1066 *Macromolecules* **1995,** *28,* 1066−1075

Associating Polymers: Equilibrium and Linear Viscoelasticity

A. N. Semenov,[†,‡] J.-F. Joanny,*,[†] and A. R. Khokhlov[‡]

Institute Charles Sadron (UPR CNRS 022), 6 rue Boussingault, 67083 Strasbourg Cedex, France, and Physics Department, Moscow State University, Moscow 117234, Russia

Received August 1, 1994; Revised Manuscript Received October 26, 1994[®]

ABSTRACT: A theory for the equilibrium and dynamic properties of a solution of telechelic polymers in the limit of high aggregation number is presented. It is shown that (1) the micelles formed by telechelic chains (flowers) in a dilute solution strongly attract each other, (2) at some concentration ϕ^* the flowers form a reversible gel where they are connected by multiple bridges, (3) the dynamics of individual micelles in the gel is governed by the bridge/loop exchange rate and by the effective barrier associated with the hopping of a micelle to a new position; this barrier is determined by the energy associated to a deformation/compression of a micelle, (4) the viscosity is changing exponentially in the region $\phi > \phi^*$ (it is increasing in the vicinity of ϕ^*); however, it can decrease (with ϕ) in a limited concentration range above ϕ^*.

I. Introduction

Amphiphilic, or associating, polymers contain hydrophobic polar or ionic groups which are capable of association and form aggregates similar to those formed by simple surfactant molecules. One of the simplest examples of associating polymers is a telechelic polymer, i.e. a water-soluble chain with relatively small associating groups at the ends. Telechelic polymers usually aggregate in micelles (or multiplets in the "ionomer" language[1−4,7]) in solution (say in water), which are very similar to block-copolymer micelles[5,8−10] (Figure 1).

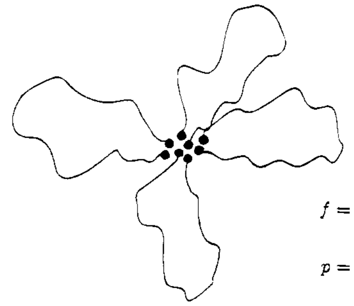

Figure 1. A flower consisting of $p = 4$ chains; the core is an aggregate of $f = 8$ insoluble end groups.

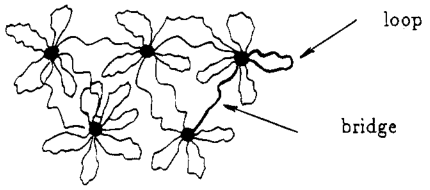

Figure 2. A transient (reversible) network of flowers connected by bridges.

A micelle consists of a compact hydrophobic core surrounded by a corona of the long soluble parts of the chains that form loops. The inner structure of a micelle is similar to that of a star polymer.[11−14] The effective functionality of a reference star $f = 2p$ (where p is the number of chains per micelle) depends on the energy of interaction between hydrophobic groups and on their size. The dependence of p on the molecular parameters has been considered theoretically.[9,15,16] Relatively large values of the aggregation number, $p = 5-50$, are often observed with associating polymers.[17−20,54,55] In the present paper we assume that p is a known fixed large number. This assumption is quite natural for the study of both the equilibrium state,[21] and the *linear* viscoelasticity. The "fixed aggregation number" assumption must however be relaxed to study nonlinear viscoelasticity; we do not consider this regime here.

Two star polymers in a good solvent always repel each other.[11,14] The important new feature of telechelic "flower" micelles is the possibility of bridging that gives rise to an attraction between micelles.[22,23] We show in section 3 that the energy of attraction can be large ($E_{\mathrm{attr}} \gg T$). The micelles then phase separate and form a macrophase of densely packed "flowers" where the neighboring micelles are connected by bridges (Figure 2).

The "flowers" form a temporary (reversible) network with hydrophobic aggregates as junction points. The functionality of the junctions is in general large. Similar reversible networks, but with a lower effective functionality were considered theoretically and by computer simulations in refs 6 and 24−30. The elastic properties of the network (gel) of "flowers" are considered in the last part of section 3.

The main dynamical effect related to the gel formation is an enormous increase of the solution viscosity. This is known as the thickening effect of associating polymers.[31] The viscosity of the reversible gel is analyzed in section 4.

The interaction between two spherical telechelic micelles is in many respects similar to that of two planar grafted layers. We thus start the next section with the description of the relevant results for planar brushes,[23,32] and then discuss bridging between compressed layers of telechelic polymers.

II. Grafted Polymer Layers in a Good Solvent

In this section, we briefly review the relevant properties of polymer layers grafted on planar surfaces obtained in refs 23 and 32. We also derive some new results on compressed layers. We consider a system of

---

[†] Institute Charles Sadron.

[‡] Moscow State University.

[®] Abstract published in *Advance ACS Abstracts,* January 1, 1995.

0024-9297/95/2228-1066$09.00/0

flexible linear polymer chains in a good solvent. Both ends of each chain are adsorbed onto a flat surface with a high surface coverage σ (number of grafted sites per unit area). We start the discussion with a reference system of "half-chains" attached to the surface by one end obtained by cutting each telechelic chain at its middle point where its tension vanishes. The reference system is therefore a usual end-attached grafted polymer layer (also called a polymer brush). This cutting procedure is valid in the strong stretching limit where the elastic energy of each chain in the brush is much larger than kT.

II.1. Equilibrium Characteristics of a Swollen Brush. We consider a dense brush where the average distance between grafted chain ends, $d = \sigma^{-1/2}$, is much shorter than the Flory radius of an isolated chain $R_F = aN^\nu$:

$$\sigma^{-1/2} \ll aN^\nu \tag{1}$$

As shown below this is the relevant limit to describe "stars" with a large functionality. Here N is the number of links per grafted chain (this implies $2N$ links per original telechelic chain), and ν is the Flory exponent ($\nu = 0.588$[33]).

