

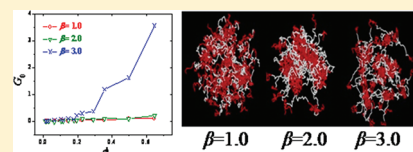
Relationship between Structural Gel and Mechanical Gel for ABA Triblock Copolymer in Solutions: A Molecular Dynamics Simulation

Cui-Liu Fu, Zhao-Yan Sun,* and Li-Jia An*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China

S Supporting Information

ABSTRACT: Polymer gel exists ubiquitously in our daily life, as in food, cosmetics, drugs, and so on. From the structural point of view, the 3D network can be found in a structural gel. In most experimental work, the gel is identified by the sharp increase in modulus; that is, the gel should have similar properties as those of a solid, which is named as mechanical gel. However, not all structural gels have strong mechanical responses. Therefore, studying the relationship between structural gel and mechanical gel is very important. In this work, we investigate the structure and mechanical properties of symmetric ABA copolymers with solvophobic end blocks during the sol–gel transition. Three typical systems with weak, middle, and strong solvophobicities are simulated. It is found that the gelation concentration, gel structure, and mechanical response of structural gel are strongly affected by the solvophobicity of ABA block copolymer. We also find that only the gel formed in strong solvophobic systems has a strong mechanical response. Furthermore, the influence of solvophobicity of A-block on the static and dynamic properties of ABA block copolymers in solutions is also studied to give a molecular understanding of physical gelation.



1. INTRODUCTION

Polymer gels have attracted much attention because of their wide application in our daily lives.¹ Lots of work on the sol–gel transition has been done both experimentally and theoretically, especially for ABA triblock copolymer solutions with solvophobic end A-block and solvophilic or athermal middle B-block.^{2–6} Krause et al.⁷ first reported that ABA block copolymers in selective solvent will form micelles that consist of inner core parts containing the insoluble A blocks and outer corona parts containing both B blocks and solvent molecules.^{8,9} Changing the temperature or increasing the concentration of ABA copolymers brings about bridging or entanglement among these micelles, which makes the structural gel form and the system undergoes a sol–gel transition.¹⁰ Nguyen-Misra and Mattice⁸ explored the structural gelation behavior of ABA copolymers using the Monte Carlo technique and pointed out that critical gel concentration depends on the size and the solvent insolubility of end block, whereas the dependence on the middle block size is weak. Tanaka et al.^{11–13} suggested that the sol–gel transition of these associating polymers was a third-order thermodynamic transition. However, Semenov et al.¹⁴ argued that it was not associated with thermodynamic singularities because structural gelation had an obvious connection with percolation. Although the percolation theory has been established to explain most of the gelation phenomena, some research has argued that the physical gelation was beyond percolation.¹⁵ Studies^{16–21} on the mechanical properties of gel showed that the modulus of gels depends on the gel structure,²² which implies that not all of the structural gel has the corresponding strong mechanical response. Experimentally, a soft gel region is found during the sol–gel transition process,^{22–29} in which soft gel is defined as a fluid with a finite yield stress but too small to confer immobility.

The soft gel is distinguished from a sol by having storage modulus more than loss modulus.²² However, the corresponding structure of soft gel is not well-investigated. Therefore, it is necessary to study the relationship between structural gel and mechanical gel.

Molecular dynamics (MD) simulation has made important contributions to our understanding of polymer self-association.^{18–20,30–32} It can give the information about chain conformation and “visualize” the structure of gel networks, which is difficult to determine by experimental methods.²⁰ In this work, we follow the system of ABA triblock copolymers in solvent that is selectively poor for the end A-block and athermal for the middle B-block using MD simulation method. Our motivation is to bring a more fundamental understanding of the sol–gel transition and show a comprehensive knowledge of the relationship between the gel structures and the mechanical properties. In our study, the effect of solvophobicity on the sol–gel transition of ABA block copolymer solutions is also investigated. Model and simulation details are given in Section 2, and results and discussion are presented in Section 3. Finally, we summarize our results in Section 4.

2. SIMULATION DETAILS

In this simulation, we focus on the gelation behavior of the symmetric ABA triblock copolymer solutions where the solvent is taken to be athermal for the middle block and poor for the end blocks. The ABA copolymer chain is described as bead–spring model, and neighboring monomers interact

Received: January 28, 2011

Revised: August 29, 2011

Published: August 29, 2011

with each other via finitely extensible nonlinear elastic (FENE) potential $U_{\text{FENE}}(r)^{33-35}$

$$U_{\text{FENE}}(r) = -\frac{k}{2}R_0^2 \ln\left(1 - \frac{r^2}{R_0^2}\right) \quad (1)$$

Here r is the distance between neighbor monomers along the chain backbone. K is the spring constant that is $7.0 \epsilon/\sigma^2$ in our system, and $R_0 = 2.0\sigma$ is the ultimate bond length,^{34,36} where σ and ϵ are the units of length and energy, respectively, which will be interpreted in the following parts.

