Simulation of self-associating polymer systems. I. Shear-induced structural changes

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We present the results of nonequilibrium molecular dynamics (NEMD) studies of self-associating polymer systems composed of flexible telechelic chains with associating end-groups (“stickers”). Formation of micellar aggregates, their structure and structural characteristics of associative polymer network (micellar gel) are studied under the influence of external shearing forces. When the association energy $\varepsilon_c$ is quite large ($\varepsilon_c \gg \varepsilon^*_e$, where $\varepsilon^*_e$ is a critical association energy corresponding to the gelation transition at rest), the spatial organization of the system as a whole is characterized by a typical network architecture with bridging chains connecting different micellar aggregates. The shearing forces cause only a slight perturbation in the structural properties of the sol (at $\varepsilon_c < \varepsilon^*_e$). However, when the association energy $\varepsilon_c$ becomes quite large ($\varepsilon_c \geq \varepsilon^*_e$), we observe sharp structural variations as the shear force is increased. At sufficiently strong attraction between stickers, the shear flow facilitates development of the aggregation process: even at rather weak shearing forces, the cluster-size distribution functions become considerably wider when the association energy is close to $\varepsilon^*_e$. Thus, aggregation processes become considerably more pronounced under shear, as compared to the same system at rest. As the shear force increases, the content of looplike chains decreases while the fraction of bridgelike chains rises. This process is accompanied by stretching of the chains. However, under a condition of high shear, many chains belonging to the associative network tend to be coiled up. This leads to the redistribution of structural elements in favor of loop chains. This exchange process can decrease the internal stress in the associative network which is mainly determined by the number and spatial topology of elastically active bridgelike chains. © 1998 American Institute of Physics. [S0021-9606(98)51843-0]

I. INTRODUCTION

Considerable interest has been paid to the principles and consequences of aggregation of self-associating amphiphilic polymers. Associative polymers represent one of the examples of polymer systems with strongly interacting groups which associate in good solvents for the polymer backbone.1–6 The most common are hydrophobic polar or ionic groups which are capable of association and form aggregates similar to those formed by surfactant molecules. Often the associating groups, referred to as “stickers,” are randomly distributed along the polymer chain. One of the simplest examples of associative polymers is a telechelic polymer, i.e., a water-soluble polymer which contains hydrophobic sticker sites only at the chain ends. Such polymers can act as model systems for associative polymers in general.

In solution, telechelic polymers usually aggregate in micelles or multiplets. The important feature of telechelic micelles is the possibility of bridging that gives rise to an effective attraction between micelles.7,8 As a result, telechelic polymers can form a temporary (reversible) network with hydrophobic aggregates as junction points. This implies that the junctions of the network can “open” and “close” in a dynamic equilibrium.

The results of Monte Carlo simulations of the self-organization in the solution of linear polymers with associating groups have been presented in Refs. 9–16. In the present paper, using nonequilibrium molecular dynamics (NEMD) simulations, we consider the behavior of the solution of associating telechelic polymers under the influence of external shearing forces. The following main question is addressed: What is the effect of a macroscopic flow of the solvent on the chain conformation and the microscopic structure of associative polymer network?

The organization of this paper is as follows. We first describe the model of associating telechelic chains as well as simulation techniques, utilizing the nonequilibrium molecular dynamics method. This is done in Sec. II. Section III represents the numerical results and our analysis of the results. The conclusions are outlined in Sec. IV.

II. THE MODEL AND SIMULATION TECHNIQUE

One of the most popular NEMD methods for introducing planar Couette flow in a fluid system is the method described by Ladd17 and termed SLLOD dynamics by Evans and Morris.18 In this method, a thermostating scheme must be
used in order to remove the local heating due to the introduction of a velocity gradient and to attain a steady state. It should be noted, however, that in the case of molecular systems (with internal degrees of freedom) the SLLOD algorithm can lead to some artifacts; at the same shear rate, the use of homogeneous thermostats coupled to different (atomic or molecular) degrees of freedom can produce very different steady states. In the Lees and Edwards work, a linearly dependent extra velocity is added in the direction of a shearing force. In this method, the normal periodic boundary conditions are removed in favor of simulation cells which slip with respect to one another. Gosling et al. (see also Refs. 22–24) proposed to use a sinusoidal transverse force to support a periodic steadyding shear wave. Because of the periodic nature of the sine (or cosine) function, normal cubic periodic boundary conditions can be applied to simulate the bulk fluid. In both these approaches irreversible heating introduced by external forces must be removed.

To simulate shearing external forces, in the present work we use a spatially periodic perturbation which generates an oscillatory velocity profile. At each time step in a conventional MD method, the external force $f_{\text{ext}}$ on the $i$th particle is applied in the $x$-direction. The magnitude of the external force depends upon the $y$-coordinate of the particle. We define $f_{\text{ext}}$ as

$$f_{\text{ext}} = f_0 \cos(q y_0) e_x,$$

where $f_0$ is a constant which specifies the strength of the applied shearing force and has been varied in the calculations reported here; $q = (0,0,0) = (0.2 \pi / L, 0, 0)$ denotes the wave vector which corresponds to a given integer $\delta = 1, 2, \ldots$ and the side of the periodic simulation box, $L$, $e_x$ is a unit vector along the $x$-direction. The question of whether such external flow field is capable of causing conformational rearrangement in the polymer system is very important since similar shearing fields are frequently used to measure the flow viscosity of polymers. It is naturally to expect that the shearing force field will align the polymer chains along the $x$-axis.