As shown by Alexander and de Gennes,[34-36] the chains in a dense brush are strongly stretched. Each chain can be considered as a nearly stretched sequence of blobs of size $d = \sigma^{-1/2}$. In a good solvent, the height of the brush, H, is[35,36]

$$H = H_0 \sim (N/g)d \sim N\sigma^{(1-\nu)/2\nu} \tag{2}$$

where $g = (d/a)^{1/\nu}$ is the number of links per blob, and where the link size, a, is chosen as a unit length.

While the original Alexander–de Gennes picture is based on a steplike polymer density profile, a more recent and refined analysis[32] shows that in fact the polymer concentration decreases monotonously and vanishes at the edge of the brush $z = H$ (the origin $z = 0$ is on the grafting plane). In the mean-field approximation, a parabolic profile, $\phi(z) = \text{const}(H^2 - z^2)$, is expected.[32,37]

A more rigorous scaling analysis for a swollen brush in a good solvent also performed in ref 32 leads to a slightly more complicated profile. In the vicinity of the brush edge, $z = H - \zeta$, with $\zeta \ll H$. The concentration profile vanishes as[32]

$$\phi(H - \zeta) \sim \phi^*(\zeta/H_0)^\beta \tag{3}$$

where

$$\beta = (6\nu - 2)/(3 - 2\nu) \tag{4}$$

and $\phi^* \sim d^{1/\nu-3}$ is the average concentration.

Close to the brush edge, the chains are less and less stretched. At a given distance $\zeta = H - z$ from the edge, the properties of the chains can be described in terms of two types of blobs: the concentration blobs are defined by analogy with a semidilute solution of concentration $\phi = \phi(\zeta)$, they contain $g_\phi = \phi^{-1/(3\nu-1)}$ monomers; the "elastic" blobs, containing g_s links, are defined as chain subunits with an elastic energy of order kT. In a free polymer brush, the two blobs are equal $g_s \sim g_\phi \equiv g$.

The description of a chain as a stretched sequence of blobs is valid if the distance from the edge ζ is larger than the size of a corresponding blob, $d \sim [g(\zeta)]^\nu$. The condition $d \sim \zeta$ gives the size of the last blob at the very edge of the brush:[23,32]

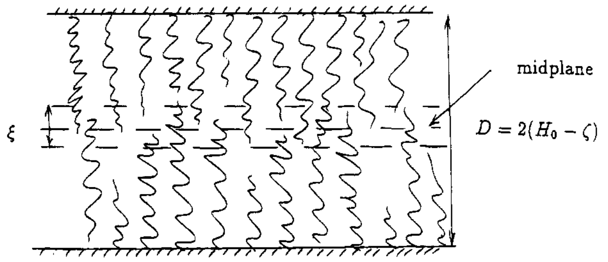

Figure 3. Two opposite slightly compressed brushes: the thickness of each is $H = D/2 = H_0 - \zeta$. The thickness of the interpenetration layer, ξ, is typically smaller than ζ.

$$d_{\max} \equiv \xi_0 \sim N^{2\nu/3}\sigma^{-1/6} \tag{5}$$

The number of links in the corresponding (largest) blob is

$$g_0 \sim N^{2/3}\sigma^{-1/(6\nu)}$$

The scale ξ_0 gives the typical amplitude of roughness of the brush edge.

From the concentration profile, we can also estimate the density of free chain ends per unit area

$$\varrho \sim \frac{\sigma}{H}\left(\frac{\zeta}{H}\right)^{(6\nu-3)/(3-2\nu)} \tag{6}$$

Equation 6 is valid in the region $\xi_0 \ll \zeta \ll H$. When $\zeta \sim \xi_0$ the density $\varrho \sim \xi_0^{-3}$ corresponds to one free end per blob.

II.2. Interaction between Two Brushes. We now consider two parallel planes at separation D, and two identical brushes grafted on these planes (Figure 3). The brushes do not interact if D is larger than $2H_0 + 2\xi_0$, where H_0 is the equilibrium brush thickness (or more precisely, the interaction energy is exponentially small in the region[23]). In the opposite limit, $D = 2H_0 - 2\zeta$, with $H_0 \gg \zeta > \xi_0$, the brushes are compressed: the compression energy, ΔF_{rep}, has been obtained in ref 32.

$$\Delta F_{\text{rep}} \sim \xi_0^{-2}\left(\frac{\zeta}{\xi_0}\right)^{(3+4\nu)/(3-2\nu)} \tag{7}$$

For compressed brushes there no longer is a unique blob size in the vicinity of the midplane (see Figure 3): one has to distinguish between concentration blobs and elastic blobs. The concentration varies very smoothly over the central layer of size 2ζ and is roughly equal to $\phi(H_0 - \zeta)$. The number of monomers in a concentration blob is

$$g_\phi \sim g_0\,(\zeta/\xi_0)^{-2/(3-2\nu)} \tag{8}$$

The size of the elastic blob can be estimated in the following way. The typical tension inside the "last" blob (near the midplane) is $f \sim g_s|\partial\mu/\partial z|_{z\approx H}$, where the force acting on a link is $|\partial\mu/\partial z|_{z=H} \sim \Delta\mu/\zeta$. The relevant chemical potential change is here $\Delta\mu \sim [\phi(H_0 - \zeta)]^{1/3\nu-1)} \sim 1/g_0(\zeta/\xi_0)^{2/3-2\nu)}$. By definition, the elastic energy (due to chain stretching) of a blob is $U_s \sim f\xi_s \sim 1$, where ξ_s is the size of the blob. An elastic blob can be considered as a nearly Gaussian chain of g_s/g_ϕ concentration blobs (the condition $g_s \gg g_\phi$ is verified below). Therefore

$$\xi_s \sim (g_s/g_\phi)^{1/2}\,\xi_\phi \sim g_s^{1/2}\,g_\phi^{\nu-1/2} \tag{9}$$

(here $\xi_\phi \sim g_\phi^\nu$ is the spatial size of a concentration blob). The number of monomers and the size of an elastic blob are then

$$g_s \sim g_0,\ \xi_s \sim \xi_0(\zeta/\xi_0)^{-(2\nu-1)/(3-2\nu)} \tag{10}$$

This last equation is valid for a weak compression, $\zeta \lesssim H_0$. The size of the elastic blob near the edge, ξ_s, is roughly equal to the thickness of the interpenetration layer, $\xi \simeq \xi_s$ between two compressed brushes (see Figure 3). The result, eq 10, when considered in the limit of a fairly dense brush and high compression ($\sigma \sim 1$, $\zeta \sim H_0/2$) is consistent with an earlier prediction for the interpenetration layer thickness of molten brushes.[39] In our case, the brush in the solvent can be considered as a molten brush of blobs.

