huggins interaction

parameter χ_{ij} by the following equation

$$\begin{aligned} a_{ij}(T) &= a_{ii} + 3.497k_B T \chi_{ij}(T) & \text{for } \rho=3 \\ a_{ij}(T) &= a_{ii} + 1.451k_B T \chi_{ij}(T) & \text{for } \rho=5 \end{aligned} \quad (3)$$

where ρ is the particle density of the system. The term a_{ii} , which corresponds to the repulsion parameter between particles of the same type i , is determined by matching the water compressibility as

$$a_{ii} = 75k_B T / \rho \quad (4)$$

The dissipative force $\vec{F}_{ij}^D$ is a hydrodynamic drag force and given by

$$\vec{F}_{ij}^D = \begin{cases} -\gamma \omega^D(r_{ij})(\vec{n}_{ij} \cdot \vec{v}_{ij})\vec{n}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases} \quad (5)$$

where γ is a friction parameter, ω^D is a r -dependent weight function vanishing for $r \geq r_c$, and $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$.

The random force $\vec{F}_{ij}^R$ corresponds to the thermal noise and has the form of

$$\vec{F}_{ij}^R = \begin{cases} \sigma \omega^R(r_{ij})\theta_{ij}\vec{n}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases} \quad (6)$$

where σ is a parameter, ω^R is also a weight function, $\theta_{ij}(t)$ is a randomly fluctuating variable.

Note that these two forces $\vec{F}_{ij}^D$ and $\vec{F}_{ij}^R$ also act along the line of centers and conserve linear and angular momentum. There is an independent random function for each pair of particles. Also there is a relation between both constants γ and σ as follows,

$$\sigma^2 = 2\gamma k_B T \quad (7)$$

In our simulations, $\gamma = 4.5$ and the temperature $k_B T = 1$. As such, $\sigma = 3.0$ according to Eq. (7).

In order for the steady-state solution to the equation of motion to be the Gibbs ensemble and for the fluctuation-dissipation theorem to be satisfied, it has been shown that only one of the two weight functions ω^D and ω^R can be chosen arbitrarily,

$$\omega^D(r) = [\omega^R(r)]^2 \quad (8)$$

which, in further, is usually taken as

$$\omega^D(r) = [\omega^R(r)]^2 = \begin{cases} (r_c - r_{ij})^2 & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases} \quad (9)$$

Finally, the spring force $\vec{f}^s$, which acts between the connected beads in a molecule, has the form of

$$\vec{f}_i^s = \sum_j C \vec{r}_{ij} \quad (10)$$

where C is a harmonic type spring constant for the connecting pairs of beads in a molecule, and is chosen equal to 4 (in terms of $k_B T$).

Note that a modified version of the velocity-Verlet algorithm is used here to solve the Newtonian equation of motion

$$\begin{aligned} r_i(t + \Delta t) &= r_i(t) + v_i(t) \cdot \Delta t + \frac{1}{2} f_i(t) \cdot \Delta t^2 \\ \tilde{v}_i(t + \Delta t) &= v_i(t) + \lambda f_i(t) \cdot \Delta t \\ f_i(t + \Delta t) &= f_i[r_i(t + \Delta t) + \tilde{v}_i(t + \Delta t)] \\ v_i(t + \Delta t) &= v_i(t) + \frac{1}{2} \Delta t \cdot [f_i(t) + f_i(t + \Delta t)] \end{aligned} \quad (11)$$

In particular, we choose $\lambda = 0.65$ and $\Delta t = 0.05$ here. As such, the time evolution of morphology patterns is recorded until the systems show a stable pattern.

結果與討論

A₂B Miktoarm Star Copolymers (This part has been accepted in *Polymer*.)

In simulating the phase behavior of A₂B miktoarm star copolymers by DPD, the particle density ρ is kept equal to 3, and hence the dimensionless interaction parameter (i.e., in terms of $k_B T$) between equal particles a_{II} in Eq. (4) is set equal to 25 to resemble the Flory interaction parameters $\chi_{II} = 0$; $I = A, B$. The total number of beads for an A₂B chain is fixed at $N=20$. We adopt 3-D lattice with at least 15x15x15 grids to ensure that the side length of the simulation box is significantly larger than the radius of gyration (R_g) of A₂B chains. In our simulated systems, the value of R_g is approximately 1.6 to 2.0 grids. In each pattern, the red and green colors are used to represent A and B, respectively.

Fig. 2 displays the phase diagram of A₂B miktoarm star copolymers simulated by DPD. We also include the phase diagram determined by SCMF theory [14], which is plotted with the black curve in Fig. 2, as a comparison. Similar to linear diblock copolymers, the formation of microstructures is mainly dominated by the composition f_B . Fig. 3 illustrates the morphology variation of A₂B with f_B when $a_{AB} = 34$. It is clear that a series of transition from

$$S_B^{A15} (f_B = 0.2, 0.25) \rightarrow C_B^{\text{HEX}} (0.3 \leq f_B \leq 0.45) \rightarrow (\text{perforated lamellae of A, PL}_B) (f_B = 0.48)$$

$$\rightarrow L (0.5 \leq f_B \leq 0.7) \rightarrow (\text{perforated lamellae of B, PL}_A) (f_B = 0.75) \rightarrow C_A^{\text{HEX}} (f_B = 0.8) \text{ is}$$

observed. Moreover, when the interaction parameter a_{AB} decreases, the ordered A₂B copolymers are expected to become disordered. However, due to the effects of thermal fluctuations, we observe that between the totally disordered and the well ordered states, the systems tend to form a micelle-like structure, i.e., with chains aggregating as large droplets but no formation of well ordered structures. Here, we sort it out as the disordered state. Basically these DPD simulated microstructure regimes by varying the composition f_B are in good agreement with the SCMF results except when f_B is larger.

Recall that when f_B is larger, such as $f_B = 0.75 \sim 0.8$, the SCMF theory predicted a wide region of C_A^{HEX} , i.e., the minority A-branch arms form the hexagonally packed cylinders. In our DPD simulations, we find that when the interaction parameter a_{AB} is larger, although the A₂B copolymers can form a stable C_A^{HEX} phase (a typical example when $f_B = 0.8$ and $a_{AB} = 34$ is shown in Fig. 3) eventually, these A-formed cylinders still connect with each other after running a long simulation time. As the interaction parameter a_{AB} decreases, for example when $a_{AB} = 33$ and f_B is still fixed at 0.8, the resulting morphology pattern shown in Fig. 4 clearly demonstrates that these miktoarm star copolymers can no longer form C_A^{HEX} but instead a tube-like phase. A reasonable explanation may be given as follows. When the component with more arms per molecule (i.e., A) is a minority so that these A arms remain on the concave side of the interface, because curving the interface inward toward the A domains causes more lateral crowding of these A multi-arms and thereafter excess stretching in A, the formed microstructures become loose and less ordered. That is, the well ordered A-formed cylindrical and/or spherical phases are difficult to form and only a tube-like phase is observed. In fact, based on the TEM micrograph similar to the 2-D pattern in Fig. 4, Pochan et al. [19] reported similar results in PS-PI₂ miktoarm star copolymers that when the composition of PS, f_{PS} , is 0.81, the system is not ordered into a specific lattice but is microphase separated into worm-like micelles, as observed in DPD.

In order to quantitatively compare the phase diagram determined from both DPD and SCMF theory, we first use Eq. (3) to transform the interaction parameter in the DPD simulations, a_{AB} , into the Flory-Huggins interaction parameter in the SCMF theory, χ_{AB} . As the copolymer chains in our simulations are very short ($N=20$), due to the significant fluctuation effects which stabilize the disordered state, the expected values of $\chi_{AB}N$ at the ODT are larger than those for infinite chains, i.e., $(\chi_{AB}N)_{\text{eff}}$, predicted by SCMF theory. Therefore, we have to convert $\chi_{AB}N$ for a finite chain length into $(\chi_{AB}N)_{\text{eff}}$ for an infinite chain length. As far as we know, this conversion has not been derived theoretically for A₂B miktoarm star copolymers. We thus simulate the phase

behavior for a series of N varying from 10 to 40 at a fixed composition value of $f_B = 0.6$, and

analyze the variation of $(\chi_{AB}N)_{\text{ODT}}$ with N in Fig. 5. The value of $(\chi_{AB}N)_{\text{ODT}}$ for a specific N is determined by averaging the lowest $\chi_{AB}N$ for an ordered state and the highest one for a disordered state, which are designated with error bars in Fig. 5. The log-log plot of

$(\chi_{AB}N)_{\text{ODT}}/(\chi_{AB}N)_{\text{ODT,eff}} - 1$ and N , as shown in Fig. 5, reveals a straight line. This manifests

the fact that in A_2B miktoarm star copolymers, the decrease of the effective segregation parameter caused by fluctuations for a finite chain N obeys the equation $(\chi_{AB}N)_{\text{eff}} = (\chi_{AB}N)/(1 + \alpha N^\beta)$.

From Fig. 5, we obtain the value of $\alpha = 3.2$ and $\beta = -0.43$. We then apply this equation to convert

$\chi_{AB}N$ into $(\chi_{AB}N)_{\text{eff}}$, and compare our simulated phase diagram with that determined by SCMF

theory in Fig. 2. We observe that both phase diagrams are in quantitatively good agreement.

Recall that in linear AB diblock copolymers the corresponding ODT value of $\chi_{AB}N$ for a finite chain has been derived by including the fluctuation effects [20], and applied to quantitatively match the phase diagrams between the DPD simulation and SCMF theory [21],

$$(\chi_{AB}N)_{\text{eff}} = \frac{\chi_{AB}N}{1 + 3.9N^{\frac{2}{3}-2\nu}} = \frac{\chi_{AB}N}{1 + 3.9N^{-0.51}} \quad (12)$$

where ν is the swelling exponent for a copolymer chain with $R_g \sim N^\nu$. For short polymer chains,

they become swollen and $\nu = 0.588$. The fact that both conversion equations are quite similar reveal that the thermal fluctuation effects on the correction for the ODT for a finite chain length are almost consistent in AB linear copolymers and A_2B miktoarm star copolymers.

A_2 -star-(B-alt-C) Molecules (This part has been submitted to *Macromolecules*.)

In simulating the microphase separation behavior of A_2 -star-(B-alt-C) copolymers, we set the particle density ρ to be 3, and therefore the dimensionless interaction parameter (i.e., in terms of $k_B T$) between like particles $a_{II} = 25$ according to the work of Groot and Warren.³⁰ The DPD simulations are performed in a 3-D lattice of size $20 \times 20 \times 20$ grids with periodic boundary conditions. This box size is chosen to ensure that the formed microstructures for our model copolymer with the total number of beads per chain $N = 13$ are no longer affected by the simulation box. In each simulated morphology pattern, the red, green and blue colors are used to represent A, B, and C, respectively.