There are two methods to introduce different interactions between A and B monomers. One is by varying the prefactor in Lennard-Jones (L-J) potential with only repulsive potential that has been successfully used in modeling phase separation of polymer blends and microphase separation of block copolymers.³⁷ Another way is to introduce an attractive tail in the shifted L-J potential between A–A potentials to distinguish A and B blocks.^{33,35} Here, in this work, we choose the second method and employ a modified L-J potential $U_{\text{LJ}}^{(m)}(r)$ suggested by Lyulin³³ between A–A monomers

$$U_{\text{LJ}}^{(m)}(r) = \begin{cases} 4\epsilon \left\{ \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right] + \beta \left[\cos \frac{2\pi r}{r_c} - 1 \right] \right\} & r < r_c \\ 0 & r \geq r_c \end{cases} \quad (2)$$

where β controls the strength of the attractive interaction, which is qualitatively equivalent to varying the properties of the solvent. $U_{\text{LJ}}^{(m)}(r)$ has been successfully applied to describe the solubility of the polymer chain in selective solvent; that is, $\beta < 2.53$ represents the polymer chain in good solvent, $\beta = 2.53$ in θ solvent, and $\beta > 2.53$ in poor solvent.³³ More details of the possible physical connection between real system and the meanings of parameters β and ϵ can be found in the Supporting Information. For the nonbond interaction between B–B, B–S, S–S, A–S, and A–B particles, the original shifted L-J potential $U_{\text{LJ}}(r)$ is used to embody the excluded volume potential

$$U_{\text{LJ}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} \right] & r < r_c \\ 0 & r \geq r_c \end{cases} \quad (3)$$

For convenience, the reduced units, namely, σ , ϵ , (σ , ϵ come from the shifted L-J potential $U_{\text{LJ}}(r)$), and monomer mass μ , are used as units of length, energy, and mass. The units of other quantities can be derived from σ , ϵ , and μ , such as the time is measured in units of $\tau_{\text{ij}} = (\mu\sigma^2/\epsilon)^{1/2}$. Herein the cutoff diameter is $r_c = 2^{1/2}\sigma$ for computational efficiency. The introduction of reduced unit could allow the study of many combinations of σ , ϵ , and μ in one time simulation according to the law of corresponding states and reduce the computational error.³⁸ The side length of the simulation box ($L \times L \times L$) with periodic boundary condition is $L = 22.05\sigma$, and the particle number density of the system is selected to be $\rho = 0.864(1/\sigma^3)$.^{34,36} The equations of particle motion governing the evolution of our systems are given by

$$\dot{\vec{r}} = \frac{\vec{p}}{m} \quad (4)$$

$$\dot{\vec{p}} = -\frac{\partial U}{\partial \vec{r}} \quad (5)$$

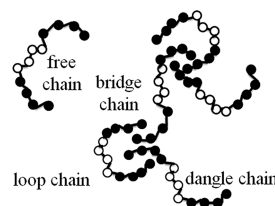


Figure 1. Schematic diagram of four types of chain conformations formed by ABA copolymers. A: solid spheres, B: hollow spheres.

which are integrated via leapfrog algorithm³⁹ with the integration time step $\delta t = 0.006\tau_{\text{ij}}$, and the Verlet-cell list method is employed to accelerate the calculation.⁴⁰ The temperature of these simulation systems is kept at $k_{\text{B}}T = 1.0\epsilon$ controlled via Berendsen thermostat.⁴⁰ To test the finite size effect, we also simulate some representative systems in a large simulation box with $L = 26.25\sigma$ and total of 15 625 particles, and the results are very similar to those obtained in the system with $L = 22.05\sigma$. For convenience, we only show the results obtained in the system with $L = 22.05\sigma$. To obtain an equilibrium structure, we first relax these copolymer chains with 4.0×10^6 time steps as normal polymer chains;³⁶ that is, we do not distinguish A and B blocks. Then, it is followed by 8.0×10^6 time steps relaxing with different potential for A and B blocks. After that, the systems reach equilibrium. Then, the data are collected in the following 7.5×10^6 time steps. In this work, five parallel samples are performed to obtain better statistic results.

The amphiphilic ABA triblock copolymer chains in selective solvent have the ability to aggregate and form micelles. In the simulation, a micelle is defined as a group of two or more chains having A–A interchain contacts. Its aggregation number p characterizes the number-average value of the number of A blocks in a given micelle,⁸ which is defined by the following equation

$$p = \frac{\sum_{i=1}^n p_i}{n} \quad (6)$$

where p_i is the number of A blocks in the i th micelle and n is the total number of micelles.⁸ ABA block copolymer in solvent can form four types of chain conformations (Figure 1), that is, loop chain (both of the two end A blocks belong to the same micelle), bridge chain (the two end A blocks are in different micelles), dangling chain (only one A block is in micelles), and free chain (none of the A blocks is in any micelles).⁸ We introduce f_{l} , f_{b} , f_{d} , and f_{f} denoting the fractions of loop, bridge, dangling, and free chains, respectively.⁸ When there is a group of interconnecting (or bridging) micelles passing through the box boundaries in all three directions x , y , and z with periodic boundary conditions, these interconnecting micelles produce an infinitely large 3-D network, and the system is defined as a structural gel.⁸ The geometric percolation method is employed to estimate the emergence of a connected network structure.²⁰

3. RESULTS AND DISCUSSION

We follow the system of ABA triblock copolymer in solvent with different solvophobicities using MD simulation method. For convenience, the chain structure of our model is fixed as

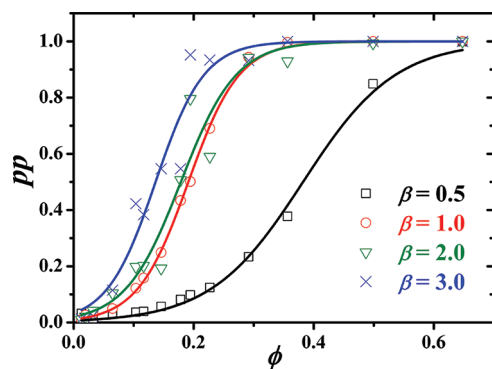


Figure 2. Percolation probability (PP) of ABA copolymer solutions with $\beta = 0.5$ (\square), 1.0 (\circ), 2.0 (∇), and 3.0 (\times) as a function of concentration Φ , where the solid lines are Sigmoidal fit lines.