In the present study, the single telechelic molecule is considered to be a linear freely-jointed chain consisting of $N$ units (‘‘beads’’), each with mass $m (= 1)$, located at positions $\mathbf{r}_i (\alpha = 1, 2, \ldots, N)$ separated by rigid bonds of fixed length $b$. The bond lengths are fixed at unity. As a model for the solution of telechelic polymers we consider a system of $n$ identical chains. Two end units of each chain are designated as end-groups (‘‘stickers’’). Thus, the total number of sticker sites in the system is equal to $n_s = 2n$. Any two nonbonded polymer–polymer particles in the system under study interact via a shifted, purely repulsive Lennard-Jones potential

$$u(r_{\alpha \beta}) = \begin{cases} \frac{4 \epsilon}{(\sigma/r_{\alpha \beta})^12} - \frac{(\sigma/r_{\alpha \beta})^6 + \frac{1}{2}}{r_{\alpha \beta} < r_0}, \\ 0, \quad r_{\alpha \beta} \geq r_0, \end{cases}$$

where $r_{\alpha \beta} = |\mathbf{r}_\alpha - \mathbf{r}_\beta|$ is the separation between monomeric units $\alpha$ and $\beta$, $\epsilon$ and $\sigma$ are the usual LJ parameters ($\epsilon = 1$, $\sigma = 1$), and $r_0(=2^{1/6}\sigma)$ is the distance at which the potential (2) is cut. This potential represents the excluded volume interactions between any two nonbonded particles. Thus, it is assumed that the polymer chain is immersed in a good solvent.

In addition to the LJ potential (2), the end-groups in each chain interact via a screened attractive Coulomb potential, $u_c(r)$, for which we use the following form: 15,25

$$u_c(r_{\alpha \beta}) = - \frac{\epsilon_c}{r_{\alpha \beta}} f(r_c, r_{\alpha \beta}).$$

In the above $r_{\alpha \beta}$ is the separation between head groups (stickers) $\alpha$ and $\beta$ of chains and $\epsilon_c$ is the energy parameter. The screening function $f(r_c, r_{\alpha \beta})$ is given by the following expression: 15,25

$$f(r_c, r_{\alpha \beta}) = \begin{cases} \left[1 - \frac{(r_{\alpha \beta}/r_c)^2}{r_{\alpha \beta} < r_c} \right], \\ 0 \quad \text{if} \quad r_{\alpha \beta} \geq r_c. \end{cases}$$

Here $r_c$ is the ‘‘screening length’’ (i.e., the cutoff distance). We have set $r_c = \sqrt{2}\sigma$.

It must be emphasized that the potential (3) is, of course, only a prototype of a realistic potential for interactions involving associating end-groups. Simplifications are introduced partly for computational efficiency but also because of our limited knowledge concerning the corresponding molecular forces. Nevertheless, we believe that the simple model (3) provides a convenient basis for interpreting (at least qualitatively) of all the important features which can be found in real systems or predicted in statistical mechanical theories. As mentioned above, the effective energy of attraction between associating end-groups must be, by definition, very strong, i.e., much larger than $k_B T$. From this point of view, the best choice would be to keep the value of $\epsilon_c$ at some sufficiently high level ($\epsilon_c = 10k_B T$).

The entire system of $N$ chains is enclosed in a periodic box with side lengths $L$ and volume $V$. The corresponding number density of the chain beads is $\rho = n N/V$, and the number density of stickers is $\rho_s = 2n / V$. In order to avoid spurious effects due to the periodic boundary conditions, it is clearly desirable that the linear size of the box be larger than the characteristic size of the stretched chain, $L_{\text{chain}} = b(N-1)$. Due to the large computational effort required to study long polymer chains, our NEMD simulations were limited to relatively short chains of length $N = 8$ and 16. The value $N = 8$ might seem rather small to describe polymeric behavior. However, it should be taken into account the following: the assumption that successive bonds of the freely-jointed chain can form arbitrary angles means that a single polymeric unit may correspond physically to a group of $\sim 10$ successive monomer units of a real flexible chain macromolecule. In other words, each bond of the model represents a statistical segment of a polymer which includes many monomer units.

In the MD simulations, the equations of motion of a polymer system in the presence of fixed constraints (the bead-rod model) are...
\begin{equation}
\sum_{k=1}^{n(N-1)} \lambda_k g_k(\mathbf{r}_1, \ldots, \mathbf{r}_{nN}) + F^\text{ext}_\alpha, \quad \alpha = 1, 2, \ldots, nN
\end{equation}

with the constraints of fixed bond lengths
\begin{equation}
g_k = \frac{1}{2}((\mathbf{r}_{k+1} - \mathbf{r}_k)^2 - b^2) = 0,
\end{equation}