First, we examine how the interaction parameters affect the resulting structure patterns of A_2 -star-(B-alt-C) copolymers. Fig. 6 displays the phase diagram in terms of a_{BC} and $a_{AB} = a_{AC}$ for the systems with $f_A = 0.54$. At a fixed value of a_{BC} , we observe that when $a_{AB} = a_{AC}$ is large enough, i.e., the immiscibility degree between the A-coil block and the BC-alternating block becomes significant, the copolymers pack into an ordered A-rich and BC-rich segregated microstructure. Moreover, various diblock-like morphologies are induced by varying the

interaction parameter a_{BC} . For instance, Fig. 7 illustrates the morphology variation with a_{BC} at $a_{AB} = a_{AC} = 100$. When a_{BC} is set to be 25, both B and C are indeed indistinguishable for A since $a_{AB} = a_{AC}$ and the A_2 -star-(B-alt-C) copolymers are identical to the so-called A_2B miktoarm star copolymers. Accordingly, the copolymer with $f_A = 0.54$ forms a complex gyroid phase G_{BC} , as have been predicted by self-consistent mean-field theory and simulated by DPD. When a_{BC} decreases from 25, due to the fact that B and C components become more attractive, the BC-alternating blocks tend to coil and transform into cylinders, and even spheres in the matrix of A-coil blocks. This transition behavior by decreasing a_{BC} is analogous to decreasing the composition of BC-alternating block. On the contrary, when a_{BC} increases from 25, one may expect that the increasing segregation degree between B and C would cause the BC-alternating chain more extended, and thus a transition from G_{BC} to lamellae to A-formed cylinders or spheres would occur. However, a series of the morphology variation with a_{BC} , $S_{BC}(a_{BC} =$

$$-20) \rightarrow C_{BC}^{\text{HEX}} (-10 \leq a_{BC} \leq 0) \rightarrow G_{BC} (15 \leq a_{BC} \leq 25) \rightarrow L_{A,BC} (30 \leq a_{BC} \leq 90) \rightarrow$$

$L_{B,C}$ -within- $L_{A,BC}$ ($100 \leq a_{BC} \leq 120$), is observed in Fig. 7. That is, as a_{BC} increases from 25,

though the segregation degree between B and C becomes more obvious, the systems still retain at a stable A-rich and BC-rich lamellar phase in a wide range of a_{BC} between 30 and 90, and no further diblock-like large-length-scale transition as mentioned above occurs. Indeed, these results are not surprising since when a_{BC} keeps increasing such that in order to reduce the contacts between B and C, the BC-alternating chain would rather fold within the original BC-rich layers to form small-length-scale B-rich and C-rich lamellae, i.e., the so-called hierarchical $L_{B,C}$ -within- $L_{A,BC}$. Moreover, the resulting hierarchical periodicity is formed in parallel direction to each other, which is different from that in comb-coil copolymers. When the value of $a_{AB} = a_{AC}$ is fixed to a lower value such as 40, similar morphology transition associated with the large-length-scale ordering has also been observed by varying the interaction parameter a_{BC} . Whereas, even when a_{BC} increases to a very large value of 120, we do not find the formation of the hierarchical structure-within-structure morphology induced by a_{BC} , as in the case of $a_{AB} = a_{AC}$ at larger values. This manifests the fact that in order to form the small-length-scale lamellar segregation between B and C within the large-scale BC-rich domains, not only the interaction parameters between B and C (a_{BC}) but also between the A-coil block and the BC-alternating block (a_{AB} and a_{AC}) have to be significantly large. If the value of $a_{AB} = a_{AC}$ continues to decrease, since the repulsion between A and B(C) becomes weaker, the ordered copolymers are expected to become disordered. Note, between the totally disordered and the well ordered states, we observe that the systems form a micelle-like or random network structure (i.e., with chains aggregating but no formation of well ordered structure), which we sort out as the disordered phases.

Next, we discuss the phase transition behavior associated with two-length-scale ordering for A_2 -star-(B-alt-C) copolymers in a wide range of composition f_A . Recall that our previous results have shown that in order for a copolymer with a particular value of composition f_A to form an ordered microstructure, the value of $a_{AB} = a_{AC}$ controls the order-disorder transition; while a_{BC}

plays a dominant role in determining the morphology geometry at large length scale as well as the formation of hierarchical structure-within-structure. Therefore, here we fix the value of $a_{AB} = a_{AC}$ at 100, which is significant enough to assure the formation of the large-length-scale diblock-like structures, and construct the corresponding phase diagram in terms of f_A and a_{BC} , as shown in Fig. 8. As can be seen clearly, when $a_{BC} = 25$, a series of morphology by varying f_A from perforated lamellae of A, PL_A , ($f_A = 0.23$) $\rightarrow$ $L_{A,BC}$ ($0.3 \leq f_A \leq 0.5$) $\rightarrow$ G_{BC} ($f_A = 0.54$) $\rightarrow$ C_{BC}^{HEX} ($0.6 \leq f_A \leq 0.7$)

$\rightarrow S_{BC}$ ($0.75 \leq f_A \leq 0.85$) is observed. These simulated microstructure regimes by varying the

composition are in good agreement with those predicted by self-consistent mean field (SCMF) theory as well as our previous DPD study. Both SCMF and DPD results revealed that the simulated phase diagram is similar to that of linear AB diblock copolymers but with a slight deviation due to the molecular asymmetry. When a_{BC} decreases from 25, it is worth noting that the regime of ordered microstructures in which the BC-blocks form the minor domains such as

G_{BC} , PL_{BC} , C_{BC}^{HEX} , and S_{BC} , is enlarged noticeably and even extended to the systems with $f_A < 0.5$. For example, when $f_A = 0.3-0.5$, although the BC-block is longer than the A-block, the majority BC component still tends to form the minor domains in the minority A-rich matrix, i.e., the so-called inverted microstructures. This is due to the fact that when B and C become more attractive, the BC-alternating blocks favor to coil together in order to reduce the contacts with the A-blocks. Note that these inverted structures have been frequently observed in block copolymer solutions by increasing the solvent selectivity and/or the solvent amount. However, this is possibly the first study to predict their presence in the A_2 -star-(B-alt-C) copolymer melts.

Now, let us continue to discuss the phase behavior shown in Fig. 8 for each copolymer with a particular value of f_A when a_{BC} increases from 25. Similar to the copolymer with $f_A = 0.54$, a significant increase in the interaction parameter a_{BC} also leads to the formation of small-length-scale B and C segregated lamellae within the large-length-scale BC-rich domains for the copolymers with other values of f_A in a wide range of 0.2-0.85. In Fig. 9 we display the various types of structure-within-structures, such as A-formed spheres in the matrix formed by B and C alternating layers (S_A -within- $L_{B,C}$) ($f_A \cong 0.14$), hexagonally packed A-formed cylinders in the matrix with B and C segregated layers (C_A^{HEX} -within- $L_{B,C}$) ($f_A \cong 0.23$), $L_{B,C}$ -within- $L_{A,BC}$ ($0.3 \leq f_A \leq 0.6$), coaxial B and C alternating domains within hexagonally packed BC-formed cylinders in the A-matrix ($L_{B,C}$ -within- C_{BC}^{HEX}) ($0.65 \leq f_A \leq 0.7$), and cocentric BC-alternating domains within BC-formed spheres in the A-matrix ($L_{B,C}$ -within- S_{BC}) ($0.75 \leq f_A \leq 0.85$), which are simulated at $a_{BC} = 120$. Note that the two-length-scale morphology of S_A -within- $L_{B,C}$ shown in Fig. 9 is obtained for the case of N increased to 21. This is simply because of the fact

that in the original case of $N=13$, the lowest value of f_A that the system can reach is 0.23.

Accordingly, in order to observe whether the S_A -within- $L_{B,C}$ structure is possible to form at smaller values of f_A , we increase N to 21. Generally speaking, the geometry of large-length-scale morphology is mainly dominated by the composition f_A . If we further examine the small-length-scale formation of B and C alternating layers within the major domains, such as C_A^{HEX} -within- $L_{B,C}$ and $L_{B,C}$ -within- $L_{A,BC}$, it is clear that these layers are parallel to the A-formed cylinders or lamellae. More interestingly, when f_A is larger than 0.5 so that B and C segregation occurs within the minor domains such as C_{BC}^{HEX} and S_{BC} , these BC-alternating chains fold in a particular way to form multiple (more than 2) B and C coaxial cylinders or cocentric spheres. Note that when f_A is 0.85 and $N = 13$, since each molecule only contains one B and one C, we only observe C-core/B-shell spheres as in Fig. 9. These multiple coaxial cylinders or cocentric spheres formed by the BC-alternating blocks in the A_2 -star-(B-alt-C) copolymers are possibly reported for the first time. Though it has been shown that the ABC linear triblock copolymers can form core-shell types of cylinders or spheres, the number of segregated layers within the domains is generally two instead of the multiple (more than two) layers that the A_2 -star-(B-alt-C) can form.

In Fig. 9 we also plot the schematic molecular alignment in detail for each structure-within-structure. Compared with the A-block-(B-graft-C) coil-comb copolymers as presented in Fig. 10, we observe a completely different packing behavior of molecules due to the difference of molecular architecture. Hence, the hierarchical structure-within-structures that these two copolymers can form are significantly different. In particular, the small-length-scale lamellae formed by the B-alt-C and B-graft-C chains display a parallel and perpendicular direction, respectively, with respect to the large-length-scale structure. We believe this characteristic difference could impose different influences upon various properties of polymers, such as photoelectronic properties, and lead to different potential applications.

Finally, we would like to address whether these characteristic structure-within-structures simulated at $N = 13$ can be preserved when N increases. Here, we double each arm length and thus the total number of beads per chain N increases to 25. Fig. 11 displays the resulting structure patterns for $N = 25$, $f_A \cong 0.54$ and 0.69 , at the same interaction parameters ($a_{AB} = a_{AC} = 100$ and $a_{BC} = 120$) as in Fig. 9. Note that when N increases from 13 to 25, the value of f_A should be slightly changed from 0.54 to 0.52 and 0.69 to 0.68, respectively. However, in the following comparison between both results with different N , we only denote the value of f_A for $N=13$.

When $f_A \cong 0.54$, we find that the copolymer still forms $L_{B,C}$ -within- $L_{A,BC}$ with increasing N from 13 (in this case, the number of BC-blocks per chain, n , is 3) to 25 ($n = 6$), but the formed B and C alternating layers within the BC-rich lamellae vary from B-C-B three to B-C-B-C-B five thin layers. This is not surprising since when N increases, more B and C segments per copolymer chain can fold freely, and hence more sublayers within the large-length-scale lamellae are

possible. Recall that in the *A-block-(B-alt-C)-B-block-A* copolymers, Matsushita and co-workers predicted that the number of thin layers within the large-length-scale lamellae increases from 3 when the number of (B-alt-C) per chain n equals 2, to 5 when $3 \leq n \leq 6$, by simply comparing the numbers of possible conformations for each layered structure. Though we observe a three-layered small-length-scale structure instead of their prediction of five-layered structure for $n = 3$, which we believe may be due to the difference of molecular architecture, both results have pointed to the same conclusion that more-layered structures are possible to form by increasing the number of alternating blocks. However, we believe that the number of small-length-scale segregated domains formed within the large-length-scale structures has to reach a maximum when N keeps increasing due to the balance between the chain stretching energy and the interfacial energy. As far as we know, the issue that the number of allowed thin layers formed within each hierarchical structure by varying N has not been concluded yet. To examine the number of small-length-scale B and C segregated domains formed within the structure other than lamellae, we choose $f_A \cong 0.69$ and increase $N = 13$ ($n = 2$) to 25 ($n = 4$). As can be seen clearly in Figs. 9 and 11, three B-C-B coaxial cylinders within C_{BC}^{HEX} are formed for both cases, although the formed cylinders for $N = 25$ are slightly elliptic. The reason that the number of B and C segregated domains in the $L_{B,C}$ -within- C_{BC}^{HEX} remains a constant of three when N increases from 13 to 25 may be given as follows: (1) the number of minority B and C segments per chain increases slightly ($n = 2-4$) so that the most possible chain conformation still remains to form three-layer segregation; (2) the number of thin coaxial layers allowed to form within the cylinders is three. In order to systematically investigate this matter, a further simulation for larger N values needs to be performed in a larger simulation box, which is too time consuming and not our concern here. Though the number of possible formed small-length-scale layers may differ when N increases, our above results have still revealed that the formed hierarchical structure types for small value of $N = 13$ are maintained for large N . Hence, we believe that the self-assembling behavior associated with two length scales simulated for small value of $N = 13$ in this study should also hold true qualitatively for *A₂-star-(B-alt-C)* copolymers with large degrees of copolymerization N .

A-block-(B-graft-C) Molecules (This part has been accepted in *Macromolecular Rapid Communications*.)

