

Physical gels and microphase separation in multiblock copolymers

Sharon C. Glotzer¹, Rama Bansil, Patrick D. Gallagher,
Mark F. Gyure, Francesco Sciortino² and H. Eugene Stanley

*Center for Polymer Studies and Department of Physics, Boston University,
Boston, MA 02215, USA*

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We present computer simulation results of a solution of multiblock copolymers, and show that a network can form under certain conditions. This network formation is due to a bridging effect, which exists for multiblock but not for diblock copolymers. Because of this special property, we suggest that multiblock copolymers may be used quite generally to describe physical gels. Further, we find that separation of block types from each other hinders phase separation of polymers from solvent when the solvent is poor for both block types.

1. Introduction

The study of complex systems such as polymer materials is difficult both from the standpoint of performing controlled experiments and the development of universal theories. With the advent of increasingly powerful workstations and massively parallel computers, simulation promises to provide insight into these important materials from the level of individual macromolecules to long-range collective phenomena in bulk systems.

Modeling polymeric materials is particularly challenging for the computational physicist due to the existence of many length scales and time scales in these systems [1]. A single polymer chain, which typically contains as many as 10^4 monomers, exhibits structure from the scale of a single chemical bond (typically on the order of 1 \AA), to the persistence length (typically on the order of 10 \AA), to the average chain radius (typically on the order of 100 \AA). Even larger length scales may arise from collective phenomena. For example, phase

¹ Present address: National Institute of Standards and Technology, Polymers Division, Bldg. 224, Room B210, Gaithersburg, MD 20899, USA.

² Present address: Dipartimento di Fisica, Università La Sapienza, Piazzale Aldo Moro, 00185 Roma, Italy.

separation of incompatible polymer mixtures can produce structures of many lengths, from the size of a single chain to the size of a cluster of many thousands of chains.

When two incompatible polymer chains (A_i and B_j , where i and j are the chain lengths of the A-type and B-type polymers, respectively) are mixed together under the right conditions, they can phase separate into two coexisting phases, with one phase rich in one polymer type and the other rich in the second polymer type. However, when the two polymer chains are covalently bonded together at their ends as in fig. 1a to form a diblock copolymer (A_iB_j), macrophase separation of one "block" from the other cannot occur. Instead, microphase separation occurs, producing ordered structures such as lamellae or micelles [2].

Generalization of a diblock copolymer leads to a hierarchy of multiblock copolymers ($A_iB_jA_kB_l\dots$) for which blocks alternate along the chain, as depicted in fig. 1b. The complexity of the microphase-separated structures increases as the number of blocks in each chain increases, and depends on both the number of different blocks and their placement along the chain.

Indeed, the phenomenon of microphase separation in multiblock, and specifically tri-block, copolymers is well known in industry, where the special crosslinking properties of these copolymers is used to manufacture a wide variety of materials such as triblock copolymer elastomers. However, a complete theoretical description of the complex phenomenon of microphase separation is not in hand. Many fundamental questions remain unanswered; for example, equilibrium theories are lacking for even the most elementary multiblock copolymers [3]. Hence, although industry has recognized the utility of such copolymers, basic theoretical predictions for, e.g., phase diagrams or network bridging fractions remain at present intractable. One hope for providing new, fundamental understanding of such systems lies in computer

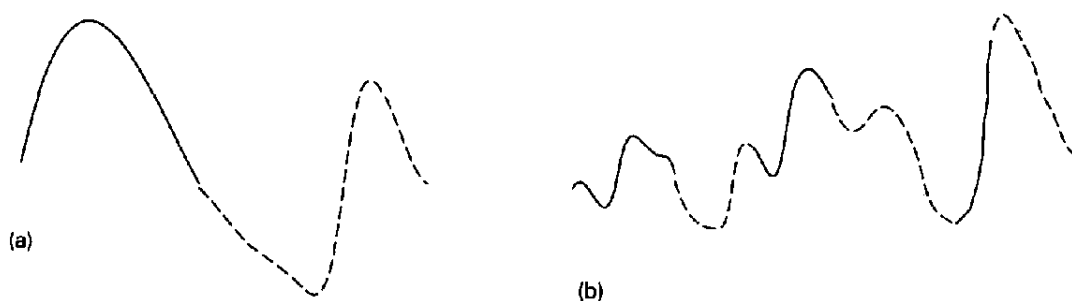


Fig. 1. (a) A diblock copolymer of the form (A_iB_j) ; (b) a multiblock copolymer of the form $(A_iB_j)_3$.

simulations. By proposing simple, coarse-grained models of block copolymers, simulations may enable the study of behavior that ordinarily would be theoretically intractable or experimentally complicated. With the computer, parameters can be independently varied and individually eliminated to an extent not possible in experiments.

