



Effect of chain composition on the mechanical response of structural gel: A molecular dynamics simulation



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ARTICLE INFO

Article history:

Received 13 December 2013

Received in revised form

21 May 2014

Accepted 6 July 2014

Available online 12 July 2014

Keywords:

Chain composition effect

Molecular dynamics simulation

Mechanical property of polymer gel

ABSTRACT

Polymer gels, defined either from the structural point of view (structural gel) or by their mechanical properties (mechanical gel), are ubiquitous in our daily life. In our previous work (*J. Phys. Chem. B*, 2011, 115, 11345), we reported that, the mechanical gel formed by strong solvophobic ABA block copolymers with fixed chain compositions shows a strong mechanical response, which meant the formed gel had a high modulus. In this work, we focus on the effect of chain composition on the relationship between structural gel and mechanical gel, where the chain length of block copolymer is lower than its entanglement chain length for simplicity. Our results show that the chain composition has a great effect on the mechanical response of the ABA copolymer solutions with a strong solvophobicity. On the other hand, for the structural gel formed by weak solvophobic block polymers, we do not find any strong mechanical responses even we change the chain composition in a wide range. Moreover, we find three typical gelation processes, accompanied with three kinds of different mechanical responses. These results may provide us an effective method to control the mechanical property of a polymer gel as expected.

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1. Introduction

Polymer gels have attracted a lot of attentions in both theory [1–12] and experiments [13–22] due to their wide applications, such as drug delivery, food processing, and material templates, etc [23–26]. A telechelic ABA copolymer, consisting of two solvophobic end A-blocks and a solvophilic or an athermal middle B-block [27–31], has become a good model to study the gelation behavior of block copolymers as it can form a physical gel reversibly when the temperature of solution is changed. Previous studies [32–34] have already reported that the gelation properties of ABA block copolymer in selective solvent depended greatly on the solvophobicity of A-blocks, including gelation concentrations and mechanical properties. Nguyen-Misra's results showed that the gelation concentration has a power-law dependence on the chain incompatibility [33]. Besides the chain solvophobicity, the chain composition [32,33,35–44] is also a key factor to influence the gelation behavior. Mattice et al. [33] reported that gelation concentration depended on the size and the solvophobicity of end A-blocks greatly, but weakly on the size of middle B-blocks by using

Monte Carlo method. Aamer [35] and Yu [39] found that the elastic modulus of ABA block copolymer gel strongly depended on the length of A-block. Kwon et al. indicated that the modulus of block copolymer solution were sensitive to the length ratio of hydrophilic to hydrophobic blocks [41–43]. Moreover, the mechanical properties depend on the gel microstructure greatly [18,19,36].

In our previous work, we found that the mechanical properties of gels formed by ABA copolymers depended on the solvophobicities of the end A-blocks, and only the structural gel obtained in a strong solvophobic system had a strong mechanical response [45]. Except for the chain solvophobicity, as mentioned above, the length and the proportion of solvophobic A-blocks also affect the property of a gel. For A-block with a long chain length or a high proportion, the effective solvophobicity of the A-block increases, hence the chain length or proportion of an A-block might be physically equivalent to its solvophobicity. Thus there might be four scenarios for the system with different solvophobicities and A-block chain length or proportion: 1) A strong mechanical gel can be formed by a long chain length or a high proportion of A-blocks with a strong solvophobicity; 2) A weak mechanical gel should be formed in the system with a short chain length or a low proportion of A-block even for a strong solvophobicity; 3) A strong mechanical gel can be formed for a short length or a low proportion of A-blocks

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with weak solvophobicity; 4) A weak mechanical gel might be formed for weak solvophobic block copolymers, when the chain length of A-blocks is long enough, or the A-block proportion is high enough. Therefore, the motivation of the present work is to show the validity of these scenarios and understand the effect of chain composition on the relationship between structural gel and mechanical gel. We study the sol–gel transition of ABA triblock copolymers with different chain compositions by using molecular dynamics (MD) simulation method since MD can give the inside information of a gel network, and has been successfully employed in the studies on polymer self-association [6,32,37,38]. It is interesting to find that, for ABA block copolymers with a strong solvophobicity, the chain composition effect makes the sol–gel transition processes exhibit three typical gelation processes together with three kinds of different mechanical responses. For the block copolymers with a weak solvophobicity, we did not find any chain composition effect on the mechanical responses of the systems. We give MODEL AND SIMULATION DETAILS in section II, RESULTS AND DISCUSSION in section III, and SUMMARY in section IV.