In order to explore the effects of the interaction parameter a_{AB} on the microstructures formed in *A-block-(B-graft-C)* coil-comb molecules, we choose $f_A = 0.2$, $N = 10$, $a_{AC} = a_{BC} = 70$, and vary the value of a_{AB} . Fig. 12 displays the resulting morphology transition from segregated AB and C

lamellae, $L_{AB,C}$, ($0 \leq a_{AB} \leq 25$) $\rightarrow$ gyroid of A, G_A , ($a_{AB} = 30$) $\rightarrow$ hexagonally packed

A-formed cylinders, C_A^{HEX} , ($35 \leq a_{AB} \leq 70$) $\rightarrow$ A-formed spheres, S_A , ($a_{AB} = 75$) $\rightarrow$ A-formed

spheres within the segregated B and C lamellae, S_A -within- $L_{B,C}$, ($80 \leq a_{AB} \leq 120$). First, the

interaction parameters of a_{AC} and a_{BC} are chosen as 70, which is large enough so that both A and B components tend to segregate with C. Accordingly, when $a_{AB} \leq 25$, i.e., A and B are highly miscible, the microstructure formed by the system is mainly caused by the segregation between AB and C, and therefore, a stable $L_{AB,C}$ is observed for the system with comparable values of volume fractions of AB and C studied here. As a_{AB} increases, due to the fact that the immiscibility degree between A and B becomes more significant, the B component would gradually depart from the original AB-rich domains into the interfaces between A-rich and C-rich domains, and further stay in the C-rich domains. This behavior is analogous to decreasing the effective composition in the AB-rich domains, and thus a transition from $L_{AB,C} \rightarrow G_A \rightarrow C_A^{\text{HEX}} \rightarrow S_A$ occurs with an increase in a_{AB} . Furthermore, it is interesting to observe that when a_{AB} keeps increasing so that most of the B chains are pushed towards the C-rich domains, whereas, the fact that there also exists significant degree of incompatibility between B and C ($a_{AC} = a_{BC} = 70$) enables a small-length-scale B and C segregated lamellar phase formed within the large-length-scale BC-rich matrix.

Not only varying the interaction parameter a_{AB} but also $a_{AC} = a_{BC}$ can induce a series of morphology transitions associated with two length scales. To illustrate this, we first perform the DPD simulations by varying $a_{AC} = a_{BC}$ for $f_A = 0.2$, $N = 10$, and a_{AB} fixed at a larger repulsion value of 100. As can be seen clearly in Fig. 13(a), a series of transition from $S_A \rightarrow$

S_A -within- $L_{B,C} \rightarrow C_A$ -within- $L_{B,C}$ occurs with an increase in $a_{AC} = a_{BC}$ from 50 to 70 to 80, respectively. It is not surprising that the small-length-scale B and C lamellae are formed with increasing the interaction parameter between B and C. Moreover, increasing the value of a_{AC} and a_{BC} simultaneously may also enhance the segregation of B from C towards A, and thus causes a large-length-scale morphology transition towards increasing the effective composition of A from S_A to C_A^{HEX} . Similar trend of morphology transition at large-length-scale with increasing $a_{AC} = a_{BC}$ has also been observed for the same system but a_{AB} at a smaller value of 50, which is displayed in Fig. 13(b). Clearly, a transition from $S_A \rightarrow C_A^{\text{HEX}} \rightarrow G_A$ occurs as $a_{AC} = a_{BC}$ increases from 50 to 70 to 100, respectively. However, in this case we observe no existence of the structure-within-structure even increasing $a_{AC} = a_{BC}$ up to a high value of 100. These results manifest the fact that in order to form the small-length-scale lamellar segregation between B and C within the large-scale BC-rich domains, not only the interaction parameters between B and C (a_{BC}) but also between the A-coil block and the BC-comb block (a_{AB} and a_{AC}) have to be significantly large. Otherwise, the continuous increase in $a_{AC} = a_{BC}$ only causes B to move towards the interfaces between the A-rich domains and C-rich domains, and trigger a morphology transition at large-length scale as we observe in Fig. 13(b).

Finally, we would like to investigate whether the DPD simulations can show the various types of structure-within-structures by varying the composition f_A , as have been frequently

observed in experiments. To illustrate this, we choose $a_{AC} = a_{BC} = 70$ and $a_{AB} = 100$. Fig. 14 displays the resulting DPD simulation results at various values of $f_A = 0.1, 0.3, 0.4, 0.6$, and $N = 10-25$. Generally speaking, with increasing the A composition f_A , the formed large-length-scale morphology varies from $S_A \rightarrow C_A^{\text{HEX}} \rightarrow G_A \rightarrow L$, as expected. More interestingly, we observe that the formation of small-length-scale segregation between B and C within the BC-rich domains is dependent of the chain length N and f_A (more precisely, the length of the BC-comb block). When f_A is 0.1, the system forms S_A -within- $L_{B,C}$ no matter whether the value of N is 10 or 20, and yet increasing N makes the separation between B and C more evident. Whereas, when $f_A > 0.1$, we find that the systems with $N = 10$ are not be able to form any structure-within-structure, but only align to form A-rich and C-rich segregated domains with B in the interfaces. Indeed, this is reasonable due to the fact that when the length of the BC-comb block becomes short, the segregation degree between B and C is not significant enough to make these B and C well aligned to form lamellae. Hence, the resulting morphology is mainly driven by the segregation between A and C, and B acts more like a component in the interfaces. By increasing the length of the BC-comb block, one may expect that B and C will separate evidently and form a lamellar structure. For example, when N increases to 20, both types of hierarchical structures of the A-formed cylinders in the matrix with B and C segregated layers (C_A^{HEX} -within- $L_{B,C}$) ($f_A = 0.3$, 0.4) and segregated B and C lamellae within the A-rich and BC-rich lamellae ($L_{B,C}$ -within- $L_{A,BC}$) ($f_A = 0.5$), are observed. When f_A increases to 0.6, though the small-length-scale B and C lamellae are not well formed within the BC-rich lamellae for $N = 20$, the formation of $L_{B,C}$ -within- $L_{A,BC}$ is still clearly observed as N increases to 25. These simulated structure-within-structures, in which the small-length-scale lamellae are typically perpendicular to the large-length-scale structures, are in good agreement with those observed experimentally in A-block-(B-graft-C) coil-comb copolymers. Note that we have not obtained other types of structure-within-structures, such as $L_{B,C}$ -within- C_{BC} and $L_{B,C}$ -within- S_{BC} . This is mainly due to the fact that these hierarchical structures are formed when f_A is larger (i.e., the comb composition is smaller). Accordingly, the total chain length N has to increase further in order to generate the small-length-scale lamellar ordering of B and C.

計畫成果自評

目前我們已具體完成了三年期計畫中的二年工作進度。從各系統的 DPD 模擬結果來看，的確改變了共聚合物的分子建構方式(architecture)，其等級結構受到了很大的影響。目前我們已完成了三篇論文。在未來的第三年度，我們計畫針對現有文獻的實驗系統來做模擬比較，期許能讓讀者對 hierarchical structures 有更全面的了解。

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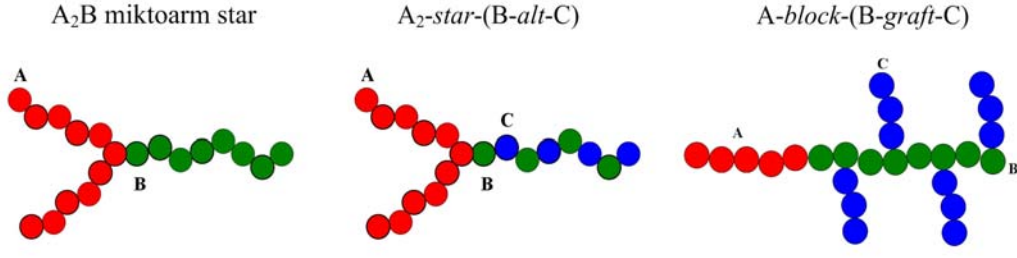


Fig. 1 Schematic plot of our simulated copolymers with different molecular architectures.

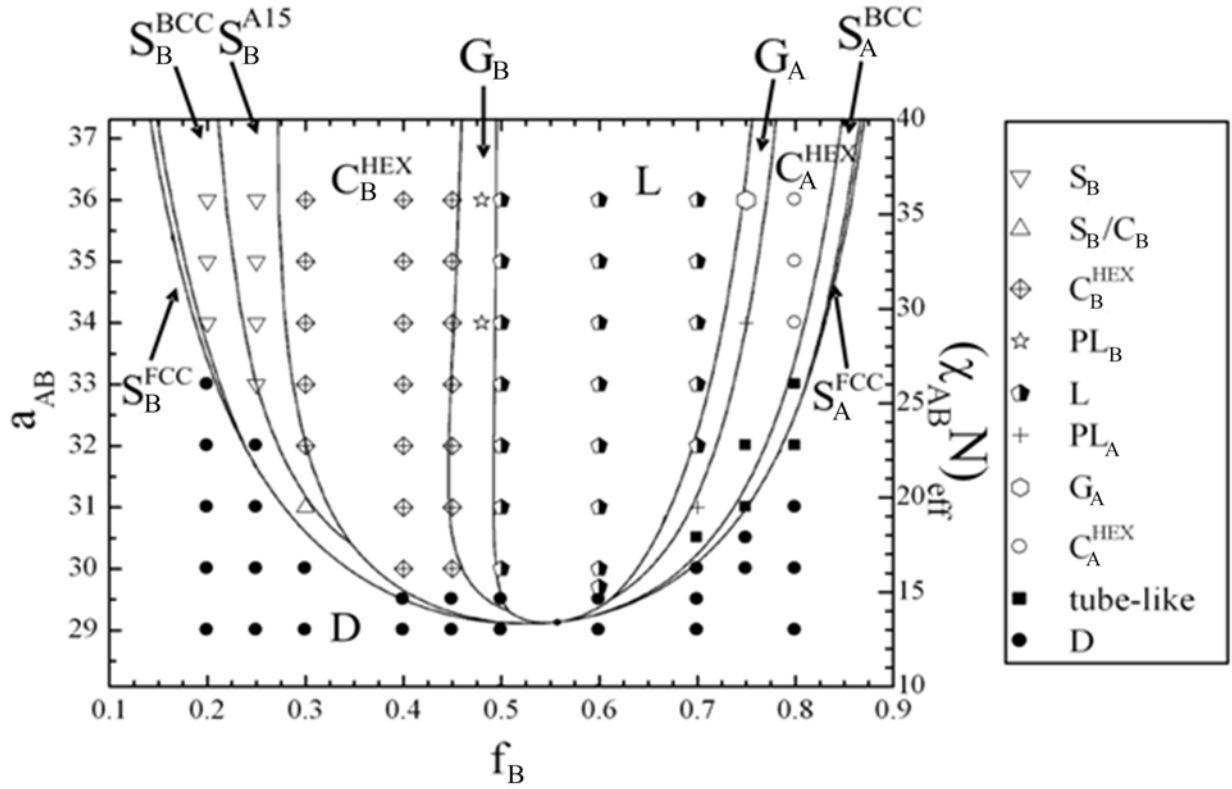
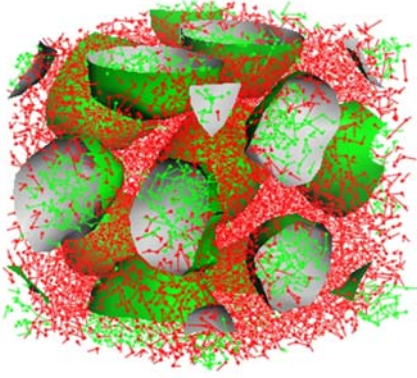


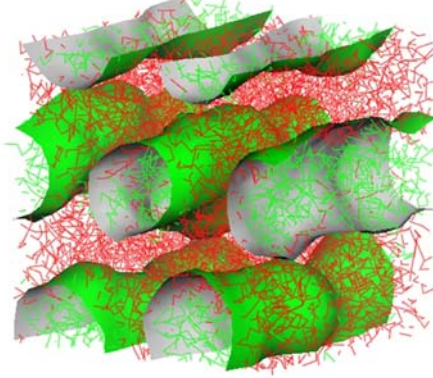
Fig. 2. Phase diagram of A_2B miktoarm star copolymers in terms of the interaction parameter a_{AB} and composition f_B . The black solid curves correspond to the phase diagram determined by SCMF theory as a function of f_B and $(\chi_{AB}N)_{\text{eff}}$, in which χ_{AB} is the Flory-Huggins interaction parameter and N is the degree of copolymerization.