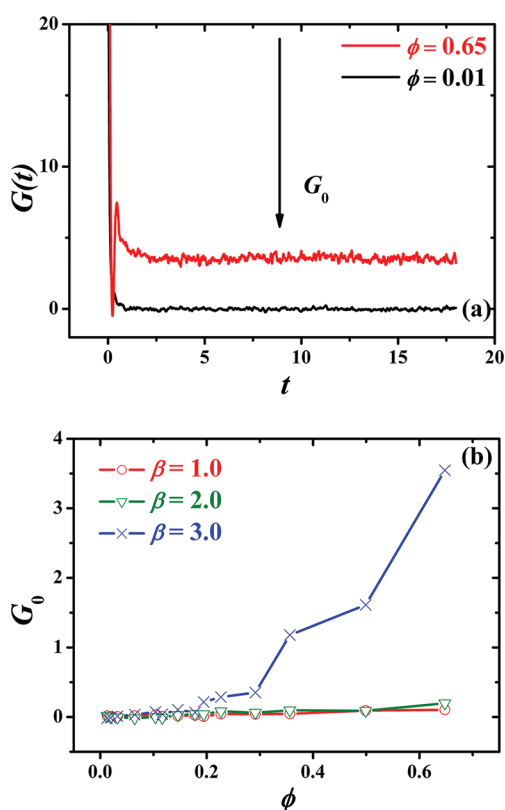


Figure 3. (a) Stress autocorrelation function $G(t)$ of the ABA copolymer system with $\Phi = 0.01$ (black) or 0.65 (red), and $\beta = 3.0$ as a function of time t . (b) Plateau value G_0 of $G(t)$ in copolymer system with $\beta = 1.0$ (\circ), 2.0 (Δ), 3.0 (\times) in terms of Φ .

$A_{10}B_{10}A_{10}$ linear block copolymers. The solvophobicity of A-block is varied by changing the parameter β in the modified L-J potential (eq 2). The percolation probabilities of $A_{10}B_{10}A_{10}$ polymer solutions with different β are shown in Figure 2. It is seen that the gelation is easy to occur for the system with high solvophobicity (i.e., $\beta = 3.0$). To understand the solvophobicity dependence on the gelation behavior of the copolymer system, we focus on three model systems, that is, ABA triblock copolymer systems with $\beta = 1.0, 2.0$, and 3.0 of A blocks, corresponding to weak, middle, and strong solvophobicities, respectively.

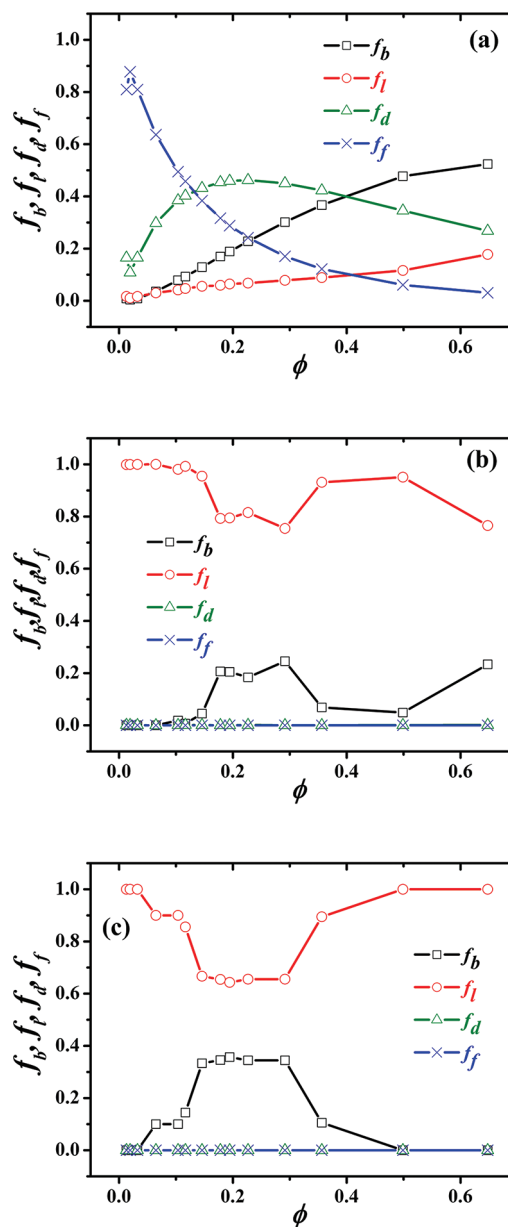


Figure 4. Concentration dependence of the fractions of bridge (f_b (\square)), loop (f_l (\circ)), dangling (f_d (Δ)), and free (f_f (\times)) chains formed by ABA copolymers with $\beta = 1.0$ (a), 2.0 (b), and 3.0 (c).