2. Model and simulation details

We consider ABA triblock copolymer systems, in which the solvent is taken to be athermal for the middle B-blocks and selectively poor for the end A-blocks [45]. In our model, an ABA block copolymer is described as a bead-spring chain, which can be considered as a freely jointed chain [46]. The neighboring monomers interact with each other via finitely extensible nonlinear elastic (FENE) potential [47–49] $U_{\text{FENE}}(r)$,

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

where r is a distance between neighbor monomers along the chain backbone. The spring constant k is $7.0 \epsilon/\sigma^2$ and the ultimate bond length R_0 is 2.0σ in reduced units [48,50]. A modified Lennard-Jones potential $U_{\text{LJ}}^{(m)}(r)$ brought forward by Lyulin [47] is employed to distinguish A and B particles by introducing an attractive tail in the shifted Lennard-Jones potential between A–A monomers [47,49],

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

here β controls the strength of the A-block solvophobicity, which is equivalent to varying the properties of solvent, i.e. $\beta < 2.53$ represents the polymer chain in good solvent, $\beta = 2.53$ in θ solvent and $\beta > 2.53$ in poor solvent [47]. For the other cases, such as B–B, B–S, S–S, A–S and A–B interactions, a usual Lennard-Jones potential $U_{\text{LJ}}(r)$ is used to embody the excluded volume interaction.

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

where, σ , ϵ , monomer mass μ are used respectively as units of length, energy and mass for convenience, resulting in that the time is measured in unit of $\tau_{\text{LJ}} = (\mu\sigma^2/\epsilon)^{1/2}$. For computational efficiency, the cutoff diameter is set as $r_c = 2^{1/6}\sigma$ in reduced units. Besides, we have made an effort to describe the system in such a way so that it can be linked to an experimental system. The simulation parameters β or ϵ can be mapped onto the Flory–Huggins interaction

parameter χ in real systems. A clear description of the connection between β or ϵ and the real experimental system is illustrated in the Supporting Information file of our previous work [45]. In this work, we only focus on the effect of solvophobicity of A-blocks on the gelation process of block copolymers. It should be noted that the change of solvophobicity of B-block will also affect the gel structure and the mechanical property of gel. However, for block copolymers with strong solvophobic B-block, the bridge chains will disappear and the gel forms through the packing of micelles. Since the gelation mechanism of such system is quite different, this will not be included in the present work.

The simulation box ($L \times L \times L$) has a side length of $L = 22.05\sigma$ with periodic boundary conditions, and its particle number density is selected to be $\rho = 0.864$ ($1/\sigma^3$) [48,50]. The simulation temperature is kept at $k_{\text{B}}T = 1.0\epsilon$ controlled via Berendsen thermostat [51]. We integrate the following governing equations of particle motions [52]

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

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

using leap-frog algorithm [51] with an integration time step of $\delta t = 0.006\tau_{\text{LJ}}$, and meanwhile, employ Verlet-cell list method for an acceleration of the computing speed [52]. We also did similar simulations for some typical systems in a larger simulation box of $L = 26.25\sigma$ to test the finite size effect caused by simulation boxes. The results are very similar as those obtained in original simulation boxes of $L = 22.05\sigma$. Therefore, the results shown in this work are obtained only for systems with $L = 22.05\sigma$ for computational efficiency. To obtain equilibrium structures, we first remove the solvophobicity of the end A-blocks (i.e., we let $\beta = 0$) and relax the polymer chains for 4.0×10^6 time steps (We do not distinguish A-blocks and B-blocks in this step), and then followed by a period of 8.0×10^6 time steps relaxing with different potentials for A-blocks and B-blocks. When the system is in equilibrium, we collect data in the next 7.5×10^6 time steps. Besides, five parallel samples are performed to obtain a better statistic result [45].

ABA block copolymers in selective solvent mainly form two kinds of aggregative structures, i.e. micelles and clusters. A micelle is defined as a group of two or more chains having A–A inter-chain contacts, whose aggregation number p is a number-average quantity in terms of the number of A-blocks in the micelle [33,45]. A cluster is defined as a group of interconnecting or bridging micelles; and its aggregation number w is presented as a function of the number of copolymer chains [33]. p and w are given by the following equations

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

$$w = \sum_{j=1}^m w_j/m \quad (7)$$

where, p_i is the number of A-blocks in the i -th micelle; w_j is the number of ABA chains in the j -th cluster; and n , m is the total number of micelles and clusters, respectively [33]. The ABA triblock copolymers can form four kinds of chain conformations, i.e. bridge, loop, dangling and free chains [33,45]. A bridge chain means the two A-blocks belong to different micelles; a loop chain means the two A-blocks are in the same micelle; a dangling chain has only one

A-block in the micelle, and a free chain means that no A-block is in the micelle [33,45]. A sketch for the four types of chain conformations is given in Fig. 1. We define f_{ml} , f_{mb} , f_{md} to represent the fractions of loop, bridge and dangling chains in the largest cluster, respectively. In the largest cluster, if there is a connective path passing through the box boundaries in all x , y , and z directions, an infinitely three-dimension network will form, and then the system can be considered as a structural gel. Based on this, we can obtain the gelation concentration ϕ^* by using geometric percolation method [38].