Over the past decade, many coarse-grained, lattice Monte Carlo (MC) polymer algorithms have been devised [4]. One of the newest and most efficient of these is the flexible-bond, or bond-fluctuation, algorithm of Carmesin and Kremer (CK) [5,6]. In this model, each bond represents several monomers in a Kuhn segment, or persistence length. Thus each pair of connected monomers actually represents a more detailed piece of the polymer chain, so that the monomers are really “effective” monomers. The bond can fluctuate in length, allowing the polymer chain more freedom to move than previous MC algorithms, such as the kink-jump method [4]. Due to this flexibility, the non-ergodicity found in previous models vanishes for all but the most dense systems. The flexible-bond algorithm recovers (1) Rouse-like motion in the dilute case (the expected dynamics when no hydrodynamic effects are present), and (2) reptation-like motion in the melt (the expected dynamics when entanglement is important).

In the CK flexible-bond model, the elementary time step in which a monomer is randomly moved by one lattice unit in a randomly chosen direction, corresponds roughly to the actual monomer reorientation time. With this coarse-grained algorithm, as with its predecessors, all details of the chemical structure as well as phenomena occurring on time scales smaller than the reorientation time are sacrificed in order to model phenomena occurring on longer time scales. Due to the relative flexibility of the chains, relaxation times are much shorter than those of the kink-jump method [5]. Moreover, if certain conditions on the bond length are adhered to, unphysical bond intersections are automatically avoided [5,6] and very long times can be simulated quite efficiently.

With this motivation, we present here computer simulation results of diblock and multiblock copolymer solutions, and investigate the phenomenon of network formation. In particular, we show that network formation is due to a bridging effect which exists for multiblock but not for diblock copolymers and suggest that this property makes multiblock copolymers useful for describing general properties of physical gels. The remainder of this paper is organized as follows. In section 2, we describe how the CK flexible-bond algorithm is used to model the chain dynamics of a block copolymer. In section 3, we discuss the simulation results, focusing on network formation in multiblock and diblock copolymer systems. In section 4, we discuss multiblock copolymers as models for physical gels.

2. The model

We begin by placing binary variables representing monomers and solvent molecules on the sites of a 200×200 square lattice^{*1}. Monomers are connected to nearest-neighbor monomers on the same chain via flexible links. The monomers can be of type A or B, and are grouped in blocks along the chain. Here we consider diblock copolymers $(A_{20}B_{20})$, where each chain consists of two blocks of twenty monomers each, and multiblock copolymers $(A_5B_5)_4$, where each chain consists of eight blocks of five monomers each. The entire system in each case contains 80 polymer chains. The effective volume fraction is $\phi_{\text{eff}} = 0.32$, since each monomer has an effective “excluded” volume of four lattice sites [5] (cf. fig. 2).

The monomers are exchanged with solvent molecules using the CK flexible-bond algorithm combined with Kawasaki dynamics. This algorithm allows all motions such that the distance between neighboring monomers on one chain (cf. fig. 2) is in the range $[2, \sqrt{13}]$ [5]. These numbers are chosen so that a polymer chain on a two-dimensional lattice can never cross itself or another chain. For longer bond lengths, constant checks are needed to see if the move intersects another link; with this choice, no intersection is possible if the initial

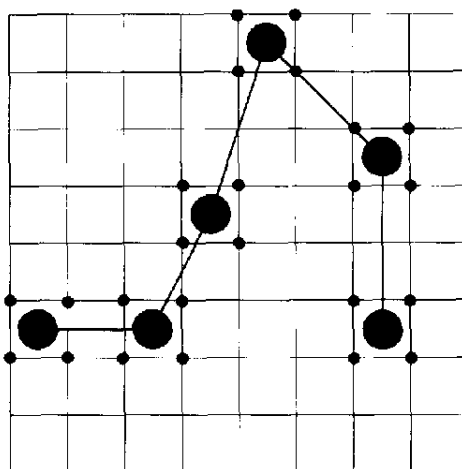


Fig. 2. Example of an allowed configuration in the flexible bond algorithm. The large circles represent monomers, and the lines which connect them represent flexible links. Each link must have a length $2 \leq l \leq \sqrt{13}$ to ensure that the chain will not intersect itself. The small circles at the vertices of each occupied plaquette represent the excluded volume of four sites associated with each monomer.