\begin{equation}
k = 1, 2, \ldots, N - 1, \ldots, n(N - 1),
\end{equation}

where \(-\nabla \alpha U(\mathbf{r}_1, \ldots, \mathbf{r}_{nN})\) represents the total nonbonded force on the particle \(\alpha\), which is due to the potentials (2) and (3), and \(\lambda\)'s are the Lagrange multipliers. The summation in Eq. (5) is performed over all the \(n(N-1)\) bonds of the polymer chains. The term \(\nabla \alpha \sum_{k=1}^{n(N-1)} \lambda_k g_k(\mathbf{r}_1, \ldots, \mathbf{r}_{nN})\) in Eq. (5) represents the forces which are due to the bond reactions. Each of the \(k\)th geometrical constraints (bonds) is associated with exactly one unknown \(\lambda_k\). The equations of motion (5) in conjunction with Eqs. (6) are solved iteratively by the Newton-type iteration. For this calculation we use the MA-TRIX algorithm. In general, 3–4 iterations are sufficient to maintain the bond lengths to within one part in \(10^8\). To integrate the equations of motion representing \(nN\) particles, we use Verlet’s explicit time-centered finite difference algorithm with a time step \(\Delta t = 0.004\tau\), where \(\tau = \sigma^2(m/e)^{1/2}\) is the characteristic microscopic time. The calculations are performed in standard reduced units, i.e., lengths are measured in units of \(\sigma\), energy in units of \(\epsilon\), and time, \(t\), in units of \(\tau\). At each time step, an instantaneous temperature of the system is computed. Note that the expression for the temperature must be written by taking into account the exact number of degrees of freedom for the system. Thus, the average temperature is defined by
\begin{equation}
T = \frac{1}{n(2N+1)} \sum_{\alpha=1}^{nN} m_\alpha \langle \mathbf{v}_\alpha^2 \rangle,
\end{equation}

where \(\mathbf{v}_\alpha^2\) is the velocity squared of the \(\alpha\)th particle at the given time step and \(\langle \cdot \cdot \rangle\) denotes a time average. \(T\) is measured in the reduced units, \(\epsilon/k_B\), standard in MD simulations. In order to maintain a given reference temperature, \(T\), during the simulation we use for our model a velocity rescaling procedure which mimics frequent collisions of the particles of the system with much lighter virtual particles of an external heat bath having a Maxwellian velocity distribution at this temperature. In other words, all velocities are rescaled with the relaxation time \(\tau_r = 0.4\tau\), if the temperature of the system, \(T(t)\), calculated from velocities at a given time \(t\), deviates from the prescribed value \(T\).

All the runs reported here were carried out at a reduced temperature \(T = 1.5\) corresponding to the fluid state. In each case a “preliminary run” of \(\approx 250,000\) time steps was carried out before the “production runs,” to eliminate transient effects.

III. RESULTS AND DISCUSSION

First of all, let us consider the behavior of chains with no attraction between end-groups (\(\epsilon_\alpha = 0\)) under the influence of external shearing forces. Later, these results will be used as reference data.

It has been generally assumed that shearing forces tend to increase the mean size of flexible-chain molecules but such effect has not been directly observed in real experiments. In each of the simulations discussed below the final configuration of the \(t = 200\tau\) run at \(f_0 = 0\) was used as the starting configuration, the external shearing force turned on, the system relaxed during \(1000\tau\) to reach a stationary state, and then the trajectories followed for an additional \(1000\tau\) at a given \(f_0\). The shear-induced changes in the mean-square end-to-end distance \(\langle R^2 \rangle\) are shown in Fig. 1(a) for the case \(N = 8\) and \(\rho = 0.4\). As can be inferred from this figure, as the shear force increases chains tend to stretch; that is, the shear flow favors more elongated chain configurations. However, this effect is quite weak under the conditions considered here (\(\approx 10\%\)). Closer examination shows that the anisotropy of the chain bonds becomes slightly stronger in the high-shearing regime. In addition, the bonds tend to align along the flow (\(x\)) direction. Of course, as the bonds align with the flow field, they also align with respect to one another. Note that the analogous weak extension (\(\approx 10\%\)) of chains has been observed by Clarke and Brown for dense liquids composed of hexanlike chain molecules undergoing planar Couette flow. The same effect has been found for long linear
alkanes under shear,\textsuperscript{31} for flexible bead-spring chains in a melt,\textsuperscript{32} and for lattice two-dimensional chains.\textsuperscript{33}

The shear-induced changes in potential energy per particle, \( U_i = \langle U/nN \rangle \), are plotted in Fig. 1(b). We find that \( U_i \) is a decreasing function of \( f_0 \), however, the effect of shear flow is quite weak. For fluids without internal degrees of freedom it is invariably found that the potential energy increases with shear rate.\textsuperscript{34} On the other hand, as seen from Fig. 1(b), this is definitely not the case for flexible chain molecules with internal degrees of freedom. Clearly the changes in thermodynamic properties, including \( \langle U \rangle \), are a reflection of structural modifications induced by external forces.