$$f_B=0.25$$



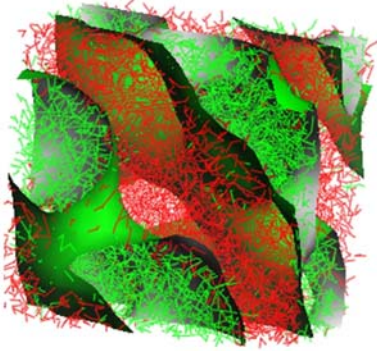
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$$f_B=0.3$$



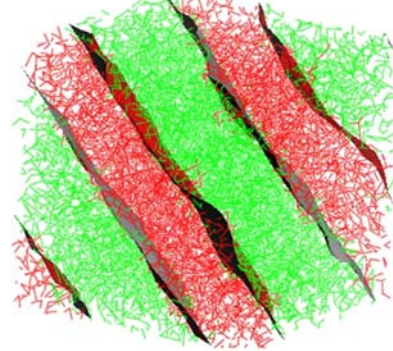
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$$f_B=0.48$$



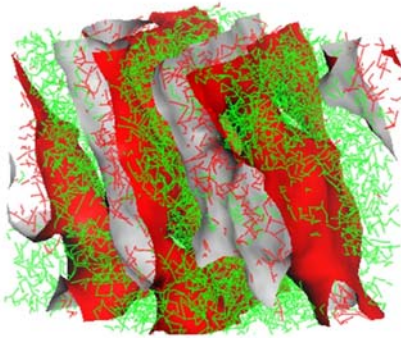
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$$f_B=0.6$$



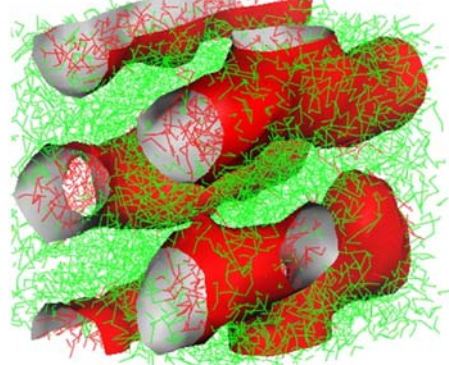
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$$f_B=0.75$$



box size=20x20x20

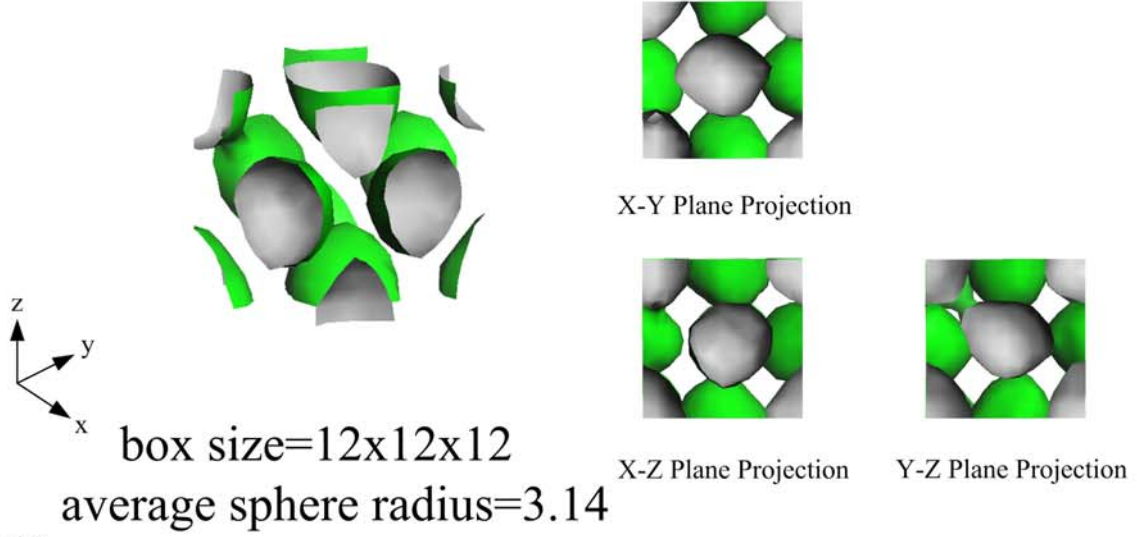
$$f_B=0.8$$



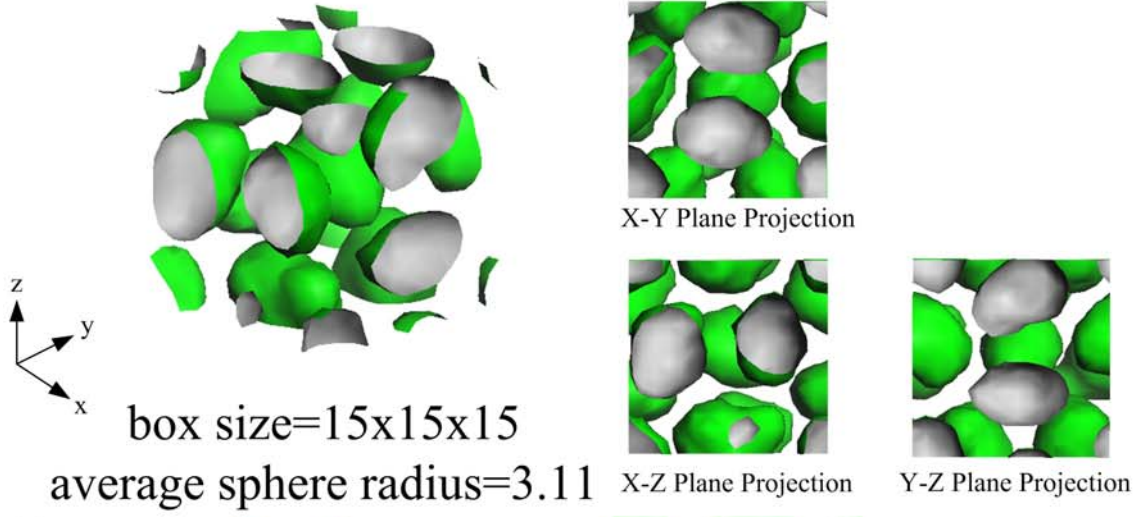
box size=15x15x15

Fig. 3. Morphology variation of A_2B miktoarm star copolymers with f_B at $a_{AB} = 34$. The red and green colors represent A and B, respectively. The red and green surfaces correspond to the isosurfaces of component A and B, respectively.

(a)



(b)



(c)

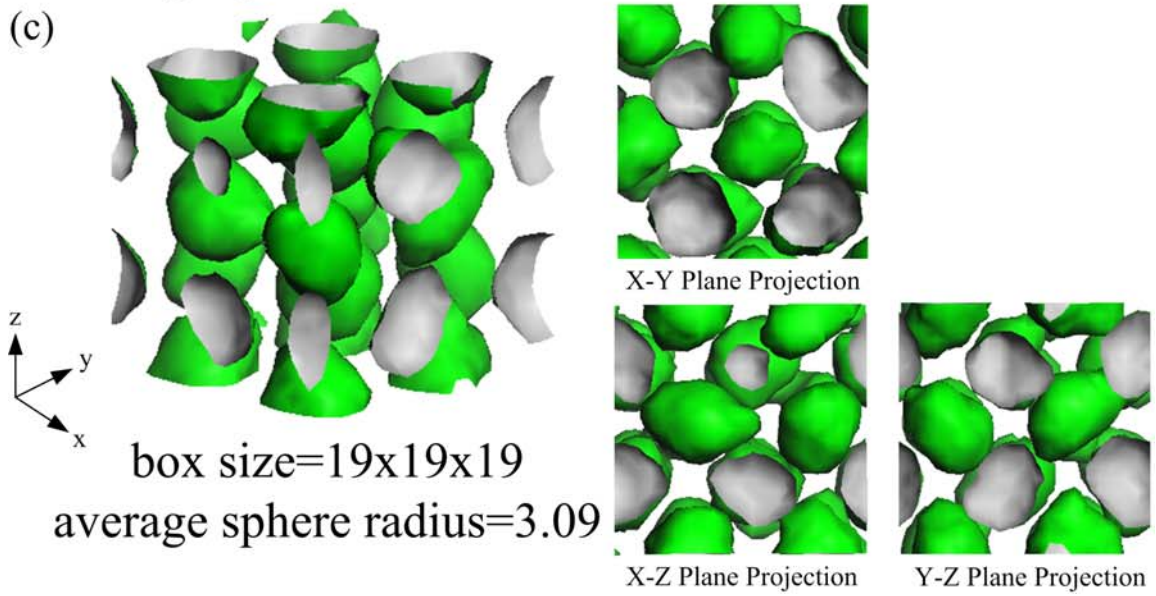


Fig. 4. Morphology pattern and projection of A₂B miktoarm star copolymers with $f_B = 0.8$ and $a_{AB} = 33$.

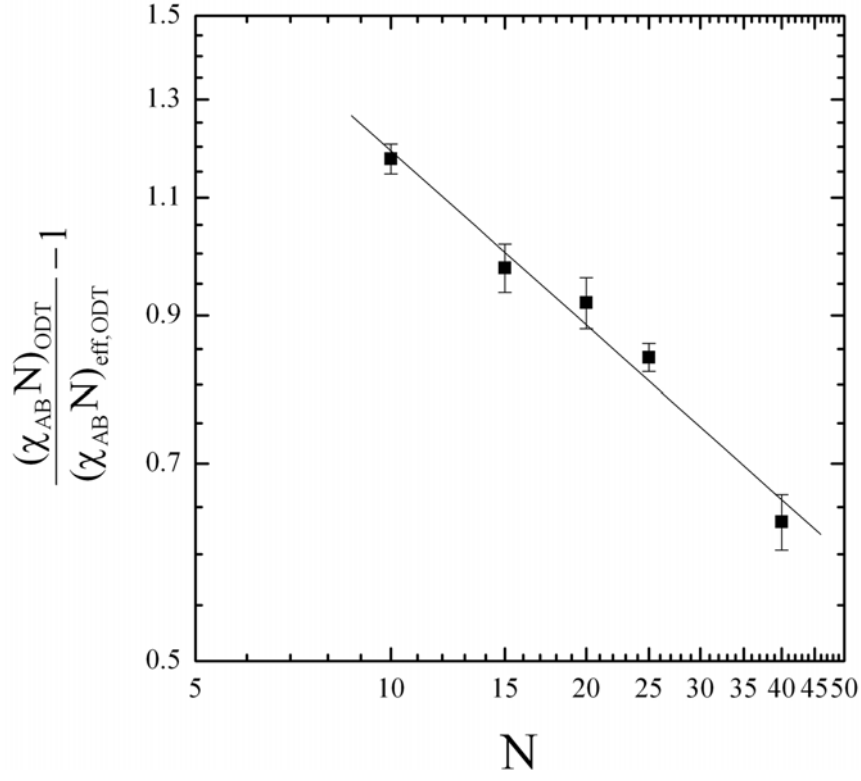


Fig. 5. Log-log plot of $(\chi_{AB} N)_{\text{ODT}} / (\chi_{AB} N)_{\text{eff,ODT}} - 1$ versus N for A_2B miktoarm star copolymers at $f_B = 0.6$.