^{*1} Larger lattices are simulated to check for finite-size effects; for the ratio of lattice size to chain length used here and higher, the results appeared to be robust. Moreover, similar results were observed in a molecular dynamics simulation of both the diblock and multiblock copolymer systems.

configuration has no intersections, and consequently the algorithm is computationally very efficient. Note that, in general, a bond length of $\sqrt{18}$ also excludes chain intersection (if diagonal moves are not permitted), but $\sqrt{16}$ does not.

Monomers of the same type interact with energies $E_{AA} = -2$ or $E_{BB} = -1$ if they are within a distance $R = \sqrt{13}$ of each other. This range R is chosen so that two nearest-neighbor monomers on a chain will interact with the same energy regardless of the distance between them, which is limited by the flexible-bond algorithm to $\sqrt{13}$. In this way chains are not energetically biased towards shorter or longer lengths. Unlike monomers do not interact except by excluded volume. Both monomer types, as well as solvent molecules, interact with other solvent molecules by excluded volume only. Thus hydrodynamic effects due to the presence of the solvent are not included in this model. Periodic boundary conditions are used in all of our simulations.

3. Network formation: diblock vs. multiblock copolymers

To investigate the main difference between diblock and multiblock copolymers in their ability to form networks in a selective solvent, we performed MC computer simulations of diblock and multiblock copolymers in a solvent that is poor for one block type but good for the other. When a solvent is good for a polymer chain, the chain behaves like a self-avoiding walk in the limit of large chain length N and small concentration, so that its mean radius of gyration $\langle R_g \rangle \sim N^{3/4}$ in $d = 2$ [8]. In a poor solvent, however, a polymer chain collapses to a globular configuration ($\langle R_g \rangle \sim N^{1/2}$) and expels the solvent, since poor solvent quality implies that the system will phase separate into polymer-rich and polymer-poor regions [8–10]. The quality of a solvent can be varied, for instance, by lowering the temperature.

Before quenching, the copolymer systems are equilibrated at high temperature, i.e., above the critical temperature. One of the diblock systems is shown in fig. 3. Each chain consists of one A block and one B block. When quenched to a temperature for which the solvent is good for the B blocks but poor for the A blocks, the A blocks collapse and form domains with other A blocks as shown in fig. 4a. The collapse of the A blocks is triggered by lowering the temperature below the critical temperature for the A blocks [11]. The B blocks, which remain in a good solvent, do not collapse. Fig. 4b shows clearly that each chain in fig. 4a participates in the formation of only one domain, and micellar-type structures are formed. Networks are not formed in this case.

Fig. 5a shows a system of multiblock copolymers for the same solvent conditions as fig. 4. Each chain now consists of four A blocks and four B



Fig. 3. An example of a high temperature ($T = \infty$) configuration of diblock copolymer chains in solvent. Black denotes a solvent molecule, red denotes a monomer of type A, and white denotes a monomer of type B.

blocks, but both the chain length, and the total number of A and B monomers per chain, are identical to those for the diblock copolymers discussed above. In this case a network forms because different A blocks on the same chain can participate in the formation of different domains, as can be seen more clearly in fig. 5b.

A form of competition, or frustration, exists in this system because the phase-separating blocks along a chain are permanently connected to one another by the non-phase-separating blocks. Thus the uncollapsed B blocks form bridges between collapsed A domains and act like tethers, preventing the