Also, it should be noted that there is no indication that the systems are in regions of shear-induced thermodynamic transitions,\textsuperscript{35} at any rate for the shearing forces considered here. For small rigid molecules, such transitions are associated with a change from an essentially amorphous liquid structure to a ”string” phase, in which particles are aligned along the shear streamlines and pack into a hexagonal lattice, when viewed in a plane orthogonal to their length. These strings have been observed in NEMD simulations of hard spheres,\textsuperscript{36} Lennard-Jones particles,\textsuperscript{37,38} and diatomic and triatomic molecules.\textsuperscript{39,40}

The local structure of the system has been examined via the radial distribution function, \( g(r) \). Two different distribution functions can be defined in the system under investigation; namely, total \( g(r) \), which characterizes correlations between all pairs of particles, and ”sticker” function \( g_s(r) \), which describes the spatial distribution of sticker sites. These are shown in Figs. 2 and 3 together with the corresponding static structure factors, \( S(q) \) and \( S_s(q) \). The total polymer function \( g(r) \) has the very sharp first (”valent”) maximum, indicating the nearest neighbor distance in chains at \( r = 1 \). The cusp of \( g(r) \) situated at \( r = 2 \) is a manifestation of the second nearest neighbors in chains. We find that the correlation functions calculated for the system in the presence of shearing forces are practically indistinguishable from those which are observed at rest. Note that at the relatively low density considered (\( \rho = 0.4 \)) the behavior of \( S(q) = \hat{w}(q) + \rho (\hat{g}(q) - 1) \) is mainly governed by the intrachain contribution \( \hat{w}(q) \) [see the inset in Fig. 2(b)].

Now we will analyze the behavior of associating telechelic chains capable of micelle formation at \( \epsilon_i > 0 \).

A central object in discussions of the thermodynamics of micelle formation is the equilibrium size distribution function

\[
W(m) = \langle S(m) \rangle / \sum_m \langle S(m) \rangle,
\]

where \( m \) is the instantaneous aggregation number (i.e., the number of molecules belonging to an aggregate) and \( \langle S(m) \rangle \) is the mean (i.e., time-averaged) number of \( m \)-particle aggregates. Thus, the average aggregation number is given by

\[
\langle m \rangle = \sum_m mW(m).
\]

In addition to \( \langle m \rangle \), we can define the instantaneous average aggregation number \( m_{2s} \), for a given configuration, as well as the time-averaged maximum aggregation number \( \langle m_{\text{max}} \rangle \) and the instantaneous maximum aggregation number \( m_{\text{max}} \).

To simulate the formation of micellar aggregates (clusters), first we need to define what is an aggregate. The standard definition implies that each associating particle is surrounded by an imaginary sphere of a given radius \( R_c \); the other particle is considered as belonging to a given cluster if there is at least one particle \( \beta (\beta \neq \alpha) \) that belongs to the same cluster and lies inside the \( \alpha \) imaginary sphere. The number of particles belonging to a cluster constructed in this manner is the instantaneous aggregation number \( m \). In our simulations, an \( m \)-mer cluster is defined as such a cluster in which each chain end-group is not further away than a radius \( R_c = 2^{1/2} \) from at least one other end-group in the cluster. This means that the cluster could assume any possible geometry. We have experimented with values of \( R_c \) ranging from \( 2^{1/6} \) to 2 and have found that the properties of the aggregates are relatively insensitive to \( R_c \), which lies within the region of strong attraction of the potential \( u_c(r) \).

We can consider the amphiphilic solution as a mixture of clusters with different aggregation numbers \( m \), where association and dissociation of the aggregates can be treated analogously to usual chemical recombination and dissociation. In other words, we can describe equilibrium association
of amphiphilic molecules to micelles consisting of two, three, etc. molecules as formation of chemical compound such as dimers \((m = 2)\), trimers \((m = 3)\), etc. There are two alternative possibilities for the associative equilibrium, \(^{41,42}\) the so-called closed and open association. In the case of closed association, only two states of the system are possible: homogeneous solution of unimers \((m = 1)\) or solution of micelles with optimum aggregation number \(m^*\). The transition between these states takes place in a critical micelle point at \(e_c = e_c^*\), where the cluster-size distribution function \(W(m)\) is bimodal. On the other hand, the open association is characterized by the equilibrium between different \(m\)-mer aggregates in the crossover region, without the existence of a well-defined optimum micellar size \(m^*\). In this case, as has been shown in recent theoretical work \(^{43}\) for the solution of associating block-copolymers, the cluster-size distribution function \(W(m)\) in the vicinity of critical micelle point \((c.m.p.)\) is rather broad and does not have a pronounced bimodal character. It has been found \(^{43}\) that the c.m.p. itself is manifested by the occurrence of the inflection point on \(W(m)\). On the other hand, one can say that the presence of the inflection point for \(W(m)\) is the criterion of the c.m.p. These conclusions have been supported by computer simulations of micelle formation in the solution of flexible chains with one attracting end-group. \(^{43}\)

Typical examples of the cluster-size distribution function \(W(m)\) for the system with attracting end-groups are shown in Fig. 4 for 8-unit chains, at \(\rho = 0.4\) and \(f_0 = 0\). Let us consider the evolution of the function \(W(m)\) with the increase of \(\epsilon_c\). At \(\epsilon_c < 20\) the function \(W(m)\) decreases monotonically with \(m\). This picture changes principally at \(\epsilon_c = 20\), when the inflection point on \(W(m)\) appears. In this case, we find that in the region \(m \approx 3\) the function \(W(m)\) decreases at the same rate as for \(\epsilon_c < 20\), but in the region \(m \approx 4 - 13\) some plateau can be observed which is the manifestation of the inflection point. With further increasing of \(\epsilon_c\), this plateau transforms to the broad second maximum, which becomes more distinct and narrow as \(\epsilon_c\) is increased. Clearly, that such a behavior corresponds to the open association model for micelle formation.