The stress autocorrelation function $G(t)^{20,40,41}$ is introduced in this work to study the mechanical properties of obtained gel for block copolymer solutions¹⁸

$$G(t) = \frac{V}{3k_B T} \sum_{\alpha\gamma} \langle \sigma_{\alpha\gamma}(t_0) \sigma_{\alpha\gamma}(t_0 + t) \rangle \quad (7)$$

$$\sigma_{\alpha\gamma} = \mu \sum_{i=1} v_{i\alpha} v_{i\gamma} + 1/2 \sum_{i \neq j} r_{ij\gamma} f_{ij\alpha} \quad (8)$$

where k_B is Boltzmann's constant, V is the volume of the simulation box, and $\langle \dots \rangle$ is a time average taken over all time origins t_0 . $\sigma_{\alpha\gamma}$ is the stress tensor of the system with $\alpha, \gamma = x, y, z$, where μ is the monomer mass, $v_{i\alpha}$ is the α component of the velocity of i th atom, $r_{ij\gamma}$ is the γ component of the vector \vec{r}_{ij}

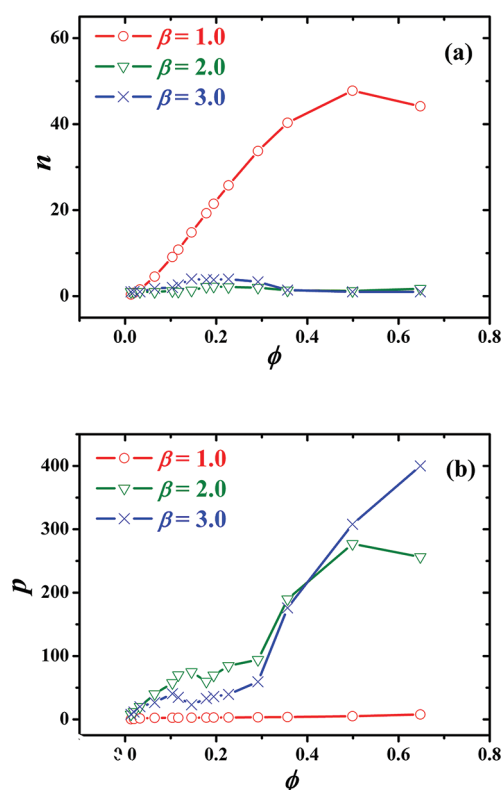


Figure 5. Concentration dependence of the number (a) and aggregate number (b) of micelles formed by ABA copolymers with $\beta = 1.0$ (\circ), 2.0 (Δ), and 3.0 (\times).

separating i th and j th monomer, and $f_{ij\alpha}$ is the α component of the force exerted on the i th monomer by the j th monomer.²⁰ The zero-shear viscosity can be derived from the integration of $G(t)$; that is, $\eta = \int_0^\infty G(t) dt$. For mechanical gel, which has similar properties as those of a solid, the value of zero-shear viscosity will diverge, and thus $G(t)$ will not converge to zero with the evolution of time. Therefore, the function of $G(t)$ could be considered as a criterion of mechanical property for a given system. As shown in Figure 3a, $G(t)$ decays to a plateau G_0 (G_0 is obtained by a statistical average method of the plateau) with the evolution of simulation time, and G_0 is close to zero for solution ($\phi = 0.01$) and nonzero for solid-like system ($\phi = 0.65$). Therefore, the nonzero of G_0 suggests the solid-like behavior of systems,²⁰ and the value of G_0 represents the strength of the mechanical response of the system. Through the observation of G_0 in the three model systems (Figure 3b), we find that the stronger the solvophobicity of A block is, the greater the mechanical response of the system is. For weak ($\beta = 1.0$) and middle ($\beta = 2.0$) solvophobic systems, because both G_0 are very close to zero, the unlimited networks formed in these systems have only very weak mechanical responses. For the strong solvophobic system ($\beta = 3.0$), G_0 is also close to zero at low ϕ and then increases rapidly after gelation concentration; that is, the network in such system already has a strong mechanical response, and thus the mechanical gel is formed.²⁰ Our results are in agreement with those of Kumar and Douglas et al.,¹⁵ who denoted two extreme types of gels formed by physically associated polymers with “stickers”; that is, geometrical percolation closely corresponds to gelation for association polymers with large sticker pairing energy ε and does not guarantee solid-like

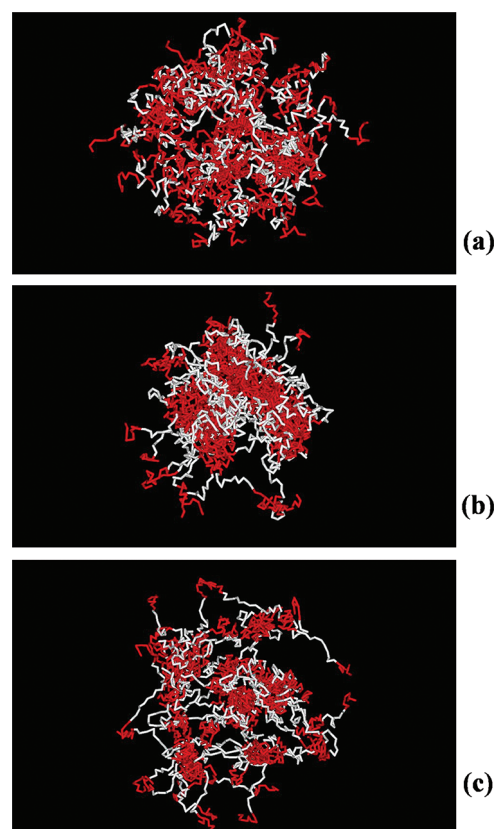


Figure 6. Snapshots of ABA triblock copolymer in solvent with $\Phi = 0.29$ and different solvophobic property (a) $\beta = 1.0$, (b) $\beta = 2.0$, and (c) $\beta = 3.0$, where A: red, B: white. The solvent particles are not shown in these snapshots.

behavior at long times for those ones with small ε proved by refs 42 and 43.