The number of links per elastic blob is nearly constant (independent of degree of compression), whereas the size is decreasing under compression (the blobs are becoming less swollen since the concentration at the midplane increases). Within the layer of thickness $\sim\zeta$ near the midplane the concentration is nearly constant, so that the concentration blob size also does not change much (it is given by eq 8). The interpenetration layer, $\xi \sim \xi_s$, is thinner than the ζ-layer ($\xi \ll \zeta$). One can also check directly that the concentration blobs are smaller than the elastic blobs ($\xi \gg \xi_\phi$).

II.3. Bridging Attraction between Telechelic Brushes. We now return to brushes formed by telechelic polymers. Each telechelic chain in a dense (highly stretched) brush can be considered as two half-chains with their free ends coinciding with the midpoint of the telechelic chain.

An important new feature of the system of telechelic chains between two adsorbing planes is their possibility to form bridges. This effect had been analyzed in ref 23 for polymers in a marginal solvent. The main qualitative results of this paper are equally applicable to the case of telechelic polymers in a good solvent.

The bridges give rise to an additional attraction between the opposite telechelic brushes, the energy of attraction being of order kT per bridge. For large separations between the planes, $D/2 - H_0 \gg \xi_0$, the number of bridges is exponentially small; thus the attraction is very weak. However the excluded volume repulsion is also exponentially small in this region, and it was shown[23] that in fact the interaction energy is dominated by attraction.[42]

For two opposite brushes just at "classical contact", i.e. for $D = 2(H_0 \pm \xi_0)$, the number of bridges per unit area, $\mathcal{N}_2$, can be estimated as the number of free ends of the reference chains (or midpoints of telechelic chains) in the interpenetration layer[23]

$$\mathcal{N}_2 \sim \xi_0^{-2} \tag{11}$$

The same criterion can be used for compressed brushes, but here we must take into account the fact that "elastic" blobs in the interpenetration region strongly overlap. Thus $\mathcal{N}_2 \sim \phi(H_0 - \zeta)\xi/g_s$, and using eqs 3 and 10 we get (for $H_0 \gg \zeta \gg \xi_0$)

$$\mathcal{N}_2 \sim \Delta F_{\mathrm{attr}} \sim \xi_0^{-2}\left(\frac{\zeta}{\xi_0}\right)^{(4\nu-1)/(3-2\nu)} \tag{12}$$

where ΔF_{attr} is the attractive free energy due to bridging. Comparing eq 12 and eq 7 we notice that the interaction between two compressed brushes is always dominated by the repulsion.

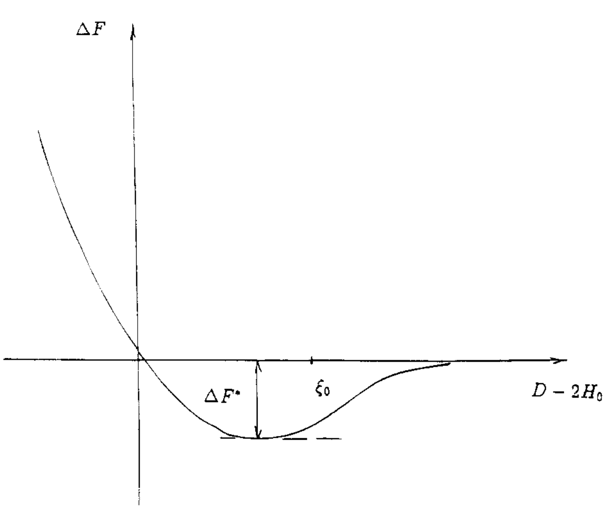

Figure 4. The energy of interaction of two opposite brushes as a function of the distance, D, between the grafting surfaces. The minimum, ΔF^*, corresponds to the distance $D - 2H_0 \sim \xi_0$, i.e. to the "classical contact" between the brushes.

The above considerations suggest that the free energy of interaction between the adsorbing planes, $\Delta F = \Delta F_{\mathrm{rep}} + \Delta F_{\mathrm{attr}}$, has a minimum in the region $D/2 - H_0 \sim \xi_0$; the depth of the minimum is[23]

$$\Delta F^* \sim \xi_0^{-2} \sim N^{-4\nu/3}\sigma^{1/3} \tag{13}$$

The schematic dependence of the free energy, ΔF, as a function of the separation D is shown in Figure 4 which is similar to Figure 2a of ref 23.

The case of strongly compressed brushes ($D \ll H_0$) can be considered just in the same way as for weak compression. Here the monomer concentration is nearly constant throughout the whole volume of the compressed brushes.

$$\phi = \sigma N/D$$

The interacting grafted layers can be considered as two opposite *molten* brushes by redefining a link as a concentration blob. Using this analogy, we obtain[38-41] the edge correlation length (the size of an elastic blob near the mid-plane which is also the interpenetration layer thickness) as

$$\xi \sim \frac{N^{2/3}}{D^{1/3}}\left(\frac{D}{\sigma N}\right)^{(2/3)[(2\nu-1)/(3\nu-1)]} \tag{14}$$

The averaged number of bridges per unit area is

$$\mathcal{N}_2 \sim \frac{D^{1/3}}{N^{2/3}}\left(\frac{\sigma N}{D}\right)^{1-(1/3)[(2\nu-1)/(3\nu-1)]} \tag{15}$$

The last two equations are applicable provided that $\xi < D$, and $\phi = \sigma N/D < 1$.