Figure 5 presents the values of \(U_1\) and \(dU_1/d\epsilon_c\) as a function of \(\epsilon_c\) for \(\rho = 0.4\) and \(f_0 = 0\). We find that \(U_1\) is a decreasing \(S\)-like function of the association energy \(\epsilon_c\). The derivative \(dU_1/d\epsilon_c\) has a rather sharp peak in the region \(\epsilon_c = 20 - 22\). The inflection point on the cluster-size distribution function appears approximately in the same region (see Fig. 4). The corresponding value of \(\epsilon_c\) \((\sim 20)\) can be treated as the critical association energy, \(\epsilon_c^*\), at which an equilibrium between a sol phase consisting of small chain clusters and a gel phase is observed for given conditions. Hereafter we will consider this characteristic energy as a critical association energy corresponding to the gelation transition.

When the external shearing forces act on the system of associating telechelic chains, essential shear-induced effects are observed.
Figure 6 shows the values of $\langle R^2 \rangle$, $U_1$, and $\langle m \rangle$ as a function of the strength of the applied shearing force $f_0$ for the system composed of 8-unit chains, at $\rho = 0.4$ and $\epsilon_c = \epsilon_c^* (= 20)$. Figure 7 presents the dependencies of $\langle R^2 \rangle$, $U_1$, and $\langle m \rangle$ on the association energy $\epsilon_c$ for the $N=8$ system at $f_0=0$ and 0.1. The same dependencies obtained for the system of 16-unit chains at $f_0=0.1$ are shown in Fig. 8. In this figure we also present the mean-square radius of gyration $\langle R_g^2 \rangle$ averaged over time and all the chains and the time-averaged maximum aggregation number $\langle m_{\text{max}} \rangle$. As can be seen, when the association energy is below $\epsilon_c^*$, the quantities under discussion show rather weak variation with increasing $f_0$. Thus, the shearing forces cause only a slight perturbation in the structural properties of the sol. However, when the association energy increases and is not far from $\epsilon_c^*$, we observe quite sharp variations with $f_0$ as the shear force is increased, especially in the range $f_0 \geq 0.1$. In this case, the values of $U_1$ and $\langle m \rangle$ change monotonically, but the mean chain size tends to increase gradually as the force parameter $f_0$ is increased and to show a very sharp decrease at a certain value of $f_0$ [see Fig. 6(a)]. A possible explanation of such a nonmonotonic behavior of $\langle R^2 \rangle$ will be given below. As seen from Figs. 7 and 8, the influence of the association energy on the structural and thermodynamic characteristics of the systems undergoing flow becomes more or less visible in the range $\epsilon_c \approx 10$. The appreciable systematic differences between the systems with and without external shearing forces are observed for $\epsilon_c \approx 20$.

As to the effect of a shear field on the average cluster size [see Figs. 6(c), 7(c), and 8(c)], in principle we might expect an opposite tendency, since at first sight, large micellar aggregates must be decomposed by the sufficiently strong shear forces. However, it turns out that the shear flow facilitates development of the aggregation process. To show this more clearly, in Figs. 9 and 10 we present the cluster-size distribution functions calculated for the systems with $N=8$ and $N=16$ at different association energies for $f_0=0$ and 0.1. As seen from these figures, even at rather weak shearing forces, the cluster-size distribution functions become considerably wider when the association energy is close to the critical threshold. In addition, for such systems we observe a distinct shift of the distribution functions to larger $m$ when the external shear force is applied. This effect appears much more pronounced for higher values of the association energy. In other words, we can say that gelation, which results in intensive binding of stickers to clusters, can be induced by shear for lower values of the association energy. Thus, in associative polymers with strongly attracting end-groups, aggregation processes become considerably more pronounced under shear, as compared to the same systems at rest. Note that a similar shear-induced gelation has been observed experimentally and in Monte Carlo simulations by Groot and Agterof. According to explanation given by Witten and Cohen, this effect is due to the fact that under conditions of high shear the polymer chains are stretched and, as a result,
more associative groups become available for binding. We do indeed find the chains to be stretched, as it is seen in Fig. 6 (a).

The effects discussed above can be related in a simple way to the free energy of micelle formation. To do this, let us consider the fraction $F_m$ of micelles with a given aggregation number $m$. The value of $F_m$ is given by the standard expression

$$F_m = \frac{k_m}{k_1},$$

where $k_m$ is the corresponding equilibrium constant. On the other hand, in the case of negligibly small intermicellar interactions we have

$$F_m = k_m \phi,$$

where $\phi$ denotes the fugacity of the associating molecules. For the free energy of formation of an $m$-particle aggregate one has

$$\Delta \mathcal{F} = -k_B T \ln(k_m \phi^m).$$

Minimization of $\Delta \mathcal{F}$ with respect to $m$ gives the most probable aggregation number $m^*$ which corresponds to the minimum of $\Delta \mathcal{F}$. As it is seen, the shearing force reduces the free energy $\Delta \mathcal{F}$ at large values of $m$ and, hence, the most probable aggregation number $m^*$ increases when shear is applied. In addition, the presence of shear perturbation results in broadening of $\Delta \mathcal{F}$ in the region close to $m^*$. From the theoretical point of view the most interesting is the behavior of $\Delta \mathcal{F}$ at $m^*$. We find that, at large $m$, $\Delta \mathcal{F}$ behaves like $\Delta \mathcal{F} \propto m$ (see Fig. 11). Such a dependence agrees with the theoretical prediction. 47–49