From the above discussion, we know that the mechanical responses of gel networks formed by different solvophobicities of A blocks are totally different. In another word, for block copolymers with different solvophobicities, the gelation mechanism might be different, which leads to different mechanical responses of the gels. To describe the gel structure and gelation mechanism of the ABA copolymer systems, we focus on the dependence of concentration ϕ on the fractions of bridge (f_b), loop (f_l), dangling (f_d), and free (f_f) chains in ABA copolymers.⁴⁴ As shown in Figure 4, for weak ($\beta = 1.0$, Figure 4a) solvophobic system, most of the polymer chains are free at low ϕ ; then, the increase in ϕ augments the fractions of bridge, loop, and dangling chains. The emergence of bridge chains implies the connection between different micelles, which is very helpful to the formation of gel network. Therefore, the competition among bridge, loop, dangling, and free chains dominates the formation of a gel structure in weak solvophobic system. For middle ($\beta = 2.0$, Figure 4b) and strong ($\beta = 3.0$, Figure 4c) solvophobic systems, most of the ABA chains tend to associate and form loop chains at low concentration. With increasing ϕ , bridge chains occur, but most of ABA copolymers chains still exist as loop chains. Therefore, in these two cases, the bridging interaction among micelles promotes the formation of gel network, but it is not the main reason.

To find the dominant factor of the sol–gel transition of ABA copolymers with different solvophobicities, we investigate the number n (Figure 5a) and aggregation number p (Figure 5b) of

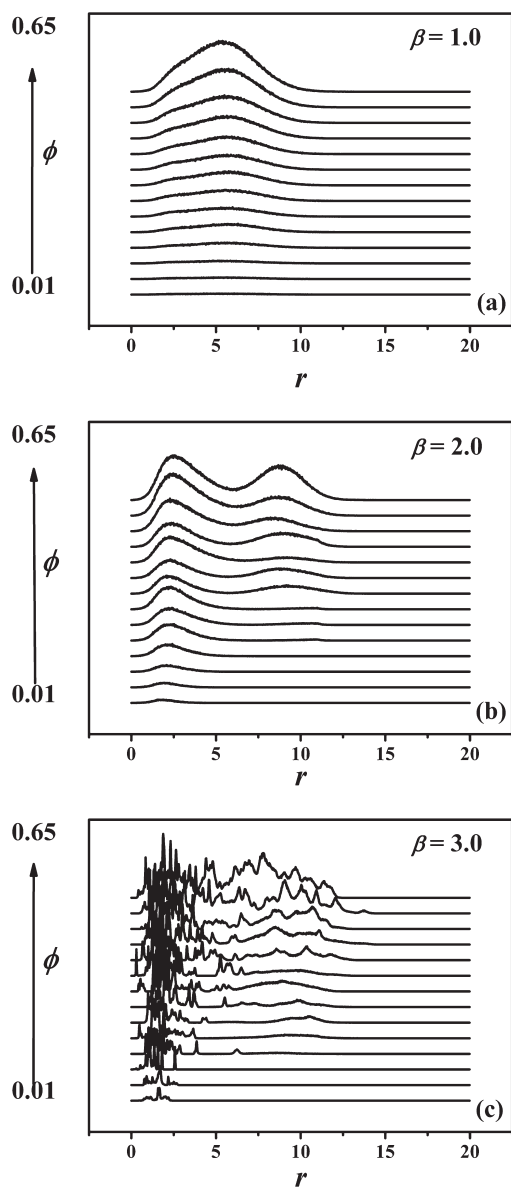


Figure 7. Φ dependence of the distribution of the mass center distance of the two A blocks in the same ABA chain with $\beta = 1.0$ (a), 2.0 (b), and 3.0 (c).

micelle dependence on the concentration ϕ in these systems with weak, middle, and strong solvophobicities. It is observed that for the system with weak solvophobicity the number of micelles greatly increases with the increase in ϕ , corresponding to the small value of aggregation number, whereas for those with middle and strong solvophobicities the number of micelles increases gradually, followed by a slight decrease until it reaches the plateau, corresponding to the slight increase first, then the decrease and finally dramatic increase in aggregation number. It should be noted, for the system with weak solvophobicity, that the size of micelles almost keeps unchanged and the number of micelles increases greatly during gelation process, which means that the bridging between different micelles is formed during gelation process (Figure 6a). However, the bridge chains between different micelles are not strong enough so that the formed gel almost has no strong mechanical response. For the system with middle and strong solvophobicities, the size of micelles grows and the