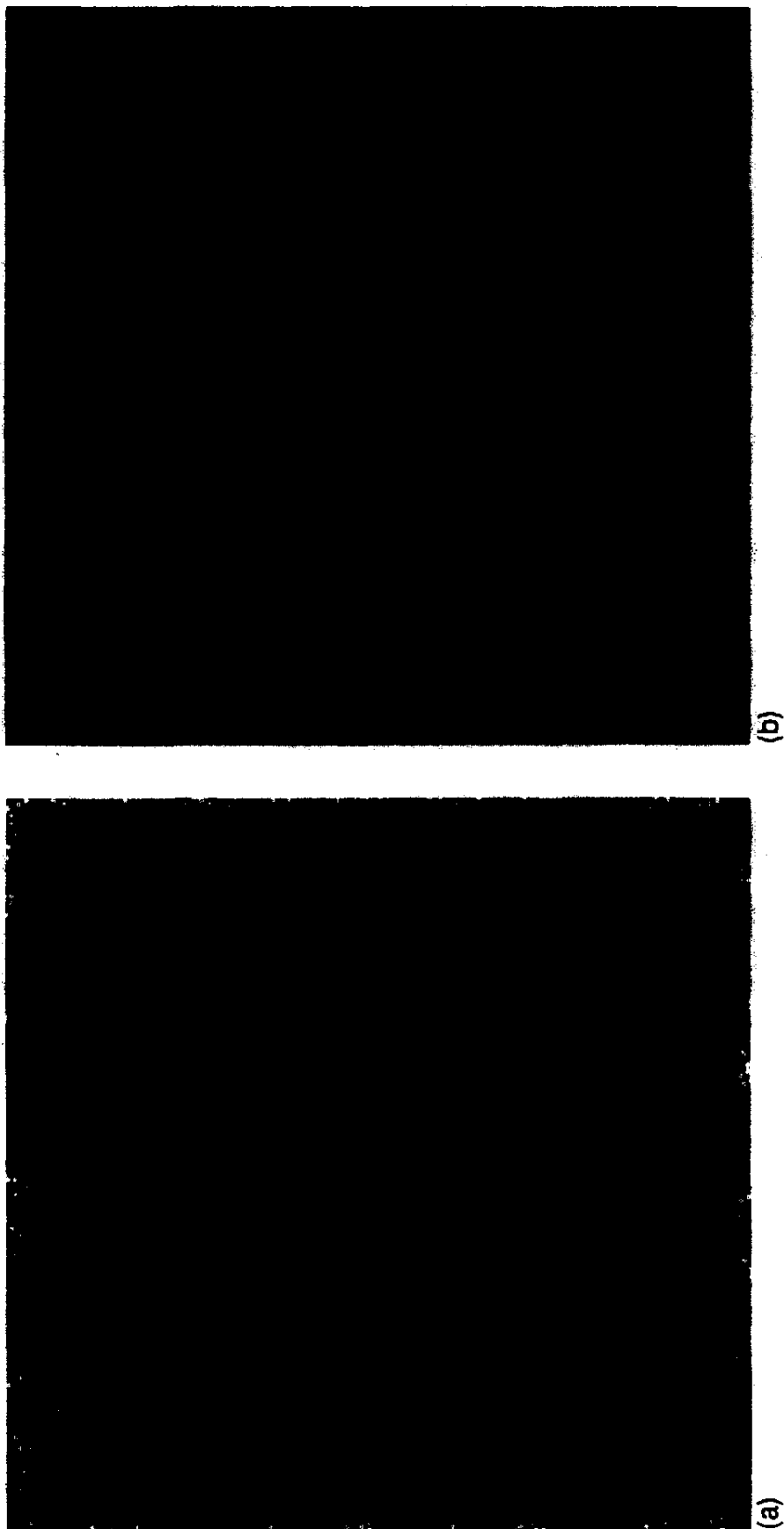
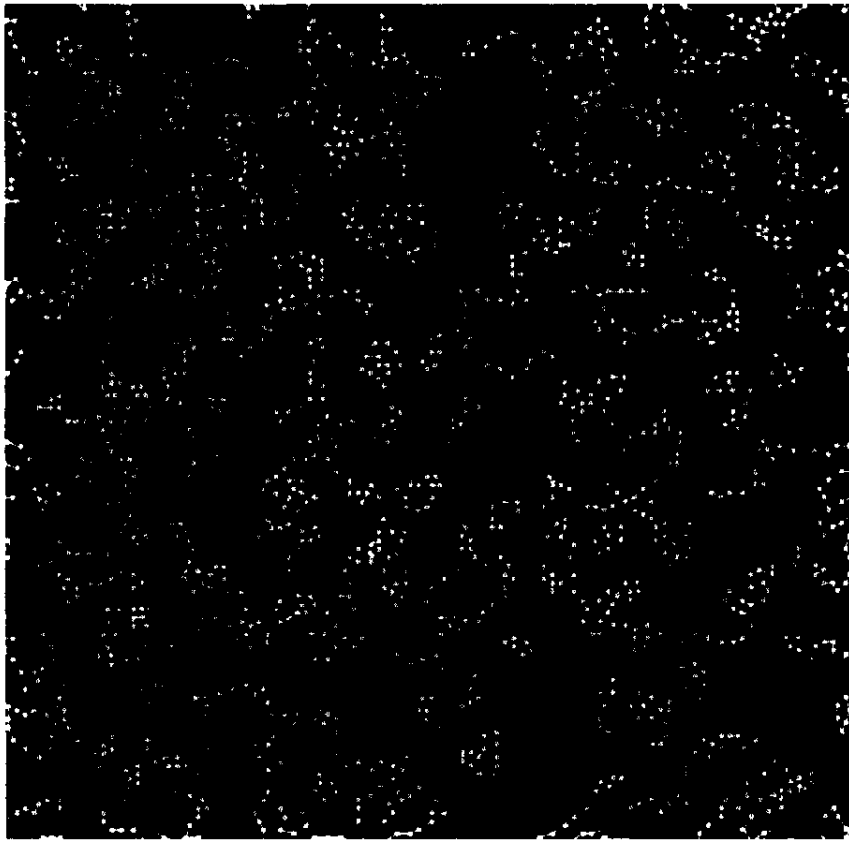