The key factor, which determines properties of associative polymer networks, is the system morphology. In principle, two limiting situations are possible for the system of telechelic polymers with strongly attracting end-groups: (i) a system constructed from isolated flowerlike micelles which contact each other by their outer soluble shells ("coronas") and (ii) a continuous spatial network of bridging chains connecting micellar cores which act as junctions of the associative network. The question is: Which type of structure is more favorable under shear? In Ref. 47 it was supposed that the dynamic properties of a reversible associative gel are primarily governed by the so-called "creep motion." In this process, a micelle can creep to a new position (new "cell") without changing its volume but with a considerable deformation of its shape and surrounding micelles. According to

FIG. 7. Dependencies of $\langle R^2 \rangle$, $U_1$, and $\langle m \rangle$ on the association energy $\varepsilon_c$ for the system composed of 8-unit associating chains, at $f_0=0$ and 0.1.

FIG. 8. The $\varepsilon_c$ dependencies of structural and thermodynamic characteristics for the system composed of 16-unit associating chains, at $\rho=0.4$ and $f_0=0.1$. 

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Ref. 47, the corresponding deformation energy must critically depend on the bridge-exchange process and on the average fraction of bridging chains, \( w_B \). Thus, it is interesting to analyze the global system architecture. To this end the structural characteristics of associative network have been studied in detail.

In principle, we can distinguish “free chains,” “pendent chains” with only one end-group entering to a micellar core, “loop chains” with both ends belonging to the same micellar core, and “bridging chains” with the ends well separated in space and belonging to different aggregates. Below we denote the average fractions of these structural elements as \( \varphi_F \), \( \varphi_P \), \( \varphi_L \), and \( \varphi_B \), respectively.

In Fig. 12 we show a typical snapshot of the micellar system under conditions of shear \( (f_0=0.1) \). For visual clarity, we present only a fragment (slab) of the whole system. A vast variety of structural elements can be noticed in Fig. 12. One can see the formation of microdomain structure: chain stickers group into clusters (multiplets) which are separated by internal (soluble) sections of amphiphilic polymer chains. The spatial organization of the system as a whole is characterized by a typical network architecture with bridging chains connecting different aggregates. As seen, the bridging chains are strongly stretched.

In Fig. 13 we present the fractions of pendent, loop, and bridging chains plotted vs \( f_0 \) at three different values of the association energy \( \epsilon_c \). The first conclusion which can be drawn is that the shearing forces have no or little effect when attraction between end-groups is weak. Only when the association energy becomes quite large \( (\epsilon_c=\epsilon_c^*) \), we observe a strong effect of external forces; as the shear force increases, the content of pendent and loop chains decreases while the fraction of bridging chains rises in the region \( f_0>0.13 \). In the range \( f_0<0.13 \) (at \( \epsilon_c=20 \)), the value of \( \varphi_B \) begins to drop, while the value of \( \varphi_L \) increases. An analogous non-monotonic behavior has been observed for \( \langle R^2 \rangle \) [see Fig.

**FIG. 9.** Cluster-size distribution functions \( W(m) \) for the system composed of 8-unit associating chains at \( \rho=0.4 \), measured at rest \( (f_0=0) \) and under shear \( (f_0=0.1) \) for several values of the association energy \( \epsilon_c \).

**FIG. 10.** Cluster-size distribution functions \( W(m) \) for the system composed of 16-unit associating chains at \( \rho=0.4 \), measured at rest \( (f_0=0) \) and under shear \( (f_0=0.1) \) for an association energy \( \epsilon_c \) above the threshold of the sol/gel transition.

**FIG. 11.** The free energy of cluster formation as a function of \( m \) for the \( N=8 \) system at rest \( (f_0=0) \) and under shear \( (f_0=0.1) \), calculated at an association energy \( \epsilon_c \) above the threshold of the sol/gel transition. Lines of limiting slope at high values of \( m \) are given.
6(a)]. A simple way to explain this phenomenon could be the following. Under conditions of sufficiently high shear the flexible chains tend to be stretched [see Fig. 6(a)]. This effect becomes more pronounced as the association energy is increased. This is due to the fact that, at sufficiently strong attraction between stickers, the telechelic chains begin to form a physical network which is more susceptible to stretching by the shear in comparison to nonassociating (or weakly associating) chains. The mechanical behavior of this system is determined by the distribution of intramolecular and intermolecular reversible junctions. The stretching of the chains can dissociate intramolecular junctions between stickers and make these stickers available for intermolecular junctions. As a result, the mean fraction of polymer bridges increases [see Fig. 13(a)]. However, additional stretching of the chains is unfavorable by entropic reasons. When the association energy is not very high and the external shearing force is above a critical level, the intermolecular junctions that are formed by the strongly stretched chains begin to dissociate. After a given intermolecular junction breaks off, the corresponding free chain ends can either recombine in their previous (well separated) micellar aggregates or they can exchange in the associated state and recombine in new micellar aggregates. It is clear that, when the new aggregates are formed by looplike chains, this exchange process can decrease the internal stress in the associative network which is mainly determined by the number and spatial topology of elastically active bridgelike chains. As a result, many chains show folded configurations, aligned with the shear flow. Thus, we can conclude that, under a condition of high shear, many chains belonging to the associative network tend to be coiled up. This leads to the redistribution of structural elements in favor of loop chains which make approximately the same contribution to the potential energy of micellar cores as the bridging chains. That is why both \( U_1 \) and \( \langle m \rangle \) are monotonic functions of \( f_0 \) and \( \epsilon_c \), as it can be seen from Figs. 6–8.