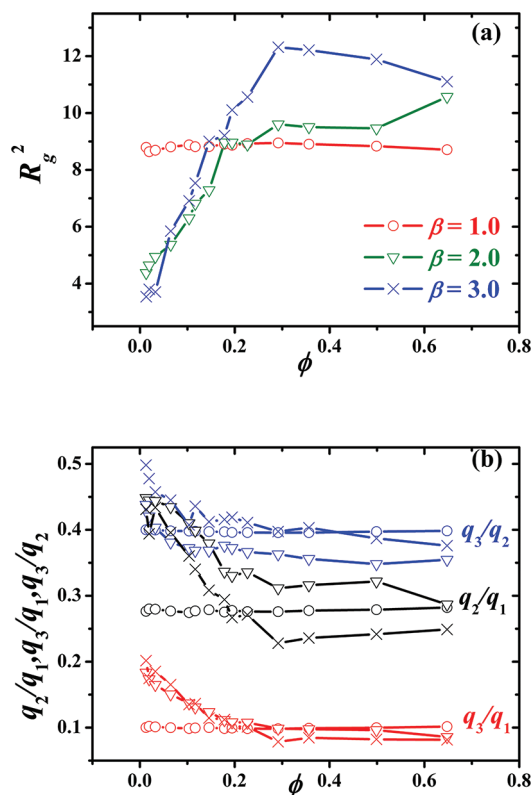


Figure 8. Mean square radius of gyration (a) and the shape (b) of ABA copolymer with $\beta = 1.0$ (\circ), 2.0 (Δ), and 3.0 (\times) as functions of Φ , where q_2/q_1 (black), q_3/q_1 (red), and q_3/q_2 (blue).

aggregation number p of micelle first increases then decreases and finally increases rapidly with the increase in ϕ . Moreover, the micelles in the system with $\beta = 2.0$ are much looser than those in $\beta = 3.0$ system; because the A blocks with attractive interaction of $\beta = 2.0$ are not strong enough, A blocks have the ability to exclude B blocks or solvent particles and associate with each other but not close enough to make other A blocks have no opportunity to approach the micelles (Figure 6b,c). This means that the coalescence between neighbored micelles occurs during the gelation process, which makes the obtained gel have a strong mechanical response. This result is consistent with those of Hamley et al.,²² who pointed out that the mechanical properties of physical gel depend on the gelation mechanism and gel structure, which distinguishes which kind of structural gel has strong mechanical response. Our results also tell us the reason why there is a soft gel region during the sol–gel transition, which has already been observed in experiment.^{22–29}

The mechanical response of a given gel is greatly related to its microscopic structure. To get a much clearer picture of gel structure, we studied the distribution $H(r)$ of the distance of mass center of the two A-blocks in the same ABA chain (Figure 7), where $H(r)$ is obtained by an average over all samples. For the weak solvophobic system ($\beta = 1.0$), the distribution curve has a single peak at $r \approx 5.5\sigma$ for weakly stretched bridge chains or dangling chains and a very weak shoulder peak at $r \approx 2.3\sigma$ for close-end ring chains (Figure 7a), whereas for $\beta = 2.0$ system (Figure 7b), there are two peaks in the distribution curve, that is, a peak at $r \approx 2.3\sigma$ for close-end ring chains and a peak at $r \approx 9.4\sigma$ for strongly stretched chains. For the system with strong solvophobicity ($\beta = 3.0$), the distribution of the distance of mass center $H(r)$ shows a multipeak,

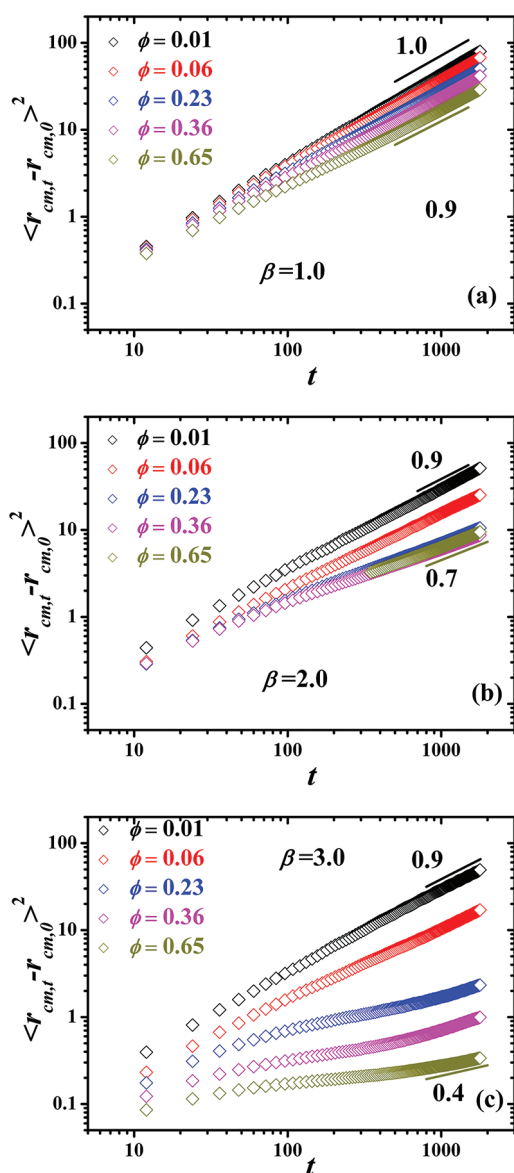


Figure 9. Mean square distance of the mass center of the ABA copolymers with $\beta = 1.0$ (a), 2.0 (b), and 3.0 (c) in terms of time t , where different color means different concentration Φ .

which implies the heterogeneity of chain structure of gel network (Figure 7c).