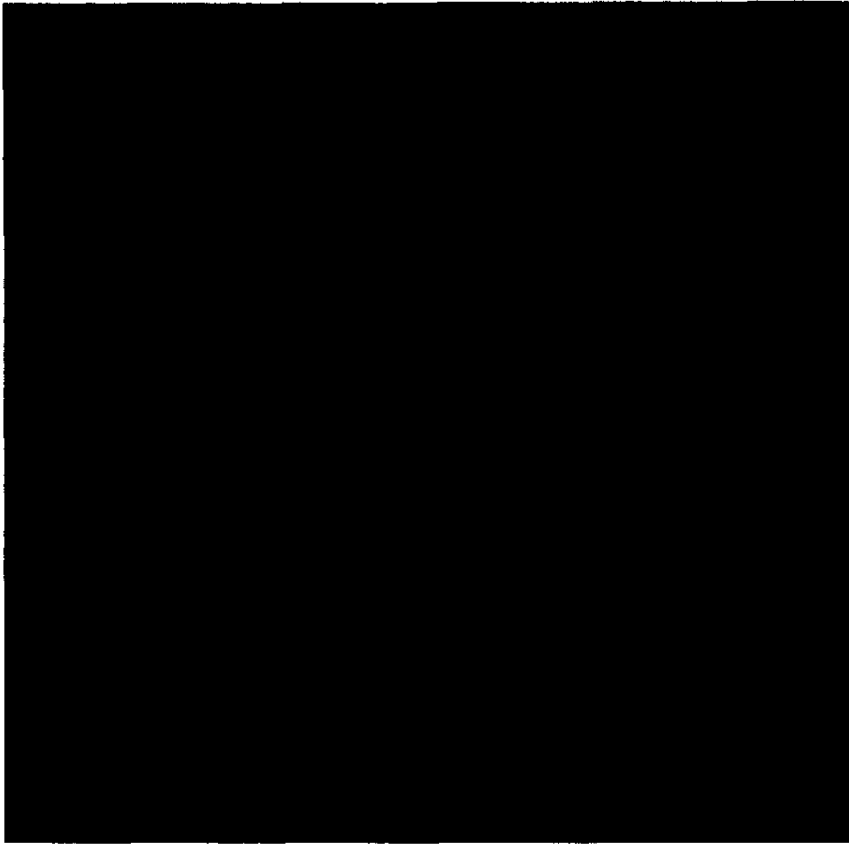