III. Equilibrium Properties of Micelles Formed by Telechelic Chains

We consider a dilute solution of telechelic chains and assume that the end groups of the chains strongly attract each other and thus tend to form aggregates. Each aggregate contains $f = 2p$ groups. The telechelic chains then form micelles, or "flowers" as shown on Figure 1. The equilibrium number of chains per micelle

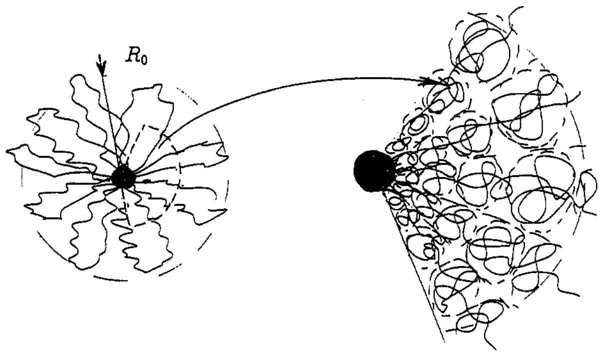

Figure 5. A blob picture for the polymer chains in the corona of a flower (the corona radius is R_0).

(p) depends on the interactions between end groups, and on some geometrical constraints[16] (the weak concentration dependence of p is neglected here). In the current section we analyze the structure of these micelles assuming that $p \gg 1$ is a fixed parameter.

III.1. Properties of an Isolated Micelle. In analogy with the planar case considered in the previous section, it is useful to introduce a reference system for a "flower" micelle namely a star polymer consisting of $f = 2p$ half-chains (Figure 5). As in the planar case, the cutting procedure to obtain half-chains is legitimate if the chains are strongly stretched in the micelle, i.e. if the aggregation number is large enough. The free energy, the size, and the local chain conformations are nearly the same for a "flower" and for the reference star. The relevant results for stars with a high functionality in a good solvent obtained in refs 11 and 14 are now applied to "flowers".

Each micelle consists of a core filled by the attracting end groups and of a corona of swollen middle chain parts. Each half-chain (branch of the reference star) can be represented as an almost stretched sequence of blobs which fills the whole volume of the corona (see Figure 6). The blob size d is roughly proportional to the distance r from the core (the core is considered as a point here): $d \sim r/\sqrt{p}$. This picture implies that the free energy of the corona is

$$F_0 \sim p^{3/2} \ln N \tag{16}$$

and its radius

$$R_0 \sim N^{\nu} p^{(1-\nu)/2} \tag{17}$$

The average polymer concentration inside the micelle is

$$\phi^* \sim \left(\frac{\sqrt{p}}{N}\right)^{3\nu-1} \tag{18}$$

We assume here that ϕ^* is small, i.e. $p \ll N^2$. Well inside the corona ($r \ll R_0$) the monomer concentration decreases with the distance from the core:

$$\phi(r) \sim \phi^* \left(\frac{r}{R_0}\right)^{1/(\nu-3)}$$

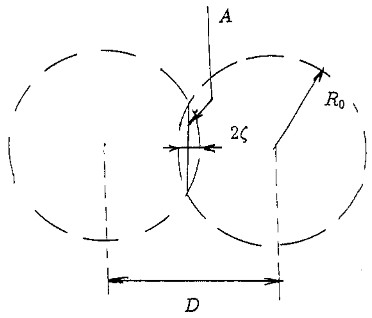

Figure 6. Two interacting flowers at the distance $D = 2(R_0 - \zeta)$. The compressed surface area can be determined geometrically as $A \approx R_0\zeta$.

The last equation is not applicable at the edge of the corona (r close to R_0): the concentration profile is similar to that of a planar brush.[43] In fact it can be argued that the asymptotic properties of the corona near its edge are the same as those for the edge of the corresponding planar brush with an effective "surface coverage" (number of chains per unit area)

$$\sigma \sim p/R_0^{\,2} \sim p^{\nu} N^{-2\nu} \tag{19}$$

In particular using eq 3 we get the density profile near the edge (for $\zeta \equiv R_0 - r \ll R_0$):

$$\phi \sim \phi^* \left(\frac{\zeta}{R_0}\right)^{(6\nu-2)/(3-2\nu)} \tag{20}$$

Substituting eq 19 into eq 5 we also get the edge correlation length of the corona:

$$\xi_0 \sim N^{\nu} p^{-\nu/6} \tag{21}$$

As for a planar brush[23] the monomer density tends to zero exponentially in the region $r - R_0 \gg \xi_0$ (outside the corona).

III.2. Interaction between Two Telechelic Micelles. The interaction between micelles ("flowers") can be described just in the same way as for two opposite planar brushes. As in the "planar" case there is bridging attraction between micelles if the separation, D (distance between their centers) is larger than $2(R_0 + \text{const } \xi_0)$, and repulsion for $D < 2(R_0 - \text{const } \xi_0)$, where the constant is of order 1. Thus the schematic picture of Figure 5 is also valid for micelles.

We first consider the interaction of two micelles which effectively repel each other: $D = 2(R_0 - \zeta)$, and we assume that $\xi_0 \ll \zeta \ll R_0$. The coronas of the two micelles are deformed over an area $A \sim R_0\zeta$ (Figure 6). There are two possible scenarios for the coronas deformation: (i) a part of each corona corresponding to the "cone of contact" becomes compressed, or (ii) some of the polymer chains move out of the "cone of contact" thus decreasing the local corona radius in the compression region. The second possibility can be easily ruled out for $\zeta \ll R_0$ as it implies a much higher deformation energy. Therefore we consider that the effective "surface coverage" is fixed and we estimate the deformation free energy, ΔF_{rep} using the results obtained for planar brushes (see eq 7):

$$\Delta F_{\text{rep}} \sim A \Delta F_{\text{rep}}(\text{planar}) \sim p^{1/2-\nu/3} \, (\zeta/\xi_0)^{(6+2\nu)/(3-2\nu)} \tag{22}$$

Note that for $\zeta \sim R_0$ the interaction energy is quite large: $\Delta F_{\text{rep}} \sim p^{3/2}$.