The variation of \( \varphi \) with the association energy for the \( N=8 \) system under shear is presented in Fig. 14 for states at \( \rho=0.4 \) and \( f_0=0.1 \). As seen from this figure, the functions \( \varphi_L \) and \( \varphi_B \) are the increasing functions of \( \epsilon_c \). The fraction of free chains decreases with \( \epsilon_c \) and approaches zero at \( \epsilon_c \approx 24 \). On the other hand, the fraction of pendent chains maximizes at \( \epsilon_c \approx 15 \) and only then decreases.

Thus, our main conclusion which follows from structural analysis is, at sufficiently strong attraction between stickers, most of the telechelic chains (>90%) adopt either a looplike or a stretched conformation, the most typical morphology of micellar gel being a combination of these two structural elements. In a gel, neighboring micellar “flowers” formed by looplike chains are connected by one or several bridgelike chains.

To demonstrate shear-induced intramolecular structural changes, we have calculated the intrachain static structure factor

\[
\hat{\omega}(q) = \frac{1}{N} \sum_{\alpha,\beta} \exp(iq(r_{\alpha} - r_{\beta}))
\]  

(13)
and the intrachain mean-square separation

$$\langle r_{ab}^2 \rangle = \frac{1}{N-\rho} \sum_{\alpha=1}^{N-\rho} \langle (\mathbf{r}_\alpha - \mathbf{r}_{\alpha+p})^2 \rangle, \quad p = |\alpha - \beta|,$$

(14)

where $\mathbf{r}_\alpha$ is the position vector of the $\alpha$ bead and $(\mathbf{r}_\alpha - \mathbf{r}_{\alpha+p})^2$ is the squared distance between beads $\alpha$ and $(\alpha+p)$ on the chain. Note that the values of $\langle r_{ab}^2 \rangle$ are related to the local fractal dimensionality ($D_p = \ln[p/(p-1)]/\ln(r_{ab}^2/(r_{ab-1}^2))^{1/2}$, where $p = |\alpha - \beta|$) which represents the extent to which the chain molecule is winding. If the chain is a straight line, then $D_p = 1$ and $\langle r_{ab}^2 \rangle = (\alpha - \beta)^2$, whereas for a Gaussian chain, $D_p = 2$ and $\langle r_{ab}^2 \rangle = |\alpha - \beta|$ for all $|\alpha - \beta|$. The results are shown in Fig. 15, where $\hat{w}(q)$ and $\langle r_{ab}^2 \rangle$ are plotted for the $N=16$ system at $f_0 = 0$ and 0.1. These data indicate that the polymer chains in the associative network (at $\epsilon_c = 23$) are highly stretched in the external force field imposed on the system. The influence of the external field is more pronounced on large scales (or at small wave numbers belonging to the range $N^{-1} \leq q \leq \sigma^{-1}$), where the $\langle r_{ab}^2 \rangle$ function is nearly a parabola. For systems composed of anisotropic molecules it is expected that the flow field should not only induce chain stretching but that there should be some preferential orientation with respect to the direction of flow giving rise to first order flow birefringence.

As mentioned above, the chains with strongly attracting end-groups form a microdomain structure (see Fig. 12). This result can be understood as follows. Strong attraction between the stickers stabilizes the clusters that serve as junction points of a temporary network (micellar gel). Strong repulsion arising between the looplike chain sections forming micellar coronas prevents further aggregation of the clusters. On the other hand, bridgelike chains, forming structural frame of the system, keep micellar cores at a finite distance from each other preventing disintegration of the associative network. Of course, the network is living in a sense that the steady-state structure of the system is mobile; the micellar aggregates and other structural elements can disappear and

FIG. 14. Fractions of different structural elements as a function of the association energy for the $N=16$ system under the influence of external shearing forces ($f_0 = 0.1$), $\rho = 0.4$.

FIG. 15. Shear-induced intramolecular structural changes illustrated by the functions $\hat{w}(q)$ and $\langle r_{ab}^2 \rangle$ for the $N=16$ associative polymer system at rest ($f_0 = 0$) and under shear ($f_0 = 0.1$); $\rho = 0.4$ and $\epsilon_c = 23$.

FIG. 16. Function $g_s(r)$ for the $N=16$ associative polymer system at rest ($f_0 = 0$) and under shear ($f_0 = 0.1$), calculated at $\rho = 0.4$ and $\epsilon_c = 23$. 
reappear again. These features of spatial organization result in the special form of pair correlation functions.