Fig. 4. (a) The diblock copolymer system of fig. 3 is quenched to a temperature which is very poor for the A (red) blocks (effective temperature $T = 0.5$ in units of E_{AA}) and very good for the B (white) blocks (effective temperature $T = \infty$). The A blocks collapse and the copolymers form micellar structures. The figure shows the system 10^5 MCS following the quench. (b) Same configuration as in (a) with each polymer chain colored independently to illustrate how individual chains interact to form micelles. Note that each chain participates in the formation of only one domain.



(a)



(b)

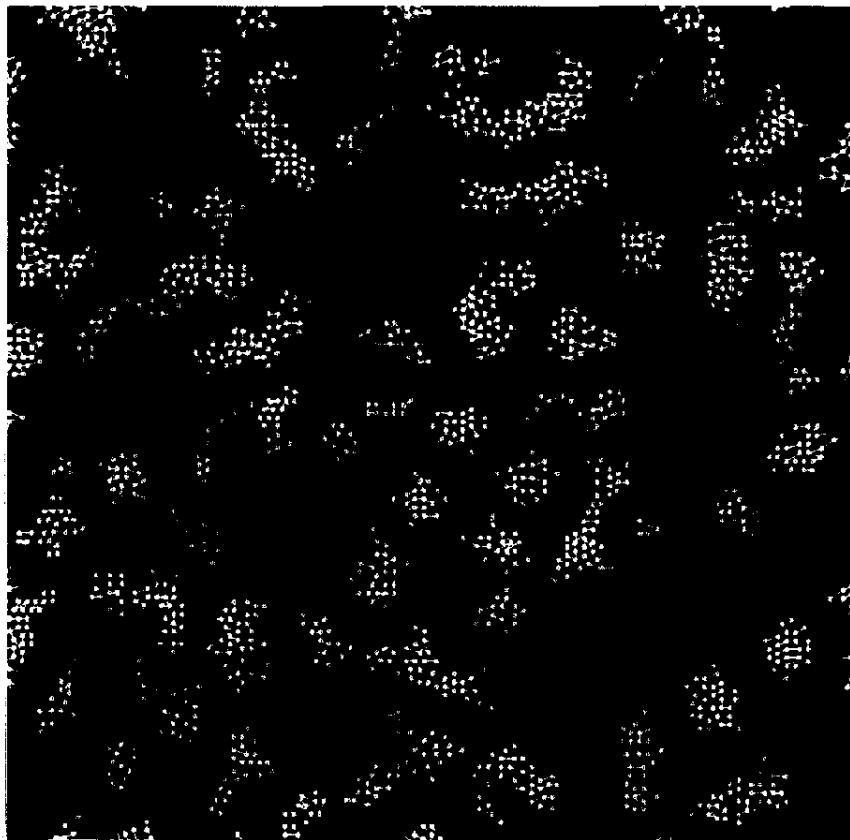
Fig. 5. (a) A system of multiblock copolymers is quenched from high temperature to a temperature which is very poor for the A (red) blocks (effective temperature $T = 0.5$ in units of E_{AA}) and very good for the B (white) blocks (effective temperature $T = \infty$), exactly as in fig. 4. The system is shown 10^5 MCS following the quench. (b) Same configuration as in (a) with each polymer chain colored independently to illustrate how individual chains participate in network formation. Note that each chain is involved in the formation of several different domains, in contrast to the diblock copolymers of fig. 4b.

A blocks from undergoing further phase separation. Consequently, the system is referred to as “microphase separated”. The existence of such bridges has been proposed in recent theoretical [3] and experimental [12] work on triblock copolymers ($A_i B_j A_k$), but this work is the first to directly investigate the formation of such structures. Note that this phenomenon is independent of the dimension, since in both two and three dimensions blocks will collapse in poor solvent and bridges of uncollapsed blocks will connect domains. Furthermore, the resulting network is thermoreversible, because it is destroyed simply by raising the temperature. Thus we find quite generally that the conditions for network formation in a selective solvent are (1) that the polymers have at least three distinct blocks, (2) that domains of one block type form, and (3) that different parts of the same chain participate in different domains [13].