3. Results and discussion

3.1. The sol–gel transition of ABA block copolymer solutions with a strong solvophobicity

We first concentrate on the relationship between structural gel and mechanical gel for strong solvophobic systems (i.e. $\beta = 3.0$, where β is illuminated in equation (2)). A structural gel can be determined from its microstructure based on the percolation theory, and the mechanical gel can be determined from the stress autocorrelation function [45]. The chain compositions of ABA copolymers are set as $A_{N_A}B_{N_B}A_{N_A}$ (The corresponding numbers of N_A and N_B are given in Table 1). It should be noted that the entanglement effect is not included in this work, because the polymerization degree N ($N = 2N_A + N_B$) of a polymer chain is less than 40, which is much lower than the entanglement length N_e of a bead-spring chain (In our simulation, polymers do not show entanglement behavior up to the chain length 120, which implies N_e is higher than 120 in the present bead-spring model). We track the formation of a structural gel network and characterize the gelation concentration ϕ^* via percolation probability. The mechanical response is calculated from a stress autocorrelation function $G(t)$ [52,53], which can be calculated based on the following equations [38,52,53]:

$$G(t) = \frac{V}{3k_B T} \sum_{\alpha\gamma} \langle \sigma_{\alpha\gamma}(t_0) \sigma_{\alpha\gamma}(t_0 + t) \rangle \quad (8)$$

$$\sigma_{\alpha\gamma} = \mu \sum_{i=1} v_{i\alpha} v_{i\gamma} + \frac{1}{2} \sum_{i \neq j} r_{ij\gamma} f_{ij\alpha} \quad (9)$$

$\sigma_{\alpha\gamma}$ ($\alpha, \gamma = x, y, z$) is a stress tensor of the system and $\langle \dots \rangle$ is a time average taken over all time origins t_0 . The parameter V represents the volume of the simulation box, k_B is Boltzmann's constant, μ is the mass of a monomer, $v_{i\alpha}$ is the α component of the velocity of i -th particle, $r_{ij\gamma}$ is the γ component of a vector separating i -th and j -th particle, and $f_{ij\alpha}$ is the α component of the force exerted on i -th particle by j -th particle [45].

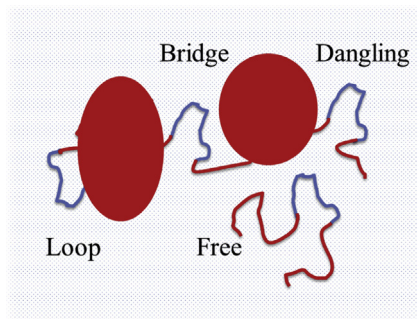


Fig. 1. A sketch for the four types of chain conformation of ABA block copolymer chains.

Table 1

The values of N_A and N_B in the $A_{N_A}B_{N_B}A_{N_A}$ triblock copolymers.

N_A	4	6	6	8	10	10	10	14	12	13
N_B	22	18	10	14	14	10	6	10	6	4

According to Green–Kubo relation [52,53], we could derive zero-shear viscosity from an integration of $G(t)$, i.e. $\eta = \int_0^\infty G(t) dt$. For mechanical gel, the value of zero-shear viscosity will diverge, thus $G(t)$ will converge to a non-zero value G_0 with an evolution of time. Therefore, the function of $G(t)$ can well describe the mechanical response of a given system. Its plateau value G_0 could reflect the strength of the mechanical property of a gelation system [37,38]. Table 2 lists the gelation concentration ϕ^* for strong solvophobic ABA block copolymers ($\beta = 3.0$) with different chain compositions at fixed total chain length N ($N = 2N_A + N_B$, Table 2). It is seen that the gelation concentration ϕ^* decreases with increasing A-block proportion f_A , which indicates that the chain composition affects the gelation concentration greatly. Fig. 2 also shows the value of G_0 for the samples listed in Table 2, which illustrates that f_A affects the value of G_0 greatly, i.e., an ABA block copolymer with higher f_A shows a higher value of G_0 , indicating a much stronger mechanical response. This result agrees with Aamer's [35]. We also did simulations for the similar systems at fixed chain length of A-blocks N_A or B-blocks N_B , which are shown in Table S1 and Fig. S1 of the Supplementary information file. Our results show that N_A and N_B have similar effect on the gelation concentration and mechanical response of the gel formed by strong solvophobic ABA triblock copolymers. The increasing N_A (at fixed N_B) or decreasing N_B (at fixed N_A) leads to the decrease of gelation concentration ϕ^* and an increase of the strength of their mechanical response (Fig. S1). The result for the solvophobic A-block length N_A dependence of the gelation concentration ϕ^* and mechanical property of a gel is consistent with Nguyen-Misra [33]'s results. Yu et al. [39] also confirmed this observation by studying the storage moduli and loss moduli of the thermoreversible gels formed by ABA type triblock copolymers in a selective solvent for the central B-block. More interestingly, we find the B-block length N_B also affects the mechanical responses of structural gels formed by these triblock copolymers, which has not been observed in Mattice et al. [33]'s work by using Monte Carlo method.

The strong solvophobicity makes block copolymer chains tend to associate and form micelles. When a group of interconnecting (or bridging) micelles pass through the box boundaries in three dimensions [33], the system can be defined as a structural gel. There are four different configurations in ABA block copolymer solutions, which are bridge, loop, dangling, and free chain configurations. Among these configurations, bridge and loop chains are mainly occurred in the micelles, and their contents can be used to identify the bridging or coalescence process of micelles. So we only focus on the fraction of bridge (f_{mb}) and loop (f_{ml}) chains in the largest

Table 2

The gelation concentrations ϕ^* for ABA copolymer systems with a strong solvophobicity ($\beta = 3.0$) at fixed N and different f_A , where f_A is the fraction of A-blocks in an ABA chain.