The microscopic properties, such as the mean square radius of gyration $\langle R_g^2 \rangle$, the shape, and the mean square displacement of molecule, will also change during the gelation process. The mean square radius of gyration $\langle R_g^2 \rangle$ (Figure 8a) is given by

$$\langle R_g^2 \rangle = \frac{1}{2N^2} \sum_{i=1}^N \sum_{j=1}^N (\vec{r}_i - \vec{r}_j)^2 \quad (9)$$

where \vec{r}_i and \vec{r}_j are the position vectors of the i th and the j th monomers, respectively.^{34,36} A tensor \mathbf{Q} describing the mass distribution of a polymer chain is introduced to characterize the shape of ABA copolymer, whose component is⁴¹

$$q_{\alpha\gamma} = \frac{1}{N} \sum_{i=1}^N (r_{\alpha i} - \bar{r}_\alpha)(r_{\gamma i} - \bar{r}_\gamma) \quad (10)$$

where $r_{\alpha i}$, $r_{\gamma i}$, \bar{r}_α , and \bar{r}_γ are the α and γ components of the position vector of the i th monomer and the mass center of polymer chain, respectively. The ratios among the three eigenvalues q_1 , q_2 , and q_3 of \mathbf{Q} reflect the shape of the polymer chain, which satisfy $q_1 > q_2 > q_3$ and $q_1 + q_2 + q_3 = \langle R_g^2 \rangle$. For example, if $q_2/q_1 = q_3/q_1 = q_3/q_2 = 1$, then the chain is spherical.⁴¹ As shown in Figure 8, the sizes and shapes of the ABA copolymers in the system with weak solvophobicity ($\beta = 1.0$) change a little with increasing ϕ , whereas in the systems with middle ($\beta = 2.0$) or strong ($\beta = 3.0$) solvophobicities, the polymer chain shrinks strongly at low ϕ , then its size increases and the shape tends to be a thinner ellipsoid with increasing ϕ , resulting in the polymer chain stretching strongly at high ϕ . Moreover, for the system with strong solvophobicity, the polymer chain shrinks strongly at low ϕ and stretches greatly at high ϕ , which makes the strong mechanical response at high ϕ .

The mean square displacement⁴⁵ of the mass center of ABA triblock copolymer is given by

$$s = \langle (\vec{r}_{cm}(t_0 + t) - \vec{r}_{cm}(t_0))^2 \rangle \quad (11)$$

where $\vec{r}_{cm}(t_0 + t)$ is the position vector of the mass center of ABA chain at time $t_0 + t$. Figure 9 shows the solvophobicity dependence on the diffusion behaviors of copolymer chains. At low ϕ , the diffusion of ABA copolymers with weak (Figure 9a), middle (Figure 9b), and strong (Figure 9c) solvophobic A blocks behaves as Brownian motion, which follows Einstein relation⁴⁵ ($s \approx t^\delta$, $\delta = 1.0$) but deviates from Einstein relation at high ϕ . The lines with scaling index $\delta = 1.0, 0.9, 0.7$, and 0.4 are also drawn in this Figure as the guide to the eye. As can be seen, the diffusion is slowed for high ϕ , especially for strong solvophobic systems, which is in consistency with the result of Guo and Bedrov et al.^{18,20} This indicates that the arrested dynamics resulting from the formation of aggregative structures, namely, the occurrence of aggregations, results in the localized motion of the A blocks within a certain aggregation.¹⁸ Furthermore, the diffusion behaviors of ABA triblock copolymers in a strong solvophobic system are greatly limited by the aggregations, which results from the compactness of the aggregations formed by strong solvophobic systems. This can also explain why the physical gel formed in strong solvophobic system has a strong mechanical response.

4. CONCLUSIONS

We have determined the solvophobicity effect on the sol–gel transition behavior of the ABA block copolymer system and given the relationship between structural gel and mechanical gel using MD simulation method. For weak solvophobic system, the formation of the network is caused by the bridging of micelles, and very weak mechanical response of the structure gel can be found, whereas for system with strong solvophobicity, the combination of bridging and coalescence among neighbored micelles leads to the occurrence of gel structure, and strong mechanical response is found greatly in such a system. The possible reason is that the strong solvophobicity of ABA triblock copolymer makes the formed micelles more compacted and the bridging among micelles much stronger. This result will be helpful for the further understanding of the sol–gel transition behavior of ABA copolymer systems.

■ ASSOCIATED CONTENT

S Supporting Information. More details about the reduced units used in this work and the physical connection between real system and the meanings of parameters β and ε employed in our work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: +86-431-85262969. Tel: +86-431-85262896. E-mail: zysun@ciac.jl.cn.

■ ACKNOWLEDGMENT

This work is supported by the National Natural Science Foundation of China (21074137, 21104082, 50873098 and 50930001) Programs and the Fund for Creative Research Groups (50921062). We also appreciate the financial support of National Basic Research Program of China (973 Program, 2012CB821500).