The attraction energy is again of the order of the number of bridges. The minimum of the interaction energy corresponds to the "classical contact" between the coronas, $D = D^*$, where $|D^*/2 - R_0| \sim \xi_0$. The number of bridges in this case can be estimated as $\mathcal{N}_0 \sim A\mathcal{N}_2$, where $A \sim \xi_0 R_0$ is the effective area of contact between the two coronas (see Figure 7), and $\mathcal{N}_2$ is the number of bridges per unit area for the equivalent planar case given in eq 11. The depth of the attractive minimum is

$$\Delta F^* \sim \mathcal{N}_0 \sim p^{1/2-\nu/3} \tag{23}$$

Hence the attractive energy between two "flowers" is large for large aggregation number p (it is of order of $p^{0.3}$) so that the micelles have a tendency to stick together. The second virial coefficient between micelles can be estimated as

$$B_2 \simeq R_0^{\ 3} - R_0^{\ 2}\xi_0 \exp(\Delta F^*) \tag{24}$$

where the first term in the right hand side is the excluded volume (numerical constants are omitted), and the second term accounts for the attractive bridging interaction in the layer of thickness ξ_0. Note that B_2 is negative if $\Delta F^* > \ln(R_0/\xi_0)$, i.e. if $p^{0.3} > \ln(p^{0.3})$, which is the case if p is large enough. Thus (for large enough p) the second virial coefficient is negative, with an exponentially large value.

Applying this result to a dilute system of micelles we conclude that the system phase separates into two macrophases one of them being a close packed phase of micelles. It is thus natural to consider this phase as a liquid of micelles.[44] The second phase is a very (exponentially) dilute solution of micelles and of free telechelic chains. The monomer concentration in the micellar phase is still small, of order of ϕ^*. At this point it is convenient to *define more precisely* ϕ^* as the average polymer concentration in the micellar phase at equilibrium with the dilute phase.

The micellar phase is in fact a gel since the micelles are connected by bridges. Of course this is a reversible physical gel since the bridges can relax. However the "debridging time" is expected to be very long as discussed in the next section. The elastic properties of the gel at intermediate time scales are considered at the end of this section.

III.3. Micellar Gel: Bridging. At $\phi = \phi^*$ the distance between neighboring micelles corresponds to the minimum of the interaction energy. The number of bridges between two neighboring micelles is given by eq 23.

We now consider a more concentrated solution $\phi > \phi^*$. Here the whole volume of the solution is filled by a somewhat compressed micellar gel. The degree of compression is $\epsilon = (\phi/\phi^*) - 1$. We estimate the number of bridges first for small compressions, $\epsilon \ll 1$. The distance between the centers of neighboring micelles is then $D = 2(R_0 - \zeta)$, where $\zeta = \epsilon R_0/3$. Taking into account the fact that the area of contact between the coronas is $A \sim R_0^2\ \epsilon$, and that the number of bridges per unit area is given by eq 12 we get

$$\mathcal{N}_0 \sim p^{5/6}\epsilon^{(2\nu+2)/(3-2\nu)} \tag{25}$$

Equation 25 is valid for $\zeta > \xi_0$, i.e. for $\epsilon > \xi_0/R_0$; at the crossover degree of compression, $\epsilon \sim \epsilon_c = \xi_0/R_0$, the number of bridges is of the same order as for an uncompressed gel given by eq 23.

A strongly compressed gel, $\phi \gg \phi^*$, is filled by nonspherical micelles: each micelle fills a polyhedron cell. The area, A, of contact between neighboring micelles is now of order of R^2, where the micellar size, R, can be readily estimated as

$$R \sim (Np/\phi)^{1/3} \tag{26}$$

(we still assume that the interpretation length, ξ, is much smaller than the size of a micelle). In this concentration range, the solution of micelles can be considered as a melt of stars of blobs. The effective "surface coverage" is

$$\sigma \sim p/R^2 \tag{27}$$

The number of bridges per micelle is $\mathcal{N}_0 \sim A\mathcal{N}_2$, where $\mathcal{N}_2$ is given by eq 15 for a planar brush, with σ given by eq 27. Thus we get

$$\mathcal{N}_0 \sim p^{5/6}(\phi/\phi^*)^{(1/9)[1-(3\nu-1)]} \tag{28}$$

The number of bridges increases with the concentration and all the chains form bridges at a concentration

$$\phi \sim \tilde{\phi} = (p^2/N)^{3\nu-1} \tag{29}$$

We assume here that $p^2 < N$ (otherwise the concentration $\tilde{\phi}$ cannot be reached). Around the same concentration $\tilde{\phi}$, the interpretation length, ξ, predicted by eqs 14 and 27 becomes of the order of the radius R of the micelles. Equation 28 is no longer applicable for larger concentrations, $\phi > \tilde{\phi}$. For $\phi \gg \tilde{\phi}$ the micelles overlap strongly, and nearly all chains form bridges. An important new feature in this concentration range is that bridges typically connect not the nearest neighbor but distant aggregates. We do not consider this regime in more details in this paper.