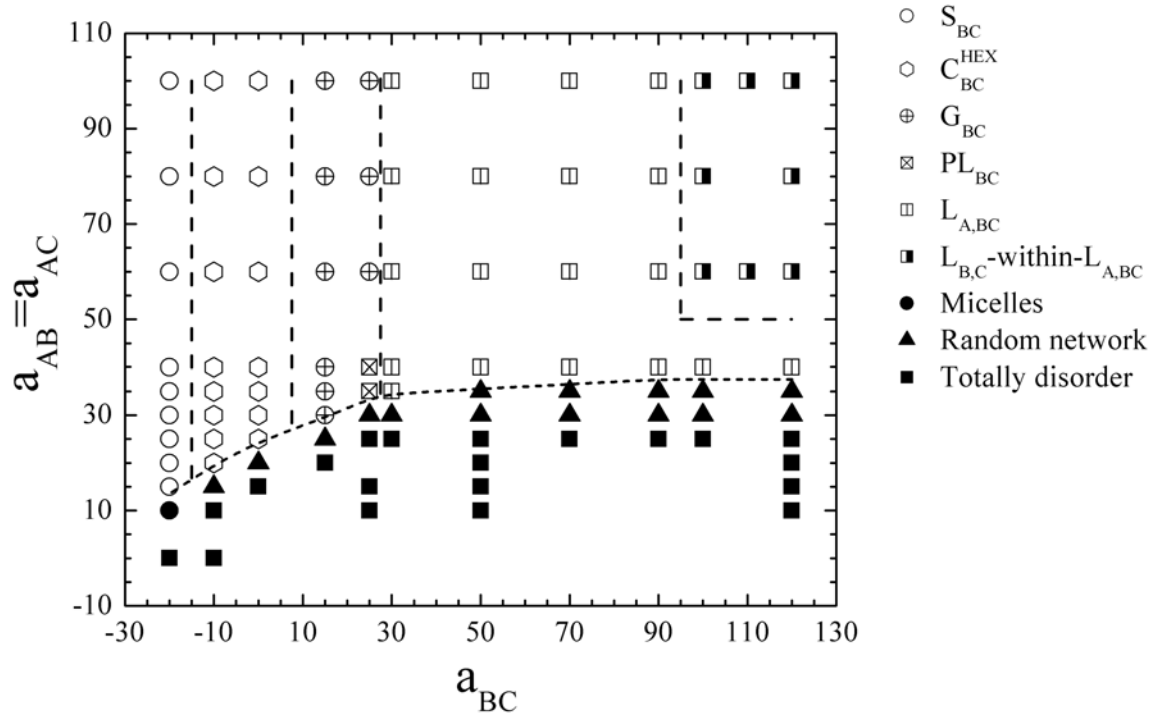


Fig. 6. Phase diagram of A_2 -star-(B-alt-C) copolymers in terms of the interaction parameter $a_{AB} = a_{AC}$ and a_{BC} when $f_A = 0.54$ and $N = 13$. The phase boundary lines are drawn to guide for the eyes.

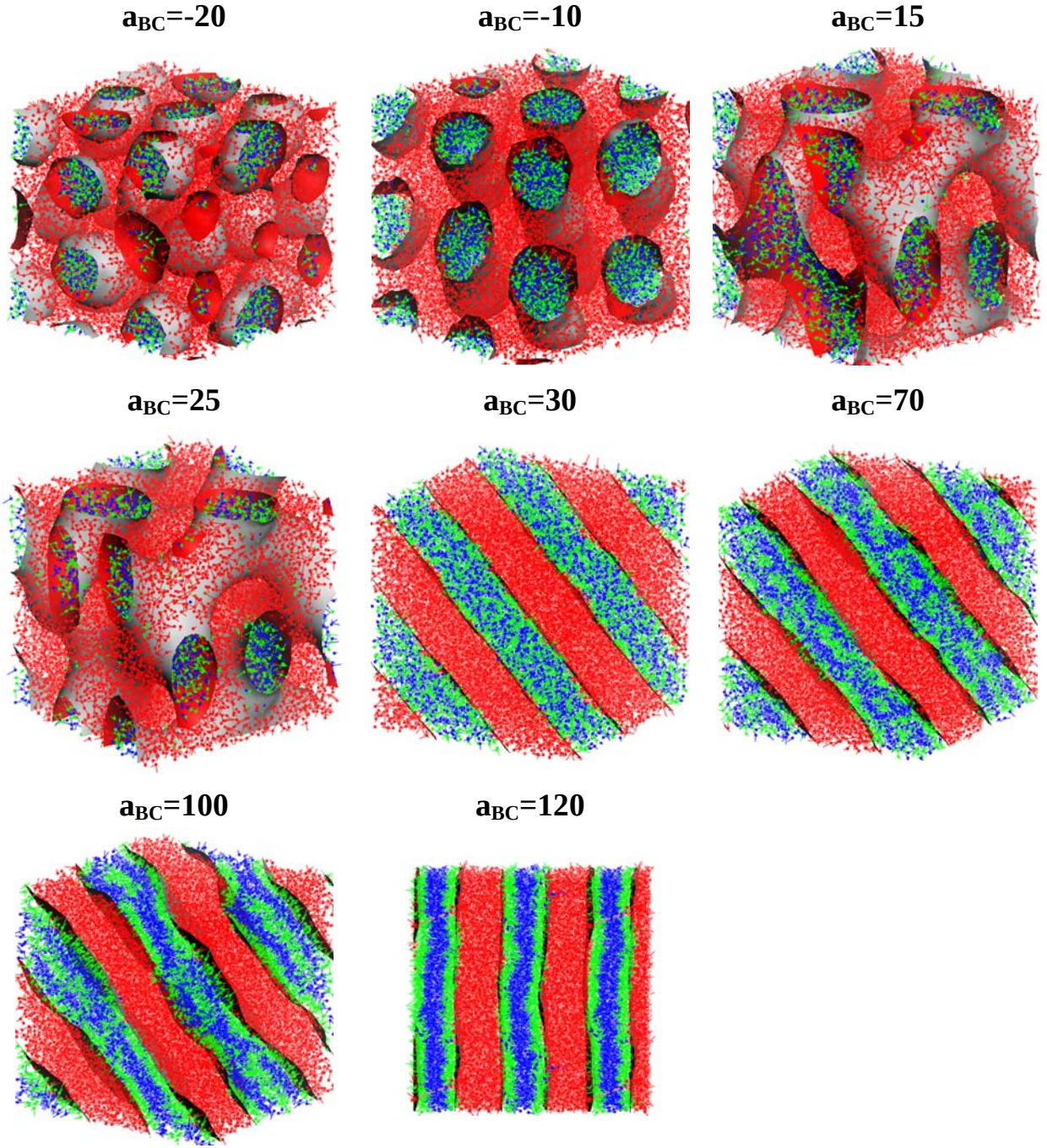


Fig. 7. Morphology variation of A_2 -star-(B-alt-C) copolymers with a_{BC} when $f_A = 0.54$, $N = 13$, and $a_{AB} = a_{AC} = 100$. The red, green, and blue colors represent A, B, and C, respectively. The red surface corresponds to the isosurface of component A.

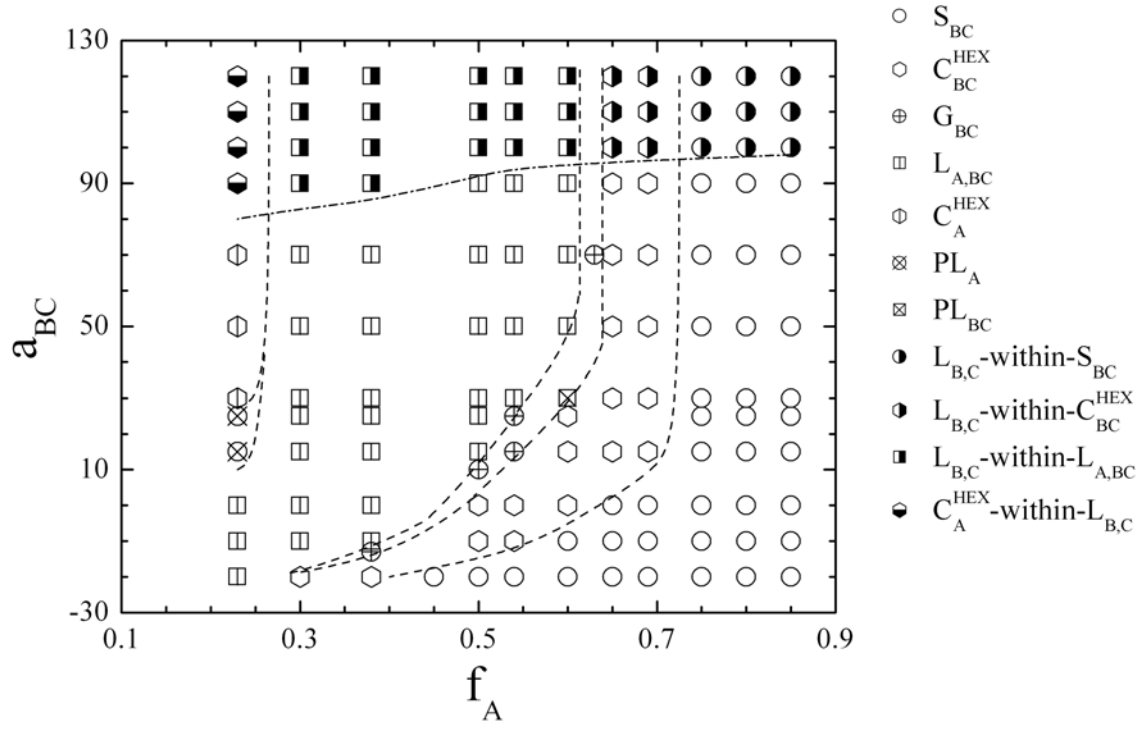


Fig. 8. Phase diagram of A_2 -star-(B-alt-C) copolymers with $N=13$ in terms of the interaction parameter a_{BC} and composition f_A when $a_{AB}=a_{AC}=100$. The phase boundary lines are drawn to guide for the eyes.