	$A_{N_A}B_{N_B}A_{N_A}$	f_A	$\phi^* (\beta = 3.0)$
Sample 1	$A_4B_{22}A_4$	0.27	0.28
Sample 2	$A_6B_{18}A_6$	0.40	0.25
Sample 3	$A_8B_{14}A_8$	0.53	0.23
Sample 4	$A_{10}B_{10}A_{10}$	0.67	0.22
Sample 5	$A_{12}B_6A_{12}$	0.80	0.19
Sample 6	$A_{13}B_4A_{13}$	0.87	0.20

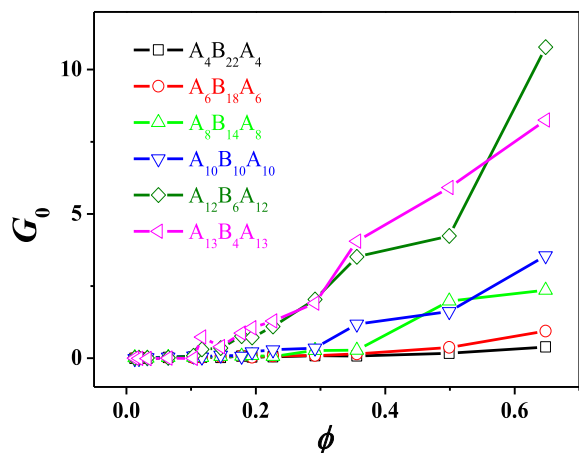


Fig. 2. The platform value G_0 of a stress autocorrelation function for an $A_{N_A}B_{N_B}A_{N_A}$ block copolymer system with a strong solvophobicity ($\beta = 3.0$) as functions of ϕ , where the chain compositions of $A_{N_A}B_{N_B}A_{N_A}$ copolymers are set as $A_4B_{22}A_4$ (\square), $A_6B_{18}A_6$ (\circ), $A_8B_{14}A_8$ (\triangle), $A_{10}B_{10}A_{10}$ (∇), $A_{12}B_6A_{12}$ (\diamond) and $A_{13}B_4A_{13}$ (\triangleleft) with the same total chain length N ($N = 2N_A + N_B$).

cluster to explore the formation of a gel during sol–gel transition [54] (Fig. 3, and Fig. S2 in supporting information file). For ABA block copolymer solutions with a low f_A and a short length of A-block, increasing ϕ leads to the increase of bridge chain fraction and the decrease of loop chain fraction, which implies the bridging effect among different micelles results in the formation of a gel network. While, for other cases, the content of bridge chains first increases, and then decreases even to a very low value with increasing ϕ .

In order to further explore the gelation processes of ABA block copolymer solutions with different chain compositions, we calculate the number of micelles n , shown in Fig. 4a (at fixed N) and Fig. S3a (at fixed N_A or N_B , Supplementary information), and the aggregation number p of micelles, shown in Fig. 4b (at fixed N) and Fig. S3b (at fixed N_A or N_B , Supplementary information). For a strong solvophobic system with a low f_A or a short N_A , such as $A_4B_{22}A_4$, the number of micelles increases gradually, micelle's aggregation number is very small and almost keeps unchanged (which means the size of micelle almost does not change during the gelation process). Therefore, the bridging among micelles results in the formation of a gel network due to an increase of bridge chain contents (the configuration is shown in Fig. 5a). While, for ABA copolymers of a moderate A-block proportion and length, increasing ϕ makes the number of micelles reach its maximum, after that, there is a short region corresponding a nearly unchanged n , then followed by a decrease of n and a rapidly increase of p , like $A_{10}B_{10}A_{10}$. This implies the gelation process for this type of ABA block copolymers is a cooperation of bridging and coalescence among micelles as analyzed in our previous work [45] (as shown in Fig. 5b). For block copolymers with a high f_A or a long length of block A, like $A_{13}B_4A_{13}$ (Fig. 5c), the number of micelles n is very small and n decreases immediately after its maximum point. Meanwhile, p increases rapidly, which means a cooperation of the coalescence among micelles and the growth of micelles leads to the formation of gel network.

3.2. The sol–gel transition of a weak solvophobic ABA block copolymer solution

From above discussion, we know that the chain composition does have a great effect on the gelation process of ABA block copolymer solutions with a strong ($\beta = 3.0$) solvophobicity. On the

other hand, for a weak solvophobic system, the results are totally different. The gelation concentration ϕ^* of the weak solvophobic systems with fixed N is listed in Table 3 (the corresponding results of ABA copolymer systems with fixed N_A or N_B are listed in Table S1 of Supplementary information). It is seen that ϕ^* decreases with increasing f_A or N_A , or decreasing N_B . The dependence of ϕ^* on N_A is much stronger than that on N_B . Compared with the results obtained in strong ($\beta = 3.0$) solvophobic systems, the gelation concentration changes greatly in $\beta = 1.0$ systems with the variation of chain compositions. However, for weak ($\beta = 1.0$) solvophobic systems, the average plateau value G_0 of a stress autocorrelation function $G(t)$ [37,52,53] is very close to zero even we have changed the chain composition of ABA block copolymers in a wide range, as shown in Fig. 6 (the results of systems with fixed N_A or N_B are shown in Fig. S4 of Supplementary information). Namely, the mechanical response of the structural gel formed by weak solvophobic ABA copolymers is very weak, which is in agreement with literatures [6,55,56]. This means that chain composition effect is invisible for the mechanical response of a structural gel formed by ABA block copolymers of a weak solvophobicity.