III.4. Elastic Moduli of the Micellar Gel. We start with a gel in an excess of solvent (uncompressed gel). The distance between micelles corresponds to the minimum of the interaction energy, $\Delta F(D^*)$, where $D^* \simeq 2R_0$. The relevant energy scale is the depth of the minimum, ΔF^* (eq 23) and the spatial scale is ξ_0 (eq 21). In the vicinity of the minimum the function, $\Delta F(D)$ can be expanded as

$$\Delta F(D) = -\Delta F^* + {}^1\!/_2 k(D - D^*)^2$$

where

$$k \sim \Delta F^*/\xi_0^{\ 2} \sim p^{1/2}N^{2\nu}$$

Thus a small compression of the gel, $\delta\epsilon$, implies an increase of the free energy of order

$$\Delta E_1 \sim k(R_0\delta\epsilon)^2$$

per micelle, where $\delta\epsilon$ is the relative volume change, $\delta\epsilon = \delta V/V$. The osmotic modulus of the gel, $K = V(\partial\Pi/\partial V)$, where the osmotic pressure Π is proportional to ΔE_1 and to concentration of micelles: $K \sim (\phi/Np)\ \Delta E_1/(\delta\epsilon)^2$. The compressional modulus of the gel is thus

$$K \sim N^{-3\nu}p^{\nu/2} \tag{30}$$

A shear deformation with an amplitude of order $\delta\epsilon$ implies the same typical change of the distance between nearest-neighbor micelles ($\delta D \sim \delta\epsilon R_0$) as a compression. Therefore the increase of the free energy is nearly the same, i.e. the shear elastic modulus, G, is of the order of the osmotic modulus:

$$G \sim K \tag{31}$$

We now consider a weakly compressed gel, $\phi = \phi^*(1 + \epsilon)$, where ϵ is small (it is also assumed that $\epsilon > \epsilon_c$). In this range, the interaction between the micelles is dominated by the excluded volume repulsion, the bridging attraction being much weaker: the ratio of the typical attraction energy to the repulsion energy is (see eqs 22 and 25)

$$q = \frac{\Delta F_{\text{attr}}}{\Delta F_{\text{rep}}} \sim \frac{\mathcal{N}}{\Delta F_{\text{rep}}} \sim \left(\frac{\epsilon}{\epsilon_c}\right)^{-4/(3-2\nu)}$$

where

$$\epsilon_c = \xi_0/R_0 \sim p^{(\nu/3)-1/2} \tag{32}$$

The relative contribution of the bridges to the elastic moduli is also of the order of q; it is thus not negligible only for an uncompressed gel at $\phi \simeq \phi^*$ ($\epsilon \sim \epsilon_c$). In the region $\epsilon \gg \epsilon_c$ the bridge contribution can be neglected.

Using the same arguments as above and the power law (eq 22) for the interaction energy between two micelles, we get the elastic moduli in the weak compression regime:

$$G \sim K \sim N^{-3\nu} p^{3\nu/2} \epsilon^{6\nu/(3-2\nu)} \tag{33}$$

This equation is valid in the region $1 \gg \epsilon \gg \epsilon_c$. At $\epsilon \sim \epsilon_c$ eq 33 crosses over smoothly to eqs 30 and 31.

In the regime of strong compression, $\phi \gg \phi^*$ we notice that the elastic free energy due to the stretching of the telechelic chains is much smaller than the osmotic free energy. The osmotic modulus is of the order of that of a semidilute polymer solution (with concentration ϕ), i.e. of the order of the osmotic free energy density:

$$K \sim \phi^{3\nu/(3\nu-1)} \sim N^{-3\nu} p^{3\nu/2} (\phi/\phi^*)^{3\nu/(3\nu-1)} \tag{34}$$

A shear deformation does not imply any change of the osmotic free energy, but does imply additional chain stretching. Therefore the shear modulus is of the order of the elastic free energy density, i.e. much smaller than the osmotic modulus K. The elastic free energy per chain is

$$E_1 \sim \phi^{\alpha}(R^2/N)$$

where $\alpha = (2\nu-1)/(3\nu-1)$, and R is the characteristic chain size given by eq 26. Therefore the shear modulus of the gel is

$$G \sim (\phi/N)E_1 \sim p^{2/3} N^{-4/3} \phi^{(3\nu-4/3)/(3\nu-1)} \tag{35}$$

Note that $G/K \sim (\phi/\phi^*)^{-(4/3)[1/(3\nu-1)]}$.

So far we have not taken into account the topological constraints due to the entanglements between chains as they are not important for equilibrium properties. However these constraints are important for the elastic properties of a micellar gel: the entanglement network formed by the polymer chains gives rise to an additional contribution to the elastic constants. Let N_e be the number of concentration blobs per entanglement (this quantity should be universal, i.e. independent of concentration, in a true semidilute regime). The shear elastic modulus of the entanglement network is proportional to the concentration of blobs:

$$G^{\text{ent}} \sim K/N_e \sim (1/N_e)\phi^{3\nu/(3\nu-1)} \tag{36}$$

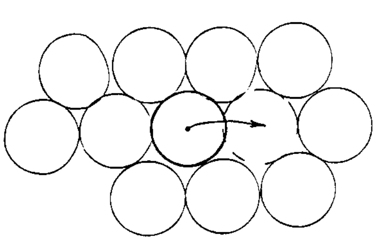

Figure 7. A jump of a micelle to a new "cell".

Comparing eqs 35 and 36 we conclude that the entanglement contribution becomes dominant if

$$\phi > \phi_e = N_e^{(3/4)(3\nu-1)} \phi^* \tag{37}$$

In the next section we consider the dynamical properties of the micellar gel in the range $\phi^* < \phi < \phi_{\max} = \min(\phi_e, \tilde{\phi})$, i.e. we ignore the effect of entanglements.

IV. Viscosity of the Micellar Gel

We restrict our considerations here to *linear* dynamical properties and more specifically to the zero-shear viscosity in the concentration range where the fraction of bridges is small ($\phi < \tilde{\phi}$), and also where entanglements do not play any role ($\phi < \phi_e$). We show that the characteristic time for stress relaxation is very long for this system (exponentially long). Thus all non-exponential (powerlike) prefactors are omitted in this section.