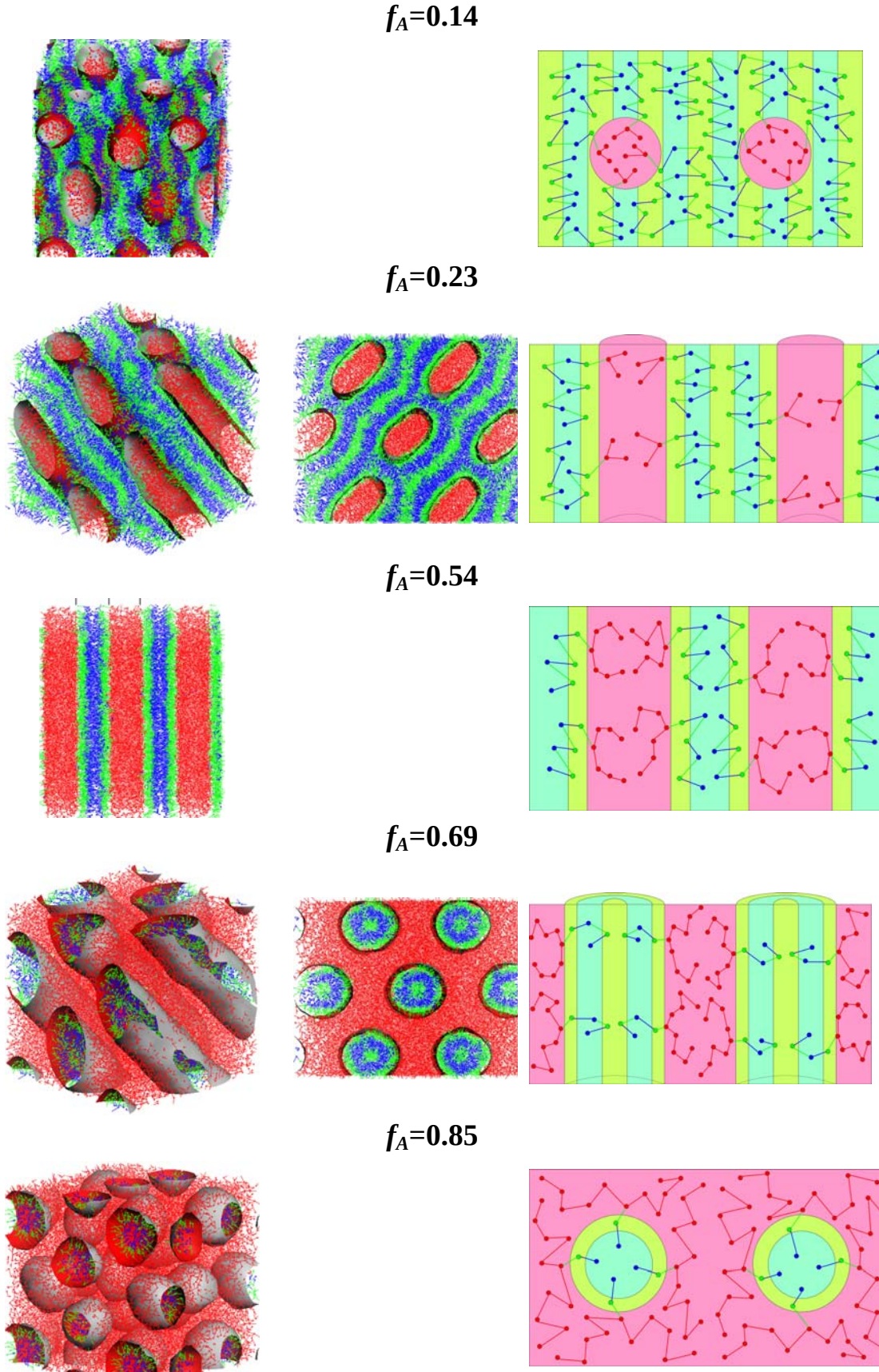
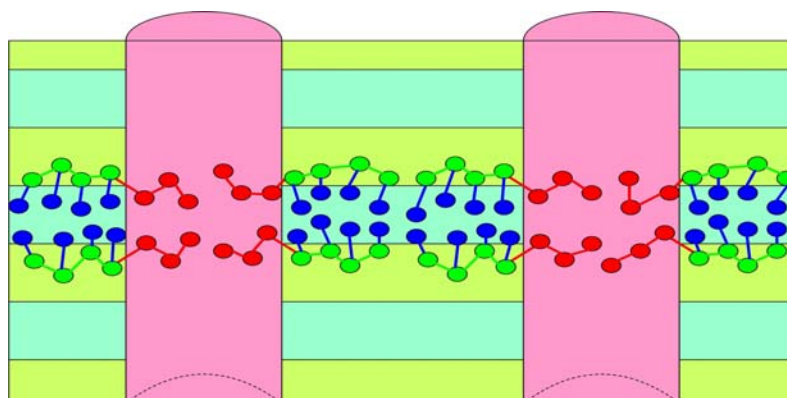
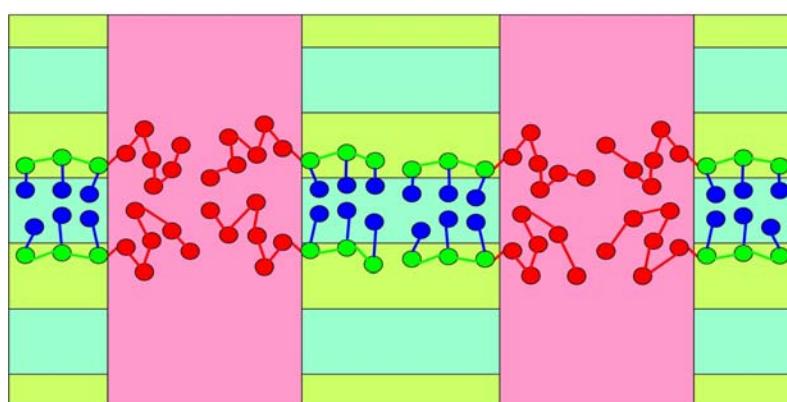


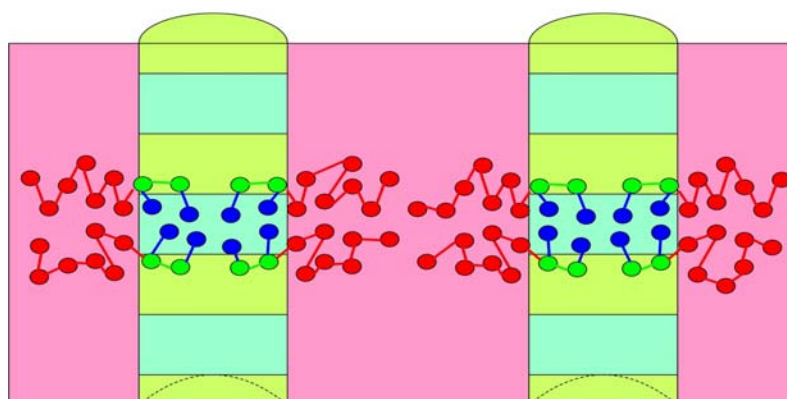
Fig. 9. Morphology variation and corresponding molecular arrangements of A_2 -star-(B-alt-C) copolymers ($N=13$) with f_A when $a_{AB} = a_{AC} = 100$ and $a_{BC} = 120$. Note that the pattern when $f_A=0.14$ corresponds to $N = 21$. The red, green, and blue colors represent A, B, and C, respectively. The red surface corresponds to the isosurface of component A.



Cylindrical-within-Lamellar



Lamellar-within-Lamellar



Lamellar-within-Cylindrical

Fig. 10. Schematic plot of molecular arrangements for A-*block*-(B-*graft*-C) comb-coil copolymers in various types of structure-within-structures.

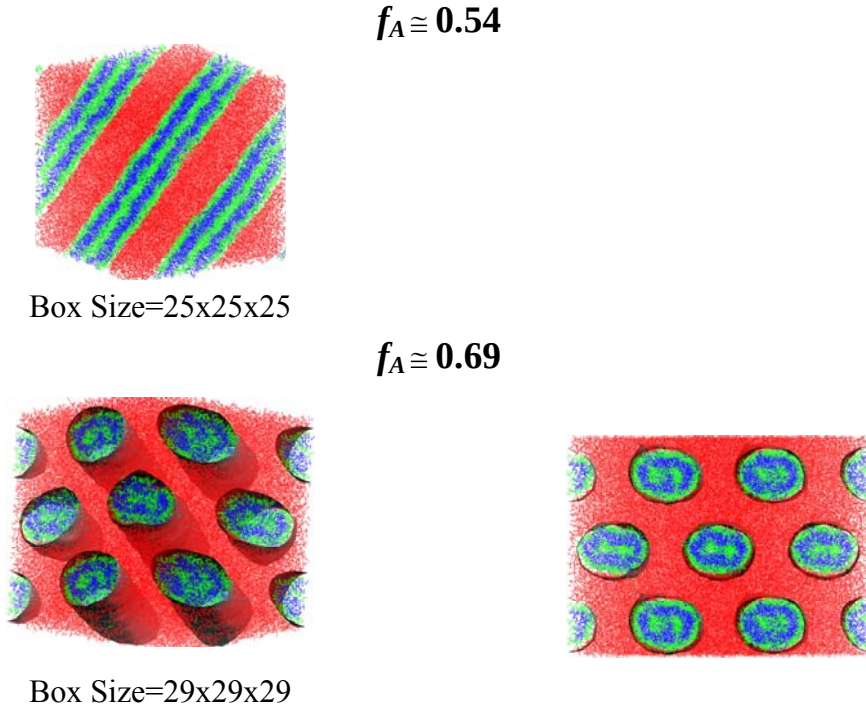


Fig. 11. Structure patterns of A_2 -star-(B-alt-C) copolymers with $N = 25$, $a_{AB} = a_{AC} = 100$, $a_{BC} = 120$, and f_A equal to 0.54 and 0.69, respectively. The red, green, and blue colors represent A, B, and C, respectively. The red surface corresponds to the isosurface of component A.

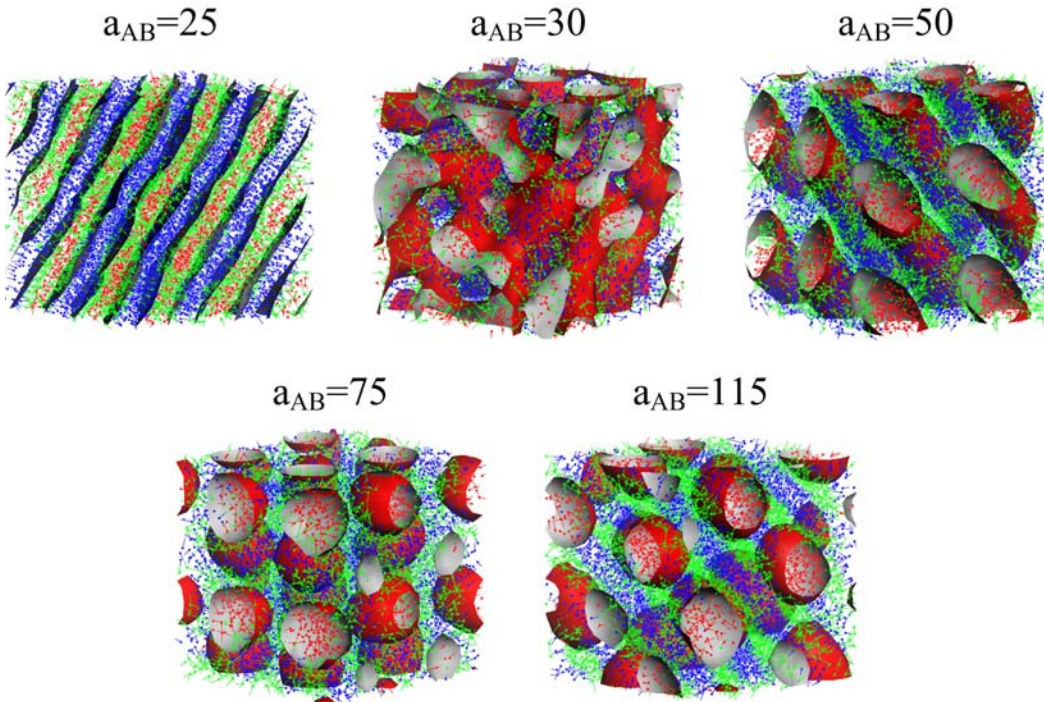


Fig. 12. Morphology variation of A-block-(B-graft-C) molecules with a_{AB} when $N=10$, $f_A=0.2$ and $a_{AC} = a_{BC} = 70$. The red, green, and blue colors represent A, B, and C, respectively. The blue and red surfaces correspond to the isosurfaces of component A and C, respectively.

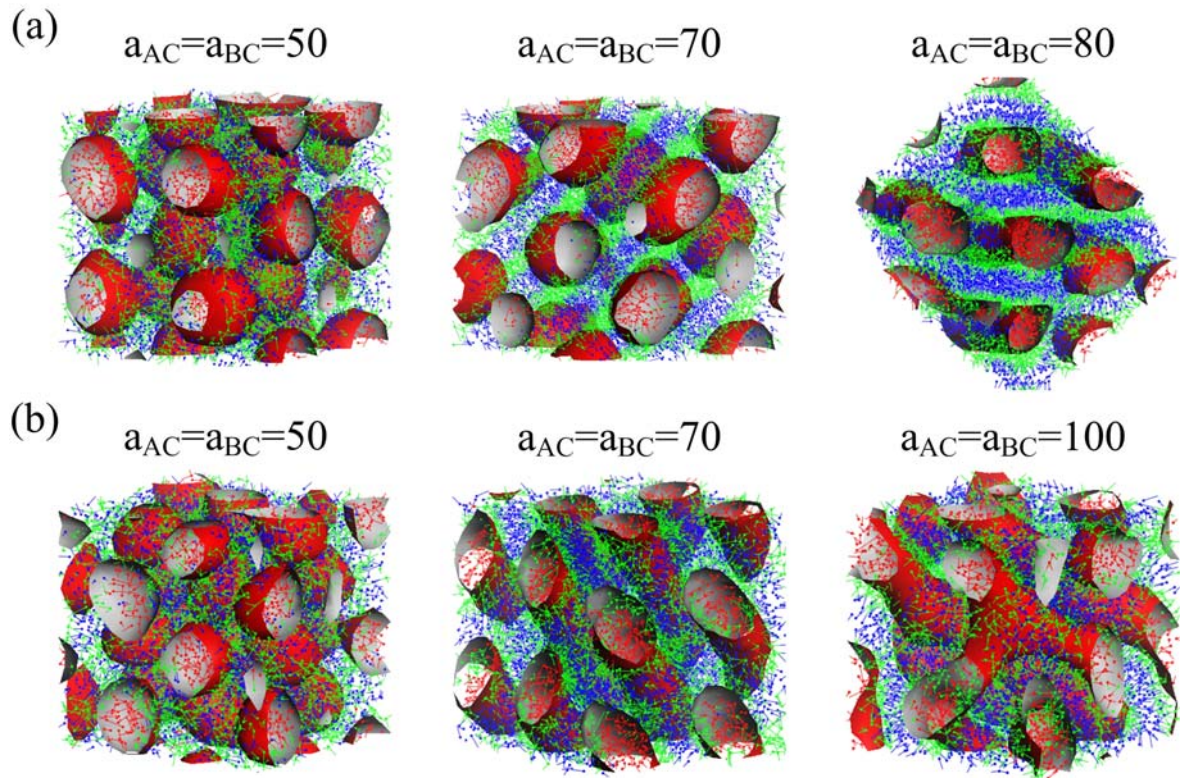


Fig. 13. Morphology variation of *A-block-(B-graft-C)* molecules with $a_{AC} = a_{BC}$ when $N=10$, $f_A=0.2$ and a_{AB} equal to (a) 100 and (b) 50, respectively.