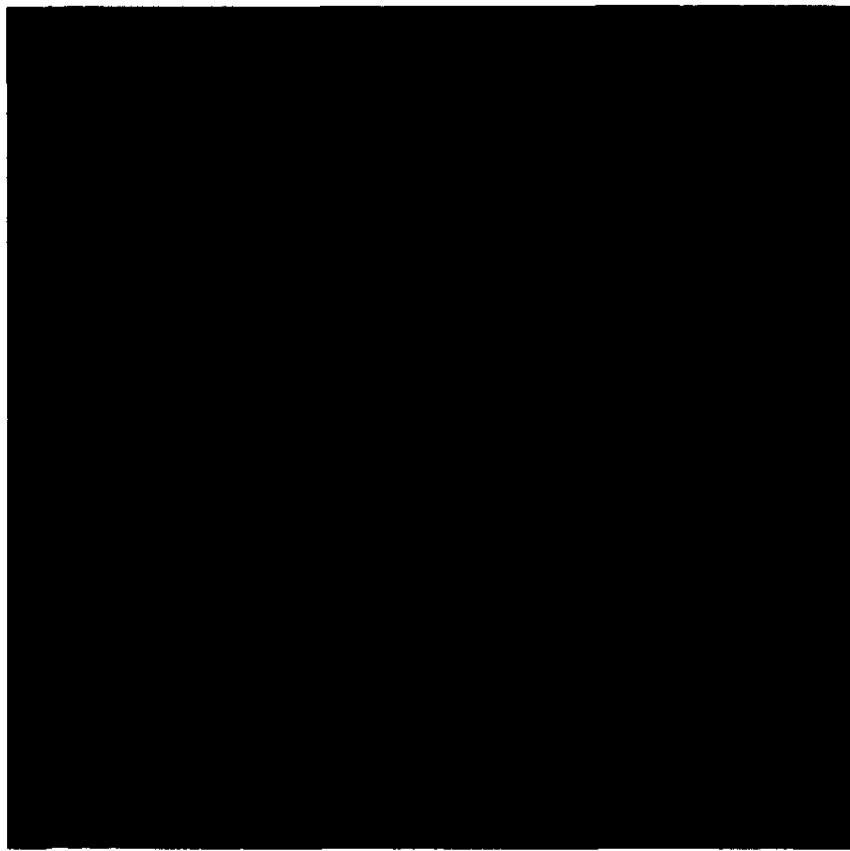
Another interesting situation is when the solvent is poor for both block types. Here one might expect to see both network formation and macroscopic phase separation of the polymer chains from the solvent. Therefore we simulated the quench of a high temperature multiblock copolymer system to a temperature for which the solvent is poor for both species but poorer for A, as shown in fig. 6. Initially, the system separates rapidly into microphases of A domains, B domains and solvent-rich domains. However, the expected continued growth of macroscopic solvent-rich domains appears to slow down due to the formation of the bridges. In fig. 7 we show the structure factor calculated for various times following the quench. Over the limited duration of our simulation, it appears that, after some time, the time evolution of the structure factor slows down considerably. Whether this will eventually lead to a pinning of the structure or to very slow expulsion of the solvent cannot be resolved from the present data. These results are qualitatively similar to experiments on the simultaneous occurrence of phase separation and gelation in gelatin–water–methanol mixtures, where it is observed that crosslinking of the gelatin chains arrests the growth of phase-separating domains [14].

4. Multiblock copolymers as a model for physical gels

Similar thermoreversible networks are observed experimentally in a wide variety of systems, including not only solutions of multiblock copolymers [15], but also chemical homopolymers such as atactic polystyrene [16–20], poly-(butyl methacrylate) [21] and poly-(vinyl chloride) [22], and biopolymers such as gelatin [14,23]. While the details of the crosslinking mechanism may differ in these systems, the resulting network formation is essentially the same. In gelatin, for example, certain amino acid sequences are thought to be pre-disposed to helix formation below a certain temperature T_{hc} , whereas other



(a)



(b)

Fig. 6. (a) A quench to a temperature which is very poor for both the A (red) blocks (effective temperature $T = 0.5$ in units of E_{AA}) and the B (white) blocks (effective temperature $T = 1.0$ in units of E_{BB}). (b) Same configuration as in (a) with each chain colored independently.