As aforementioned, the formation of a gel network is characterized by the largest cluster passing through the simulation box in three dimensions. For a weak solvophobic system, there are mainly three typical chain configurations in the largest cluster, i.e., bridge, loop and dangling chains. Therefore, we could track the variation of these chain configurations in the largest cluster during the formation of a gel network to find what happened in this process. The results are shown in Fig. 7 (at fixed N) and Fig. S5 (at fixed N_A or N_B , Supplementary information), where f_{mb} , f_{ml} and f_{md} represent the fraction of bridge, loop and dangling chains in the largest cluster, respectively [54]. At low concentrations, the content of dangling chains is very close to 1, implying that the bridging effect is very weak in the largest cluster. With an increase of increasing ϕ , bridge chains and loop chains occur and their contents increase greatly. We also calculate the number of micelles n and the aggregation number p of micelles in the system (Fig. 8 and Fig. S6 in the Supplementary information file), and we find that the aggregation number of micelle p (Fig. 8b and Fig. S6b) changes only a little but

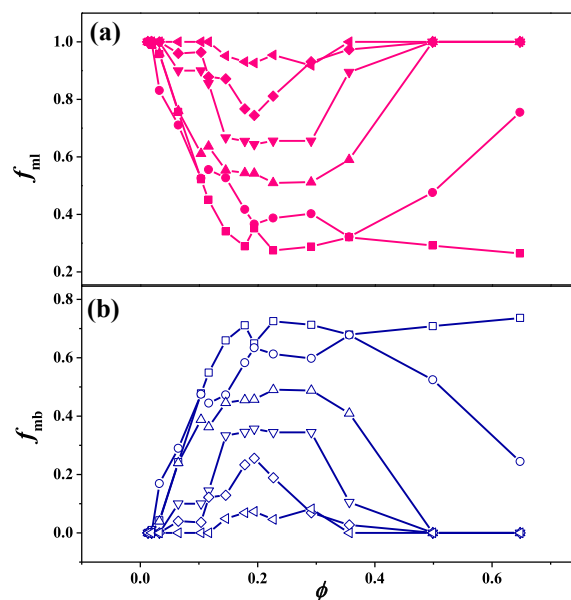


Fig. 3. f_{mb} , f_{ml} of loop (a) and bridge (b) chains in the largest cluster formed by ABA block copolymers with a strong ($\beta = 3.0$) solvophobicity and the same N in terms of ϕ . The symbols have the same meaning as Fig. 2.

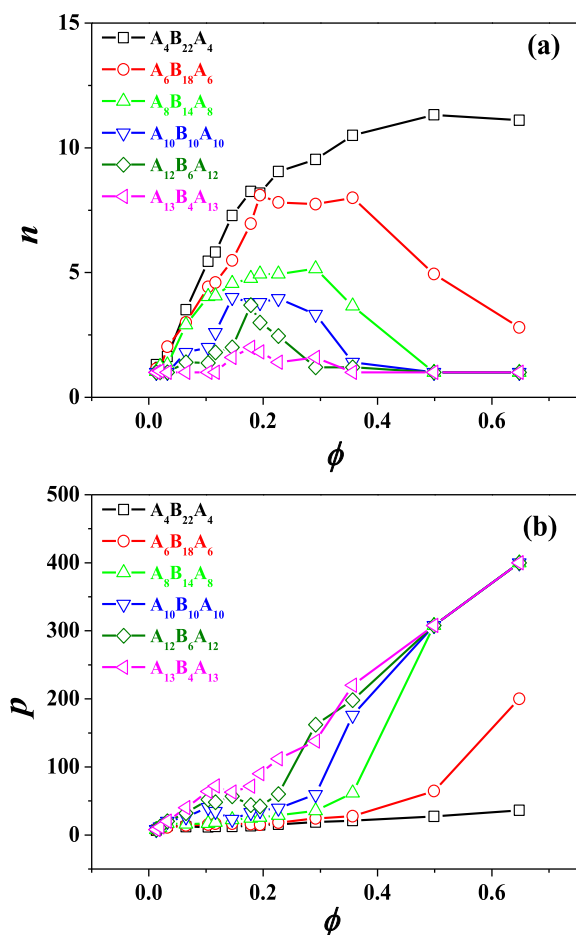


Fig. 4. The number n (a) and the aggregation number p (b) of the micelles formed by ABA block copolymers with a strong ($\beta = 3.0$) solvophobicity and the same N in terms of ϕ , where different symbols have the same meaning as Fig. 2.

the micelle number n (Fig. 8a and Fig. S6a) increases rapidly when the concentration is lower than the gelation concentration ϕ^* . This means, during the gelation process for weak solvophobic systems, the sizes of micelles only slightly change, and increasing ϕ makes more micelles formed. Therefore, for the weak solvophobic system, it is the bridging between different micelles that leads to the formation of a structural gel, and the structural gel formed in this way has no strong mechanical response.