One of the basic dynamical quantities is the characteristic time of transformation of a loop to a bridge or back (detailed balance imposes that the direct and the "reverse" time are equal within the exponential accuracy adopted in this section). This time that we call the exchange time is governed by the barrier associated with the expulsion of one adsorbing end group from the core of a micelle. The energy barrier associated to this process is the binding energy, B, per end group in the aggregate, that we consider as a known parameter. The total binding energy of a core is thus $\sim pB$ and has to be larger than the free energy of the corona given by eq 16 to insure the stability of the micelles. Therefore B must be large enough:

$$B > p^{1/2} \ln N \tag{38}$$

The exchange time can be written as

$$\tau_1 \sim \tau_0 \exp(B) \tag{39}$$

where τ_0 is the microscopic time of an end group (determined by its size and the solvent viscosity).

IV.1. Stress Relaxation Time. We first discuss stress relaxation in the gel after the application of an infinitesimal shear. The stress is carried by (i) the bridges and (ii) the additional pressure induced by the shear in the vicinity of the contact areas between micelles. It cannot be relaxed unless (1) all (or almost all) the bridges are relaxed and (2) the deformed "primitive cells" of the micelles are relaxed. Both these conditions require that a finite fraction ($^1/_2$) of micelles should change their neighbors, i.e. jump over a distance of the order of their size. After a jump a micelle occupies a new "cell" (Figure 7). The realization of a jump requires the crossing of a potential barrier due to the additional deformation of the gel. An additional hole (or void) with a diameter of the order of the micellar size must be created in the neighborhood of the original position of the hopping micelle (see Figure 8). Note that

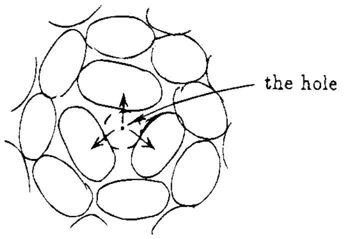

Figure 8. The process of a "hole" formation implies extension of bridges between micelles and also a radial compression of micelles in the neighborhood of the hole.

qualitatively this picture for the elementary dynamical process is similar to the one adopted in microscopic free volume theories for the viscosity of simple liquids.[45-48] Of course, the real micellar movement might be more complex; in particular one can imagine that the void is created *simultaneously* with the movement. However any micelle jump to a new position implies a locally unfavorable packing (an activation state) with a larger effective volume occupied by the given micelle and its nearest neighbors. This additional effective volume which is of the order of the volume of a micelle can be formally attributed to a hole.

A process of a hole appearance is shown schematically in Figure 8. Let us calculate the effective energy of a hole. Each micelle near the hole is compressed in the radial direction (we choose the origin, $\mathbf{r} = 0$ at the center of the hole). Also, some of the bridges between micelles in the vicinity of the hole are more stretched.

We first calculate the deformation energy associated with a hole for an uncompressed or a weakly compressed gel (the initial degree of compression ϵ, is such that $1 \gg \epsilon \gg \epsilon_c$, see eq 32). It can be checked that the additional stretching of the bridges never gives a dominant contribution to the activation energy. Thus, ignoring the bridges we approximately write the deformation energy as

$$U = 0.5K\int(\partial u/\partial r)^2\, d^3r \tag{40}$$

where $u = u(r)$ is the radial displacement of a micelle corresponding to the deformation and r is its distance from the center of the hole. The boundary conditions are

$$u(r{\sim}R) \sim R; \qquad u(r{\rightarrow}\infty) = 0 \tag{41}$$

An important point is that eq 40 is valid only if the relative deformation is weak enough, $|\partial u/\partial r| \lesssim \epsilon$. In the opposite regime, $|\partial u/\partial r| \gg \epsilon$, the elasticity of the micelles is strongly nonlinear: the density of the deformation energy is proportional to (see eq 22)

$$(\partial u/\partial r)^{(6+2\nu)/(3-2\nu)}$$

Note that the exponent, $(6+2\nu)/(3-2\nu)$, is larger than 3. This means that any increase of the characteristic deformation such that $\partial u/\partial r > \epsilon$ is unfavorable, giving rise to a larger energy. Thus in order to estimate the deformation energy we minimize the right hand side of eq 40 with the boundary conditions (eq 41) and with the additional constraint $|\partial u/\partial r| \lesssim \epsilon$. The result is

$$U \sim KR^3\epsilon^{-1} \tag{42}$$

The optimal strain is $|\partial u/\partial r| \sim \epsilon$ and the characteristic radius of the "deformation region" is $r^* \sim R/\epsilon$.

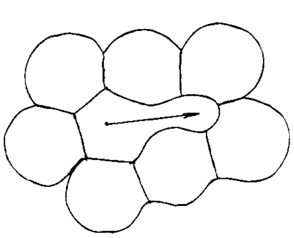

Figure 9. "Creeping" of a micelle into a new "cell" which is occurring *simultaneously* with a hole formation.

Using eqs 42 and 33 we obtain the "deformation barrier" for $\phi = \phi^*(1+\epsilon)$, $1 \gg \epsilon \gg \epsilon_c$:

$$U \sim p^{3/2}\epsilon^{(8\nu-3)/(3-2\nu)} \tag{43}$$

The last equation can be also applied to the uncompressed gel, $\phi = \phi^*$, by taking the limit $\epsilon = \epsilon_c$, so that

$$U \sim p^{(2-4\nu)/3} \tag{44}$$

For a strongly compressed gel ($\phi \gg \phi^*$) the mechanism of "elementary jump" of a micelle is different. The energy of a vacancy (a hole) is very high. However there is no need to create a hole in advance: a micelle can creep to another position without changing its volume (Figure 9). Of course, the "creep motion" requires a considerable deformation (change of the shape) of a given micelle and of its neighbors. The corresponding free energy is

$$U \sim GR^3 \tag{45}$$

where G is the elastic shear modulus (the characteristic shear amplitude is assumed to be of order 1). Note that this energy is much lower than the energy of the hole formation (which is $\sim KR^3$) since $K \gg G$ in this concentration range. Using eqs 45 and 35 we get

$$U \sim p^{5/3}N^{-1/3}\phi^{-1/3(3\nu-1)} \tag{46}$$

The stress relaxation time crucially depends on whether the "deformation barrier" U is larger than the bridge-exchange barrier B or not. If $U > B$ then the activation state for the stress relaxation is "given micelle without any bridges + deformed surrounding". The corresponding total barrier is