In Figs. 16 and 17 we present the density–density correlation function $g_s(r)$ and the corresponding structure factor $S_s(q)$. In the region of small interparticle distances $r$, the correlation function $g_s(r)$ characterizes local packing of sticker end-groups within a micellar core. In the region of intermediate $r$, intermicellar correlations are important. It is seen from Fig. 16 that the local structure of clusters becomes more perfect for the system undergoing shearing forces. Indeed, the intensities of both the first and second peaks of $g_s(r)$ increase significantly as the force constant $f_0$ is increased. At $r \approx 2.2$, the function $g_s(r)$ has a deep hollow ($g_s(r) < 1$). In this region, the effective potential, $\psi(r) = -k_BT \ln g_s(r)$, is repulsive; it describes the repulsion which is due to interaction between micellar coronas (see also Ref. 15). This region shifts towards larger $r$ as the chain length $N$ is increased (Fig. 17). The microstructure of the system is modulated as a result of the competition between the short-range attraction and the nonlocal repulsive interaction. The initial rather homogeneous state (with a liquidlike or gaslike $S_s(q)$ at $\epsilon_c = 0$) is destroyed by the growth of density fluctuations caused by the aggregation of stickers [see Figs. 3(b) and 17(b)]. The increase of the intensity of $S_s(q)$ in the region of small $q$ is due to the increase of the density fluctuations caused by the cluster formation. The characteristic period, $\xi = 2\pi/q_{\max}$, of locally ordered micellar array is related to the position $q_{\max}$ of the main maximum of $S_s(q)$. This period reflects the features of microheterogeneous spatial organization of the system which are characterized by the formation of a quasiperiodic pattern of alternating microdomains composed of micellar cores and the regions filled by soluble chain sections, as it is clearly seen from snapshot pictures.

IV. CONCLUSION

We have presented the results of extensive nonequilibrium molecular dynamics studies of self-associating polymer systems composed of flexible linear telechelic chains with associating end-groups ("stickers"). Formation of micellar aggregates, their structure and structural characteristics of associative polymer network (micellar gel) have been studied under the influence of external shearing forces.

It has been shown that when the association energy $\epsilon_c$ is quite large ($\epsilon_c \geq \epsilon^*_{\text{c}}$, where $\epsilon^*_{\text{c}}$ is a critical association energy corresponding to the gelation transition at rest) the spatial organization of the system as a whole is characterized by a typical network architecture with bridging chains connecting different micellar aggregates. Our conclusion which follows from structural analysis is the following: at sufficiently strong attraction between stickers, most of the telechelic chains (>90%) adopt either a looplike or a stretched conformation, the most typical morphology of micellar gel being a combination of these two structural elements. In a gel, neighboring micellar "flowers" formed by looplike chains are connected by one or several bridgelike chains. The characteristic period, $\xi = 2\pi/q_{\max}$, of locally ordered micellar array is related to the position $q_{\max}$ of the main ("small-angle") maximum of static structure factor. This period reflects the features of microheterogeneous spatial organization of the system which are characterized by the formation of a quasiperiodic pattern of alternating microdomains composed of micellar cores and the regions filled by soluble (inner) chain sections. The microstructure of the system is modulated as a result of the competition between the short-range attraction between end-groups and the nonlocal repulsive interaction between soluble chain sections. Of course, the network is living in a sense that the steady-state structure of the system is mobile; the micellar aggregates and other structural elements can disappear and reappear again. These features of spatial organization result in the special form of pair correlation functions.

We have found that the shearing forces cause only a slight perturbation in the structural properties of the sol ($\epsilon_c < \epsilon^*_{\text{c}}$). However, when the association energy $\epsilon_c$ becomes quite large ($\epsilon_c \approx \epsilon^*_{\text{c}}$), we have observed sharp structural variations as the shear force is increased. At sufficiently strong attraction between chain end-groups, the shear flow facilitates development of the aggregation process; even at rather weak shearing forces, the cluster-size distribution functions become considerably wider when the association energy is close to the critical threshold. In other words, we can say that gelation, which results in intensive binding of stickers to clusters, can be induced by shear for lower values of the association energy. Thus, in associative polymers with strongly attracting end-groups, aggregation processes be-
come considerably more pronounced under shear, as compared to the same system at rest. A similar shear-induced gelation has been observed experimentally.\(^{14,45}\) As the shear force increases, the content of looplike chains \(\varphi_L\) decreases while the fraction of bridgelike chains \(\varphi_B\) rises. This process is accompanied by stretching of the chains. The influence of the external field on chain stretching is more pronounced on large scales (or at small wave numbers belonging to the range \(N^{-1} \leq q \leq \sigma^{-1}\)). Under the influence of very strong shearing forces, the value of \(\varphi_B\) begins to drop, while the value of \(\varphi_L\) increases. This is due to the fact that additional stretching of the chains is unfavorable by entropic reasons. When the association energy is not very high and the external stress is small enough, molecular junction breaks off, the corresponding free chain ends will be discussed further in the context of rheological properties of structural elements in favor of loop chains which are well separated from each other.

This leads to the reformation of looplike bridges. When the association energy is not very high and the external shear is large enough, many chains belonging to the associative network tend to be coiled up. This leads to the reformation of looplike bridges. This exchange process can decrease the internal stress in the associative network which is mainly determined by the number and spatial topology of elastically active bridgelike chains. As a result, many chains show folded configurations, aligned with the shear flow. Thus, we can conclude that, under a condition of high shear, many chains belonging to the associative network tend to be coiled up. This leads to the redistribution of structural elements in favor of loop chains which make approximately the same contribution to the potential energy of micellar cores as the bridging chains. These results will be discussed further in the context of rheological properties in our next paper of this series.

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