Based on the results obtained in systems with a strong ($\beta = 3.0$) solvophobicity or a weak ($\beta = 1.0$) solvophobicity, we can give a sketch for the state behavior of the sol–gel transition of ABA block copolymer in solvent, which is shown as Fig. S7 in the

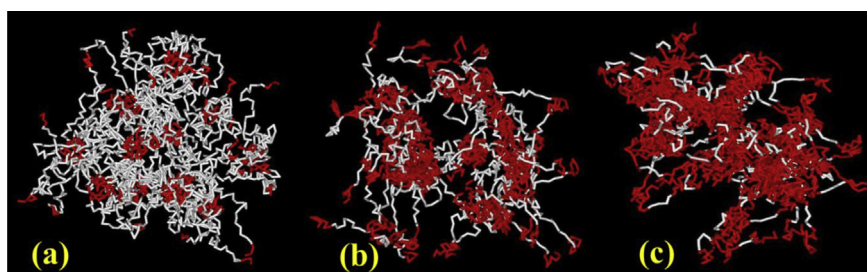


Fig. 5. The snapshots of $A_6B_{18}A_6$ (a), $A_{10}B_{10}A_{10}$ (b), $A_{13}B_4A_{13}$ (c) block copolymers solutions with $\phi = 0.3$ and $\beta = 3.0$, where A: green, B: white. The solvent particles are not shown in these snapshots. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

The gelation concentrations ϕ^* for ABA copolymer systems with a weak solvophobicity ($\beta = 1.0$) and different chain compositions. f_A has the same meaning as Table 2.

	$A_{N_A}B_{N_B}A_{N_A}$	f_A	$\phi^* (\beta = 1.0)$
Sample 1	$A_6B_{18}A_6$	0.40	-0.60
Sample 2	$A_{10}B_{10}A_{10}$	0.67	0.28
Sample 3	$A_{12}B_6A_{12}$	0.80	0.21

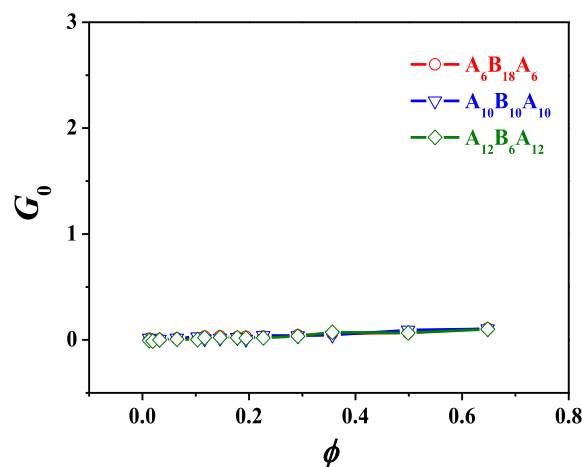


Fig. 6. The platform value G_0 for ABA block copolymer systems with a weak ($\beta = 1.0$) solvophobicity and the same N as functions of ϕ , whose symbols have similar meaning as Fig. 2.

Supplementary information file. When f_A is increased up to 0.5, the structure gel formed in a strong solvophobic system will have a strong mechanical response.

3.3. The structure of polymer gel

The radius distribution function $Q(r)$ can well describe the structural detail of these gels, which is defined as the probability of finding a pair of particles at distance r apart [53,57,58].

$$Q(r) = \frac{V}{N_{\text{tot}}} \left[\frac{n(r)}{4\pi r^2 \delta r} \right] \quad (10)$$

where $n(r)$ is the number of particles between r and $r + \delta r$ from a given particle and N_{tot} is the number of counted particles. $Q(r)$ of ABA block copolymer solutions with a strong ($\beta = 3.0$) or weak ($\beta = 1.0$) solvophobicity is shown in Fig. 9, in which Q_{tra} , Q_{ter} and Q_{ps} represents the probabilities of a monomer contacting monomers of its own chain, monomers of other chains and the solvent particles,

respectively. Fig. 9a gives the $Q(r)$ for $A_4B_{22}A_4$ and $A_{13}B_4A_{13}$ block copolymer systems at $\phi = 0.3$. Comparing these two results, we observed that there are more peaks in the curves of Q_{tra} and Q_{ter} for $A_{13}B_4A_{13}$ copolymers. The multi-peaks imply the multi-level microscopic aggregation structures of monomers. To get a clear understanding of the chain composition effect on the gel structure, we concentrate on the variation of the value of the first peak of $Q(r)$ for ABA block copolymers with different chain compositions in terms of ϕ . It is shown that Q_{tra} , Q_{ter} and Q_{ps} have respectively similar ϕ dependence for a strong solvophobic system and a weak solvophobic system. Increasing ϕ makes polymers have more probability to contact inter-chain monomers and have less probabilities to contact intra-chain monomers or solvent particles. For a