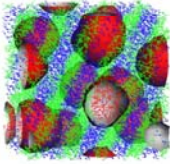
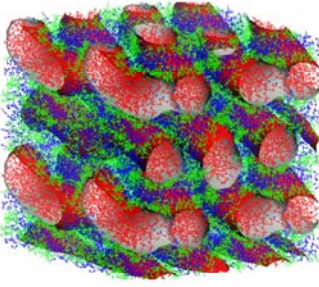
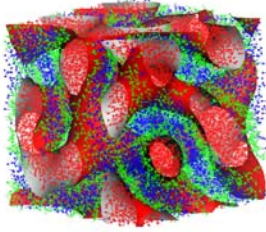
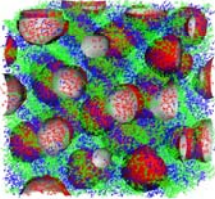
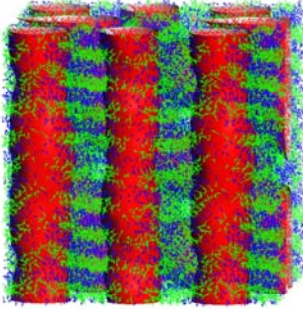
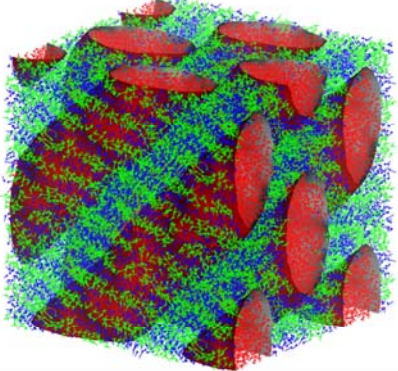
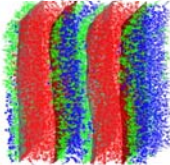
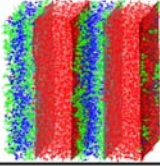
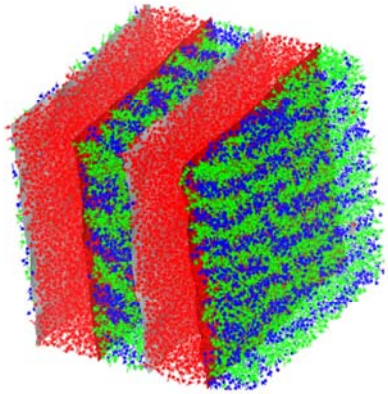
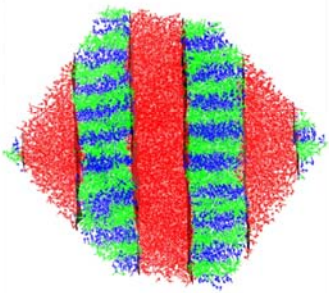
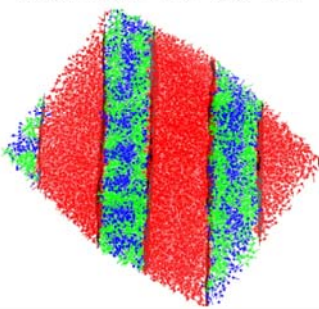
	$f_A=0.1$	$f_A=0.3$	$f_A=0.4$
N=10	Box size= $15 \times 15 \times 15$ 	Box size= $25 \times 25 \times 25$ 	Box size= $20 \times 20 \times 20$ 
N=20	Box size= $20 \times 20 \times 20$ 	Box size= $30 \times 30 \times 30$ 	Box size= $30 \times 30 \times 30$ 
	$f_A=0.5$	$f_A=0.6$	
N=10	Box size= $15 \times 15 \times 15$ 	N=10 Box size= $15 \times 15 \times 15$ 	N=25 Box size= $25 \times 25 \times 25$ 
N=20	Box size= $20 \times 20 \times 20$ 	N=20 Box size= $20 \times 20 \times 20$ 	

Fig. 14. Morphology variation of A-block-(B-graft-C) molecules with f_A and N at $a_{AC} = a_{BC} = 70$ and $a_{AB} = 100$.

行政院國家科學委員會補助國內專家學者出席國際學術會議報告

96 年 10 月 30 日

報告人姓名	黃慶怡	服務機構	國立台灣大學 高分子科學與工程研究所
時間 地點	2007/07/15~2007/07/19 Prague, Czech Republic (布拉格, 捷克)	本會核定 補助文號	NSC-95-2221-E-002-155
會議名稱	(中文) 第四十七屆尖端光電高分子材料會議 (英文) 47 th Microsymposium: Advanced Polymer Materials for Photonics and Electronics		
發表論文題目	Packing structures in poly(3-alkylthiophene): An atomistic simulation study		
報告內容包括下列各項： 1. 參加會議經過： 07/14 抵達 07/15~07/19 參與會議 07/16 論文發表 07/20 離開捷克 2. 與會心得： 此次尖端光電高分子材料會議，為捷克化學學會所舉辦相關高分子的第四十七次國際會議。晚學這幾年來，持續地探討共聚合高分子的結構行為；尤其是透過各種複雜的分子結構，能夠將共聚合物原先僅存在一種尺寸等級的微結構，進而發展出兩種不同尺寸等級同時存在的微結構；此現象的產生導致材料之光電性質有著特殊的變化，進而增加共聚合物於光電材料上的應用與發展。因此，晚學選擇參與此次國際會議，期望可從各國所發表的高分子相關論文中，吸取更多知識，將結構性質與光電性質之間的關係了解得更深入，期能對光電高分子材料的應用發展有所貢獻。 此次國際會議，聆聽了各國頂尖研究團隊對於其國家在尖端光電高分子領域的介紹及發展。其中，最大的收穫，尤其是認識了韓國 Pohang 科技大學的 Prof. K. Cho，			

並與他有了很深入的交談。Pro. Cho 向我展示了他的研究團隊，藉著改變表面的官能基，能夠有效地控制光電高分子的排列行為及其所對應的光電性質。他並對於晚學的研究展現出高度的興趣，鼓勵我可以與他的研究團隊合作，運用模擬之技術，探討光電高分子的結構排列；進而將現在所關注的結構內有結構的特殊排列行為，能更提升至光電材料未來之應用。

3. 攜回資料名稱及內容：

會議論文摘要紙本

部分參與人員名片或電子郵件地址

4. 附件：

此次國際會議中，晚學投稿發表之論文。將收錄在捷克化學學會集結所有參與此次會議發表論文之論文集當中。

Structure and Dynamics of Water Surrounding the Poly(methacrylic acid): A Molecular Dynamics Study

Ching-I Huang, Wei-Zen Cheng, and Yong-Ting Chung

Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan

Abstract. All-atom molecular dynamics simulations are used to study a single chain of poly(methacrylic acid) (PMAA) in aqueous solutions at various degrees of charge density. We observe that local arrangements of water molecules, surrounding the functional groups of COO^- and COOH in the chain, behave differently and correlated well to the resulting chain conformation behavior. Furthermore, water molecules often act as a bridging agent between two neighboring COO^- groups. These bridged water molecules are observed to stabilize the rod-like chain conformation that the highly charged chain reveals, as they significantly limit torsional and bending degrees of the backbone monomers. In addition, they display different dynamic properties from the bulk water. Both the resulting oxygen and hydrogen spectra are greatly shifted due to the presence of strong H-bonded interactions.

Keywords: molecular dynamics, ENCAD, PMAA, polyelectrolyte

PACS: 02.70.Ns, 36.20.Ey, 47.11.Mn

INTRODUCTION

Polyelectrolytes are of great importance due to their extensive presence throughout biological systems and use in a wide range of practical applications, such as sensors, detergents, drug delivery, and gene therapy. In general, polyelectrolytes, when in a solution, dissociate into polyions and counterions. The associated electrostatic interactions that involve the polyions, counterions, and the solvent, make the chain conformation behavior of polyelectrolytes quite distinct from that of neutral polymers. Polyelectrolyte conformation has been, and continues to be, an important research area, not only for its relevance to physical properties but also for a deeper understanding of biological phenomena and applications.

Experiments have shown that polyelectrolyte conformation in dilute solutions depends on the charge density that exists along the chain, salt concentration, ionic strength, and the solution pH value [1-3]. For example, highly charged polyelectrolyte chains in low ionic strength monovalent salt solutions exhibit an extended conformation due to the net repulsion between the charged monomers. When the added salts

are multivalent, a series of transitions from extended $\rightarrow$ collapsed $\rightarrow$ re-expanded conformations often occurs upon increasing the salt concentrations. Though current theoretical studies have captured most of the phenomena associated with the conformational variation in polyelectrolytes [2,4-7], solvent effects that involve direct electrostatic interactions between solvent and polyelectrolyte, the local arrangement of the solvent molecules around the polyelectrolyte chain, and the formation of the hydrogen bonds between the solvent molecules and monomers, have not yet been addressed.

We thus employ all-atom molecular dynamics (MD) simulations to study the local structure and dynamics of water in the vicinity of a single polyelectrolyte chain. We consider a single molecule of syndiotactic poly(methacrylic acid) (PMAA) in an aqueous solution. We show that due to the strong attractive interactions between water and charged monomers, the water molecules form highly bonded structures surrounding the chain via the formation of hydrogen bonds. These bridged water molecules significantly affect the resulting chain conformation behavior as well as their dynamic properties.

MODEL AND SIMULATION METHODS

We employ an Energy Calculations and Dynamics (ENCAD) simulation program [8], which is an all-atom model, to calculate the atomic interaction parameters between the PMAA and the solvent water. The total potential energy function U is given as follows,

$$U = U_{bond} + U_{bend} + U_{torsion} + U_{vdw} + U_{els} \quad (1)$$

where U_{bond} , U_{bend} , and $U_{torsion}$ describe the bonded interactions contributed from bond stretching, bond angle bending, and torsion angle twisting, respectively, with the remaining two terms, U_{vdw} and U_{els} representing van der Waals interactions and electrostatic Coulomb potential energy, respectively. The detailed terms were shown in our previous work [9].

All the parameters of the ENCAD are derived from *ab-initio* quantum mechanics, spectroscopy, and crystallography, and can be obtained from refs. [8] and [10]. In addition, the solvent water is treated explicitly via a flexible three-centered (F3C) model, in which the associated water potential still adopts the same type of the force fields as in the ENCAD program [10]. This F3C water model has proved suitable for describing the structural and dynamic properties of liquid water.