■ REFERENCES

- (1) Li, Y.; Shi, T.; Sun, Z.; An, L.; Huang, Q. *J. Phys. Chem. B* **2006**, *110*, 26424–26429.
- (2) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1989**, *30*, 170–177.
- (3) Nagarajan, R.; Ganesh, K. *J. Chem. Phys.* **1989**, *90*, 5843–5856.
- (4) Munch, M. R.; Gast, A. P. *Macromolecules* **1988**, *21*, 1360–1366.
- (5) Noolandi, J.; Hong, K. M. *Macromolecules* **1983**, *16*, 1443–1448.
- (6) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550–3557.
- (7) Krause, S. *J. Phys. Chem.* **1964**, *68*, 1948–1955.
- (8) Nguyen-Misra, M.; Mattice, W. L. *Macromolecules* **1995**, *28*, 1444–1457.
- (9) Semenov, A. N.; Joanny, J. F.; Khokhlov, A. R. *Macromolecules* **1995**, *28*, 1066–1075.
- (10) Baljon, A. R.; Flynn, D.; Krawzsenek, D. *J. Chem. Phys.* **2007**, *126*, 044907.
- (11) Tanaka, F. *Macromolecules* **1998**, *31*, 384–393.
- (12) Tanaka, F.; Matsuyama, A. *Phys. Rev. Lett.* **1989**, *62*, 2759–2762.
- (13) Tanaka, F.; Stockmayer, W. H. *Macromolecules* **1994**, *27*, 3943–3954.
- (14) Semenov, A. N.; Rubinstein, M. *Macromolecules* **1998**, *31*, 1373–1385.
- (15) Kumar, S. K.; Douglas, J. F. *Phys. Rev. Lett.* **2001**, *87*, 188301.
- (16) Aamer, K. A.; Sardinha, H.; R.Bhatia, S.; Tew, G. N. *Biomaterials* **2004**, *18*, 1087–1093.
- (17) Eiser, E.; Molino, F.; Porte, G.; Pithon, X. *Rheol. Acta* **2000**, *39*, 201–208.
- (18) Bedrov, D.; Smith, G. D.; Douglas, J. F. *Europhys. Lett.* **2002**, *59*, 384–390.
- (19) Groot, R. D.; Agterof, W. G. M. *Macromolecules* **1995**, *28*, 6284–6295.
- (20) Guo, L.; Luijten, E. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 959–969.
- (21) Yu, J. M.; Dubois, P.; Teyssié, P.; Jérôme, R.; Blacher, S.; Brouers, F.; L'Homme, G. *Macromolecules* **1996**, *29*, 5384–5391.
- (22) Hamley, I. W.; Mai, S. M.; Ryan, A. J.; Patrick, J.; Fairclough, A.; Booth, C. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2972–2980.
- (23) Tang, J.; Xie, Y.; Sun, Z.; An, L. *Chem. J. Chin. Univ.* **2010**, *31*, 383–386.
- (24) Li, H.; Yu, G. -E.; Price, C.; Booth, C. *Macromolecules* **1997**, *30*, 1347–1354.
- (25) Hyun, K.; Nam, J. G.; Wilhelms, M.; Ahn, K. H.; Lee, S. J. *Rheol. Acta* **2006**, *45*, 239–249.
- (26) Yang, Z.; Crothers, M.; Ricardo, N. M. P. S.; Chaibundit, C.; Taboada, P.; Mosquera, V.; Kelarakis, A.; Havredaki, V.; Martini, L.; Valder, C.; Collett, J. H.; Attwood, D.; Heatley, F.; Booth, C. *Langmuir* **2003**, *19*, 943–950.
- (27) Mingvanish, W.; Kelarakis, A.; Mai, S. M.; Daniel, C.; Yang, Z.; Havredaki, V.; Hamley, I. W.; Ryan, A. J.; Booth, C. *J. Phys. Chem. B* **2000**, *104*, 9788–9794.
- (28) Yu, G. -E.; Li, H.; Fairclough, A.; Ryan, A. J.; Mckeown, N.; Ali-Adib, Z.; Price, C.; Booth, C. *Langmuir* **1998**, *14*, 5782–5789.
- (29) Chaibundit, C.; Ricardo, N. M. P. S.; Ricardo, N. M. P. S.; Costa, F. M. L. L. C.; Wong, M. G. P.; Hermida-Merino, D.; Rodriguez-Perez, J.; Harmley, I. W.; Yeates, S. G.; Booth, C. *Langmuir* **2008**, *24*, 12260–12266.
- (30) Khalatur, P. G.; Khokhlov, A. R.; Kovalenko, J. N.; Mologin, D. A. *J. Chem. Phys.* **1999**, *110*, 6039–6049.
- (31) Khalatur, P. G.; Khokhlov, A. R.; Mologin, D. A. *J. Chem. Phys.* **1998**, *109*, 9602–9613.
- (32) Anderson, J. A.; Travesset, A. *Macromolecules* **2006**, *39*, 5143–5151.
- (33) Lyulin, A. V.; Dünweg, B.; Borisov, O. V.; Darinskii, A. A. *Macromolecules* **1999**, *32*, 3264–3278.
- (34) Dünweg, B. *J. Chem. Phys.* **1993**, *99*, 6983–6997.
- (35) Soddemann, T.; Dünweg, B.; Kremer, K. *Eur. Phys. J. E* **2001**, *6*, 409–419.
- (36) Fu, C.; Ouyang, W.; Sun, Z.; An, L. *J. Chem. Phys.* **2007**, *127*, 044903.
- (37) Grest, G. S.; Lacasse, M.-D. *J. Chem. Phys.* **1996**, *105*, 10583–10594.
- (38) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; Academic Press: San Diego, 2002.
- (39) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. *J. Chem. Phys.* **1984**, *81*, 3684–3690.
- (40) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon: Oxford, U.K., 1987.
- (41) Rapaport, D. C. *The Art of Molecular Dynamics Simulation*; Cambridge University Press: New York, 1995.
- (42) Grant, M. C.; Russel, W. B. *Phys. Rev. E* **1993**, *47*, 2606–2614.
- (43) Bergenholtz, J.; Fuchs, M. *Phys. Rev. E* **1999**, *59*, 5706–5715.
- (44) Li, Y.; Sun, Z.; Su, Z.; Shi, T.; An, L. *J. Chem. Phys.* **2005**, *122*, 194909.
- (45) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University: Oxford, U.K., 2003.