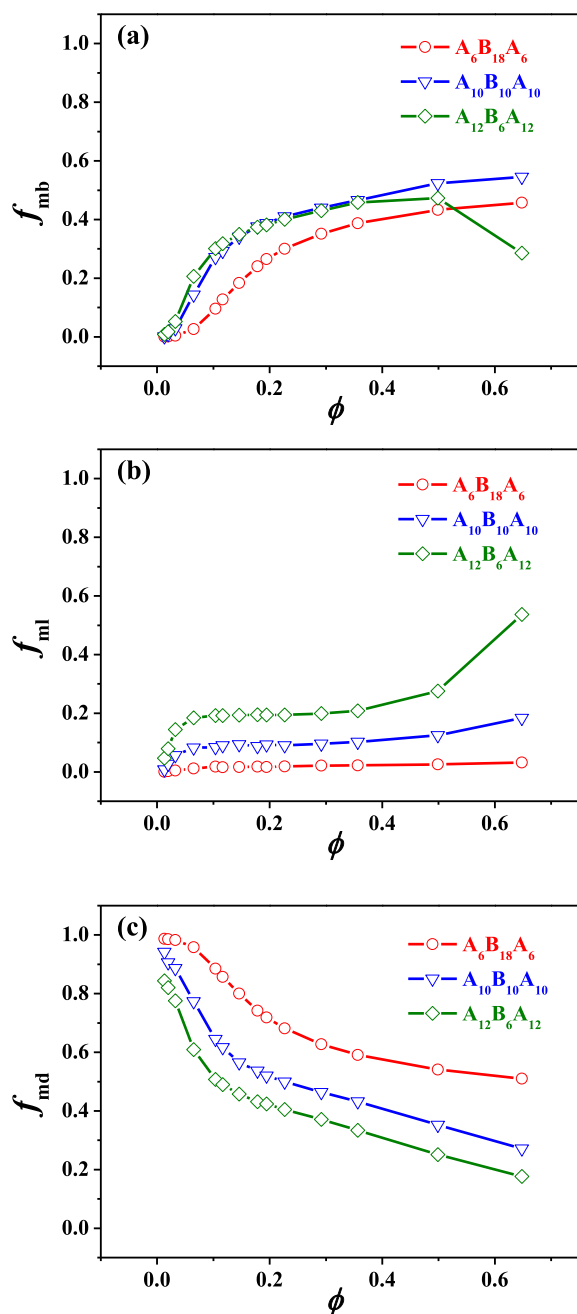


Fig. 7. The ϕ dependence of f_{mb} (a), f_{ml} (b), f_{md} (c) for bridge, loop and dangling chains in the largest cluster formed by ABA block copolymers with a weak ($\beta = 1.0$) solvophobicity and the same N , whose symbols have the same meaning as Fig. 2.

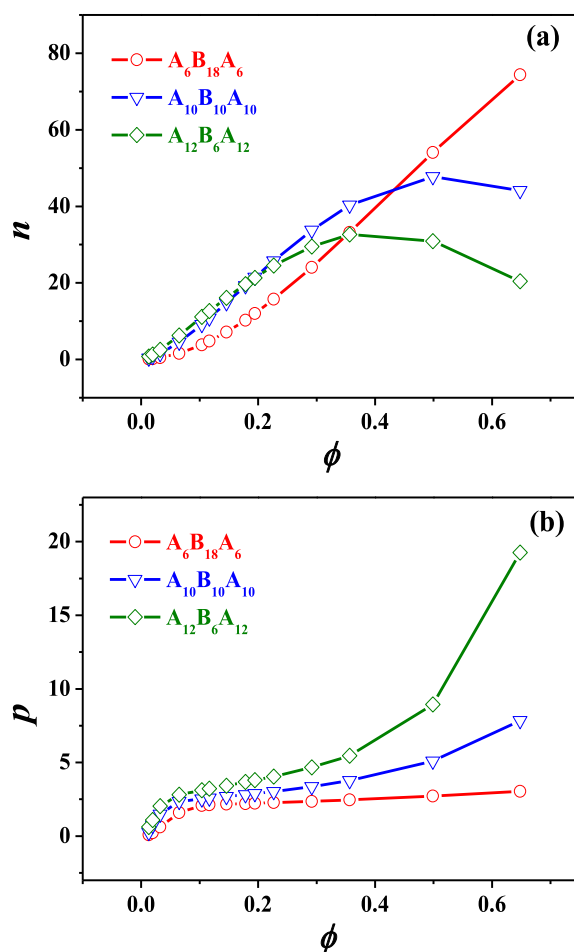


Fig. 8. The ϕ dependence of number n (a) and aggregation number p (b) of micelles formed by ABA block copolymers with a weak ($\beta = 1.0$) solvophobicity and the same N . Different symbols have the same meaning as Fig. 2.

strong solvophobic solution (Fig. 9b), with an increase of the A-block proportion f_A , the value of the first peaks of Q_{tra} and Q_{ter} increase gradually, and that of Q_{ps} decrease monotonously. Namely, the increasing A-block proportion makes the block copolymer have more abilities to aggregate together and the system shows a multi-aggregated state. While, for weak solvophobic systems with different chain compositions, the radius distribution function shows very little difference, indicating the chain composition effect on the gelation behavior is almost invisible for the weak solvophobic systems (Fig. 9c). Therefore, for ABA block copolymer systems with a strong or a weak solvophobicity, the chain composition effects are different, and only the strong solvophobic system shows a very strong chain composition effect on the gelation behavior.