The system contains a single chain of syndiotactic PMAA with a degree of polymerization N equal to 48 in the presence of approximately 1700 water molecules. In our simulations, we used Materials Studio (MS) molecular modeling software to construct the initial atomistic structure of the PMAA, and varied the number of charged monomers N_C , which were equally distributed along the chain. In particular, the charge density $f (= N_C / N)$ for the PMAA chain is equal to 1, 0.5, 0.33, 0.25, and 0, respectively. We assumed that no counterions were present in the study. The molecular dynamics simulations were performed by integrating the positions and velocities of all atoms according to the velocity-Verlet algorithm [11,12]. The initial temperature was set at 300 K and the integration time step was chosen as 1 fs. The PMAA chain was first put in a vacuum box with a side length of 40 Å and a periodic boundary condition, then the box was gradually filled with water molecules to a density of 0.791 g/cm³. Prior to simulation, the steepest descent minimization method was adopted to relax and equilibrate the initial structure. To clarify, the PMAA chain was fixed and the water solvent was relaxed to populate the relevant hydration sites on the PMAA for 30 ps in a canonical NVT ensemble. This minimized structure was then compressed to a density of 0.987 g/cm³ at a rate of 0.1 Å/fs, followed by a series of annealing processes. The annealing temperature was

first raised from 300 to 600 K at a rate of 5 K/1ps and kept at 600 K for 100 ps. It was then quenched to 300 K at the same rate and kept at 300 K for 20 ps. This annealing cycle was repeated 4 to 6 times to assure that the system had been equilibrated. Finally, it was followed by a long relaxation period of 100 ps at 300 K. After these processes were performed so that the system energy has reached the equilibrium value, we analyzed the radius of gyration (R_g) of the PMAA chain and the radial distribution function (RDF) every 100 fs as well as the self-velocity autocorrelation function (VACF) of water molecules every 5 fs, which were averaged out for the data collection interval of 10 ps.

RESULTS AND DISCUSSION

Fig. 1 displays the variation in the radius of gyration (R_g) with f , where we also designate the maximum and minimum values of R_g with error bars. In order to clearly manifest the significant effects contributed from water, we repeat the simulation on the same system, however, the water is treated implicitly as a comparison. To clarify, the solvent is taken into account as a continuum dielectric with a dielectric constant. It clearly shows that with the same charge density f , the value of R_g for the PMAA chain when the water is treated via a F3C model is greater than that when the water is treated implicitly. This indicates that the existence of real water causes a greater degree of stretching in the charged polymer chain. As the charge density f increases, due to the fact that the repulsive degree of the electrostatic interactions between the COO⁻ groups becomes more significant, R_g shows an increasing behavior. Later we will show that the organization of water molecules surrounding the PMAA chain also plays an important role in the PMAA chain conformation behavior.

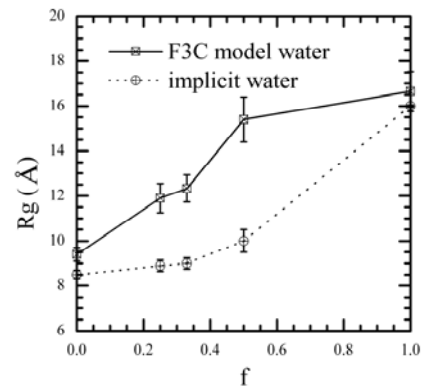


Figure 1. Plot of the radius of gyration (R_g) of PMAA versus charge density f when the solvent water is treated explicitly via a F3C model and implicitly via a continuum dielectric, respectively.

In aqueous solutions, the hydration behavior of molecules is a complex subject, but worth further exploration. In order to investigate the distribution of water molecules surrounding the PMAA chain, we analyze the radial distribution functions of the oxygen (O) and hydrogen (H) atoms of water with respect to the O atom in the COO^- group, the O atom of carbonyl ($-\text{C}=\text{O}$) in the COOH group, and the O atom of hydroxyl ($-\text{OH}$) in the COOH group of the PMAA at various values of charge density f , in Figs. 2 and 3, respectively. This radial distribution function $g_{\text{A-B}}(r)$ indicates the local probability density of finding B atoms at a distance r from A atoms averaged over the equilibrium density. In Fig. 2, where the distribution of water (H and O atoms) is analyzed from the central O atom in the COO^- group, we observe two prominent peaks for the hydrogen RDF profiles and one for the oxygen RDF profiles regardless of the charge density f values. The observed high and sharp first peaks as well as the first minimum values close to 0 for both $g_{\text{O}(\text{COO}^-)\text{-H}}$ and $g_{\text{O}(\text{COO}^-)\text{-O}}$ manifest the fact that these COO^- groups are strongly hydrophilic in nature and therefore attract a large amount of water molecules to form shell-like layers surrounding them. In addition, the first peak of the hydrogen RDF profiles occurs at 1.4 Å, which is less than the normal hydrogen bonding length of 1.8 Å [13], indicating that the interaction between the O atom of the COO^- group and the H atom of the water molecule is stronger than the strength of hydrogen bonds in bulk water. This is expected as polar water molecules and negatively charged oxygen atoms have a stronger interaction than in bulk water.

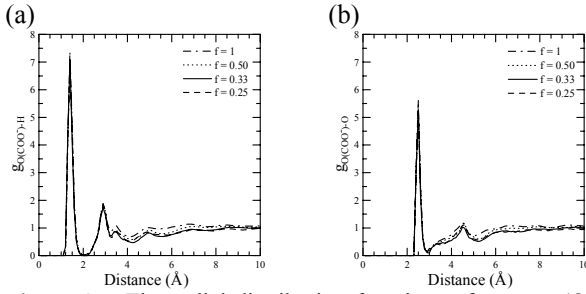


Figure 2. The radial distribution functions of oxygen (O) and hydrogen (H) atoms of water with respect to the O atom in the COO^- groups at various values of charge density f .

Next, we discuss the distribution of water surrounding the COOH group, as shown in Fig. 3. we find the height of the first peaks in Fig. 3 is less than 1, i.e., the local water density surrounding the COOH groups is even smaller than that of bulk water. To clarify, only a small amount of hydrogen bonds form between the water molecules and the COOH groups. Indeed, for the noncharged PMAA case ($f = 0$), we

observe that when the distance from the COOH group is smaller than R_g ($\approx 10\text{Å}$), all the water distribution profiles are far less than 1.0. This indicates that the COOH groups appear to be less hydrophilic in nature and therefore fewer water molecules could remain inside the coiled PMAA chain.

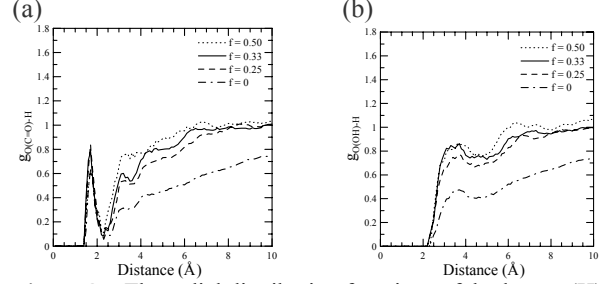


Figure 3. The radial distribution functions of hydrogen (H) atoms of water with respect to the O atom of $-\text{C}=\text{O}$ and $-\text{OH}$ in the COOH groups at various values of charge density f .

Fig. 4(a) presents the vibration spectra of the water oxygen types, O0, O1, and O2, which are obtained by applying the Fourier transformation to the VACF profiles. O0, O1, and O2 belong to the water molecules in the bulk state, with a single hydrogen bond formed with the COO^- group, and with two hydrogen bonds formed with the COO^- groups, respectively. The O0 spectrum shows a major peak centered around 58cm^{-1} and a broad shoulder peak at around $200\text{-}300\text{cm}^{-1}$, which has been observed in other MD studies [14,15]. When water molecules have stronger interactions with charged COO^- groups, through the formation of the hydrogen bonds ($\text{O2} > \text{O1} > \text{O0}$), we observe that both spectrum peaks shift to higher wavenumbers. Worthy of note, is that the second peak of the O2 spectrum (i.e., the bridged water molecules between two neighboring COO^- groups) moves significantly toward 400cm^{-1} . Moreover, the second peak becomes more significant while the first peak shows an opposite trend. Similar to the low frequency Raman spectra of liquid water reported by Walrafen et al.[16], these results imply that the second peak is primarily associated with the H-bonded O-O intermolecular stretching vibration, whereas the first peak is attributed to the non-H-bonded molecules. In Fig. 4(b) we present the hydrogen spectrum, which is typically related to the libration ($400\text{-}1200\text{cm}^{-1}$), intramolecular bending ($1200\text{-}2200\text{cm}^{-1}$) and intramolecular stretching ($2200\text{-}4000\text{cm}^{-1}$) motions. It is apparent that the presence of the charged COO^- groups has a significant influence on the resulting hydrogen spectrum. The hydrogen atoms are divided into four types of H0, H1y, H1n, and H2. Note, for the water molecules with only one hydrogen bond formed with the COO^- group, the two types of hydrogen-bonded and non hydrogen-bonded

H atoms are denoted as H1y and H1n, respectively. We find that for the H1y and H2 atoms, which are strongly connected to the oxygen atoms of the COO⁻ groups, both the libration and bending peaks shift significantly from a lower frequency for H0 towards a higher frequency, whereas the stretching peak shifts oppositely. For the H1n atoms, which are not directly adsorbed into the oxygen atoms of the COO⁻ groups, the shifting degrees of the main peak positions are not as significant as those obtained from the strongly bonded H1y and H2 atoms.

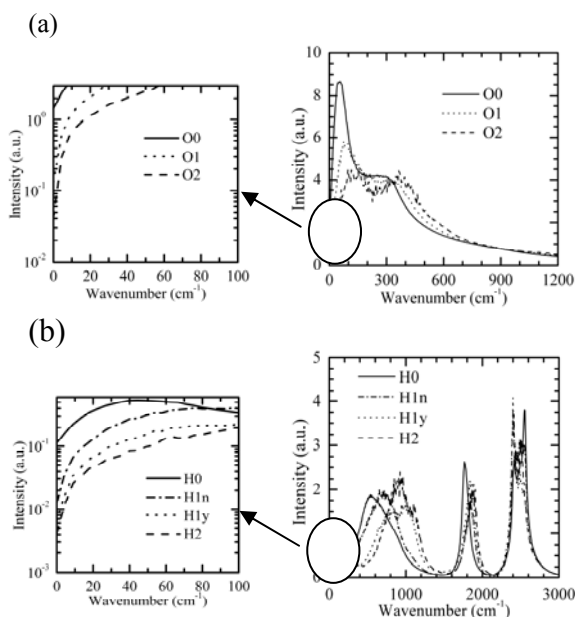


Figure 4. Vibration spectra of (a) oxygen and (b) hydrogen atoms of water in different interaction states with the COO⁻ groups.

CONCLUSION

We employ all-atom molecular dynamics simulations to study a single molecule of PMAA at

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various charge densities f in aqueous solutions. We find that in addition to the repulsive electrostatic interactions between the charged COO⁻ groups, the strong attractive interaction between the charged COO⁻ group and water via the formation of hydrogen bonds holds great influence on both the PMAA chain conformation and the dynamic properties of water. Since bridged water molecules significantly limit torsional and bending degrees of the backbone monomers, it is reasonable to conclude that the rod-like chain conformation, exhibited by the strongly charged polymer chain, is significantly enhanced via the bridged water. Furthermore, this influence slows down water diffusion and enables the two characteristic peaks of the oxygen spectrum to shift to higher frequencies. When water molecules bridge between two neighboring COO⁻ groups, we observe a significant increase to the second peak of the corresponding oxygen spectrum ($\approx 100\text{cm}^{-1}$). This is not surprising since the second peak is mainly attributed to the H-bonded O-O intermolecular stretching vibration. In addition, the strong H-bonded interaction also causes a respective increase of 386cm^{-1} and 111cm^{-1} to the libration and bending peaks of the hydrogen spectrum and a decrease of 151cm^{-1} to the stretching peak.

ACKNOWLEDGMENTS

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