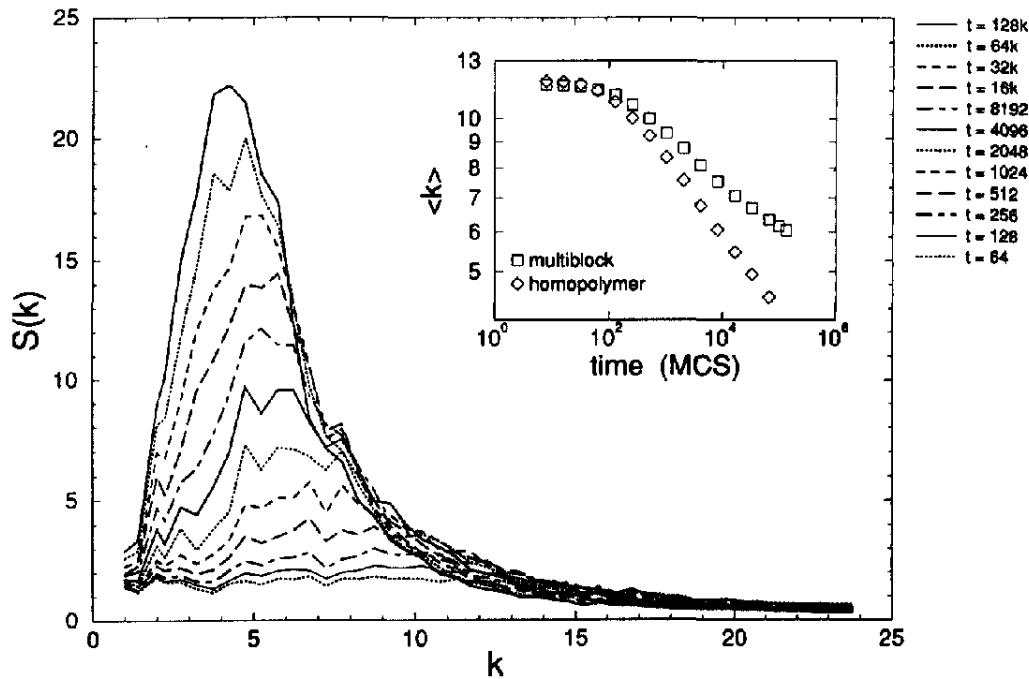


Fig. 7. Structure factor $S(k)$ vs. wave vector k for a sequence of times following the quench. The wave vector k in units of $2\pi/L$, where L is the lattice size. Inset: A double-logarithmic plot of $\langle k \rangle$, the first moment of the structure factor, as a function of time. Data for a solution of homopolymers is included for comparison.

parts of the chain remain in a random coil configuration below that same temperature. The helical portions of the chain form in association with helical portions of other chains, and not in isolation; this helix formation process is the crosslinking phenomenon that forms the gel network in gelatin. This network is thermoreversible, because by simply raising the temperature above T_{hc} , the chains undergo a helix \rightarrow coil transition, breaking the crosslinks that form the junctions of the network.

Chemical homopolymers such as atactic polystyrene have chemically identical subunits (monomers) making up the chains. However, it is now thought that the tacticity, or relative orientation, of each monomer contributes to the identification of “blocks” along the chain of similar relative orientation between neighboring monomers. That is, in an atactic polymer chain, which is defined as a chain in which the orientation of the individual monomers is random, sequences of monomers with either the identical orientation (isotactic) or alternating orientation (syndiotactic) may occur due to fluctuations during the initial polymerization process. It is now well known that isotactic and syndiotactic polymer chains tend to crystallize upon phase separation [17]; when the individual monomers are aligned in a regular fashion, it is easier for consecutive monomers to form bonds with consecutive monomers on neigh-

boring chains. Recent conjectures [19] identify the microcrystalline regions that form between the isotactic or syndiotactic sequences in phase-separating solutions of atactic polystyrene as effective “crosslinks” that can form a gel network. (The solvent may also play a role in crosslink formation in atactic polystyrene [16–18].) These microcrystalline crosslinks in atactic polystyrene are analogous to the helical crosslinks in gelatin. These gels are thermoreversible, since raising the temperature causes a change in the conformational properties of the chains and dissociates the microcrystalline crosslinks that form the network.

In our simulations, a network forms for multiblock copolymers when a difference in interaction energies between blocks causes swollen B blocks to connect collapsed A block domains. This model should therefore describe network formation in any polymer system where chemical or structural differences along the chain can be associated with “blocks” of different interaction energies. Consequently, simple models of multiblock copolymers as simulated here can describe thermoreversible gelation even when the actual crosslinking mechanism is complicated, as in gelatin and atactic polystyrene solutions.

5. Discussion

We have presented the results of simulations of diblock and multiblock copolymers and have shown that, in a selective solvent, multiblock copolymers form networks while diblock copolymers do not. While this has been known for some time, our simulations allow direct observation of the bridging effect which allows the networks to form. The essential feature in the multiblock copolymer system is the existence of blocks of energetically similar monomers which interact differently with one another than with other parts of the chain. When two or more blocks of the same chain attempt to interact with energetically similar blocks on other chains, a competition arises between that interaction and the constraint that both blocks must remain attached to each other. Hence when one block type tries to phase separate from the solvent, its progress is hindered by this competition and microphase-separated structures, such as networks, emerge. Indeed, competition and frustration has been shown to affect phase separation in a variety of systems including magnets and binary alloys as well as polymer blends and gels. In some of these systems, the existence of quenched impurities or a rigid network impedes the phase separation of a binary mixture [24–27]. However, in this work, as in many experimental systems, the same species is involved in both phase separation and network formation [14,28–30].

In many polymeric systems that form physical gels, the essential feature is the existence of chemically or structurally similar "blocks" which interact differently with one another than with other parts of the chain. Examples include the helically crosslinked domains in gelatin and the microcrystalline regions in atactic polystyrene solutions. Thus our simulations suggest that thermoreversible network formation in many polymer solutions may be described in terms of microphase separation of multiblock copolymers in selective solvents.

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