In the present work, the structure of obtained gel is normally disordered, and it is quite difficult to characterize the gel structure experimentally. Therefore, we did not give any direct experimental proof on the structure of these aggregates. Nevertheless, we still hope that our work will stimulate the experimentalist to do more work on the relationship between structural gel and mechanical gel.

4. Summary

We have investigated the chain composition effect on the sol-gel transition of ABA triblock copolymer solutions using

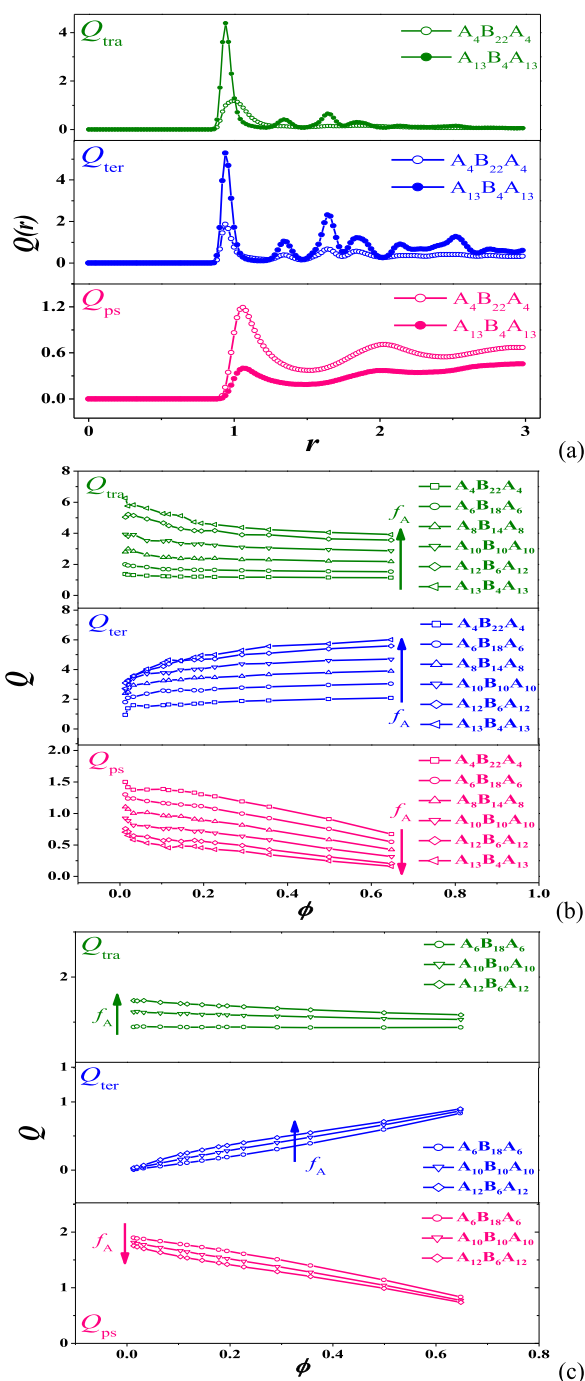


Fig. 9. (a) The pair distribution functions $Q(r)$ of $A_4B_{22}A_4$ (\square) and $A_{13}B_4A_{13}$ (\triangleleft) block copolymer solutions at $\phi = 0.3$; (b, c) The ϕ dependence of Q_{tra} , Q_{ter} and Q_{ps} for strong ($\beta = 3.0$) solvophobic systems (b) and weak ($\beta = 1.0$) solvophobic solutions (c), where different symbols have the same meaning as Fig. 2.

molecular dynamics simulation method. Our results show that the chain composition effect on the gelation behaviors of ABA block copolymer systems depends on the solvophobicities of A-blocks. For ABA block copolymer solutions with a strong solvophobicity, there are three typical gelation processes for different chain composition: 1) For a system with a low f_A or a very short chain length of A-block, the mechanical response of the formed structural gel is invisible, which is because the gel network is formed by the bridging of micelles; 2) For a system with a high f_A or a long chain

length of A-block, it is a cooperation of the bridging among micelles and the growth of micelles to make a gel structure occur, and the gel shows a strong mechanical response; 3) For a system with an intermediate f_A or a chain length of A-block, a gel network is obtained due to a cooperation of bridging and coalescence among micelles, and the strength of its mechanical response depends on the proportion of A-blocks. However, for a weak solvophobic ABA copolymer system, the bridging between different micelles leads to the gelation of copolymer solution, and the mechanical response of this structural gel is very weak. This result provides a possible method to control the mechanical property of a physical gel, and will be useful for a wide application of polymer gels [35].

Acknowledgment

This work is supported by the National Natural Science Foundation of China (21222407, 21104082 and 21074137) Programs. The authors also appreciate the financial support of National Basic Research Program of China (973 Program, 2012CB821500).

Appendix A. Supplementary information

Supplementary information related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2014.07.006>.

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