$$U^* \sim \Delta F_b + U \tag{47}$$

where $\Delta F_b \sim \mathcal{N}_0$ is the free energy penalty for "debridging" of a given micelle from its neighbors (and $\mathcal{N}_0$ is the typical number of bridges). On the other hand, if $B > U$ then a micelle can perform many "jumps" during the bridge-exchange time, τ_1. Therefore the "deformation barrier" is of no importance, and the total barrier (associated with the activation state) is

$$U^* \sim \Delta F_b + B \tag{48}$$

Finally, the stress relaxation time can be estimated as

$$\tau^* \sim \tau_0 \exp(U^*)$$

IV.2. Viscosity. The zero-shear viscosity of the micellar gel is estimated from the scaling law[49-51]

$$\eta \sim G\tau^*$$

As shown in the previous section, the gel shear modulus, G, varies as a power law of concentration. Therefore within the "exponential" accuracy it is the barrier, U^* that gives the most important contribution to the viscosity:

$$\ln(\eta/\eta_s) \sim U^* = \text{const}\,\mathcal{N} + \max(B,U) \qquad (49)$$

where η_s is the solvent viscosity. Finally, using eqs 25 and 28 for the typical number of bridges, and eqs 43 and 46 for U we get the following concentration dependence of the viscosity of the system (all numerical prefactors are omitted here as usual):

$$\ln(\eta/\eta_s) =$$

$$p^{(1/2)-(\nu/3)} + \max[B, p^{2-(4\nu/3)}] \quad \text{for} \quad (\phi/\phi^*) - 1 \lesssim p^{-(1/2)+(\nu/3)} \qquad (50a)$$

$$p^{5/6}[(\phi/\phi^*) - 1]^{(2\nu+2)/(3-2\nu)} + \max[B, p^{3/2}[(\phi/\phi^*) - 1]^{(8\nu-3)/(3-2\nu)}] \quad \text{for} \quad p^{-(1/2)+(\nu/3)} < (\phi/\phi^*) - 1 < 1 \qquad (50b)$$

$$p^{5/6}(\phi/\phi^*)^{(1/9)[1/(3\nu-1)]} + \max[B, p^{3/2}(\phi/\phi^*)^{-(1/3)[1/(3\nu-1)]}] \quad \text{for} \quad 2\phi^* \lesssim \phi < \phi_{\max} \qquad (50c)$$

where $\phi_{\max} = \min(\phi_e, \tilde{\phi})$ (see eqs 29 and 37).

The behavior of the viscosity crucially depends on the relative values of the "exchange barrier" B and of the number of chains per aggregate, p. If $B > p^{3/2}$, the viscosity of the system sharply increases at the gel-formation point, $\phi = \phi^*$, by a factor $\exp(B)$,[52] and then continues to increase in the region b by a factor $\exp(\text{const } p^{(1-\nu)/3})$, and in the region c as a power law of concentration. If $p < B < p^{3/2}$ the viscosity increases in the region $\phi^* < \phi \lesssim 2\phi^*$, but then *decreases* in the range

$$2\phi^* \lesssim \phi < \phi_2 \qquad (51)$$

with

$$\phi_2 \sim (p^{3/2}B^{-1})^{3(3\nu-1)}\phi^*$$

and again increases for $\phi > \phi_2$.

In the last regime, $B < p$ (note however that the barrier must still be much larger than $p^{1/2}$, see eq 38) the viscosity increases for $\phi^* < \phi \lesssim 2\phi^*$, and then it decreases in the range $2\phi^* \lesssim \phi < \phi_{\max}$.

The dependence of viscosity when $p < B < p^{3/2}$ on the concentration, ϕ, is shown schematically in Figure 10.

The unusual decrease of the viscosity with increasing concentration in the last two regimes is related to the fact that the telechelic chains forming the micelles are less stretched in a more concentrated gel. Therefore, it is easier for the micelles to change their shapes and the potential barrier for rearrangement of the micelles is lower at higher concentration.

V. Discussion

We have studied in this paper a model associating polymer system: telechelic copolymers with a long soluble central block and insoluble external blocks. One of the specificity of this system is that the insoluble parts associate to form micelles or flowers with a large aggregation number. Two *flowers* strongly attract each other even if the solvent is good for the soluble parts of the chains forming the coronas of the micelles. The attraction is attributed to the possibility of bridging between the flowers. This result, in fact, is not exactly new: it was first proposed by Witten,[22] and later corroborated by a detailed analysis of interaction of telechelic "brushes"[23] in the planar geometry. The same analysis has been generalized to spherical geometries and to compressed layers.

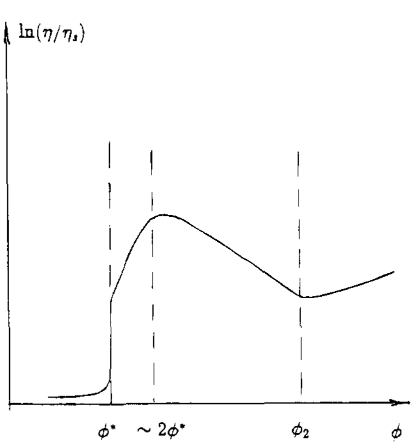

Figure 10. The typical concentration dependence of viscosity of a micellar gel (for $p < B < p^{3/2}$).

The effective binding energy (attraction energy) of two flowers is much larger than kT if the aggregation number, p (number of chains per micelle) is high: the energy is $\sim p^{0.3}kT$. One important implication of this result is that flowers tend to phase separate to form compact clusters, and eventually a macrophase of close packed flowers. This macrophase is actually a physical gel since the flowers are connected by multiple bridges.

These qualitative results should be valid not only for telechelic chains, but also for a much broader class of associating polymers including polysoaps, multiionomers containing many insoluble (hydrophobic) groups per chain. Different macromolecular architectures are also possible: the insoluble parts can be included either in the linear backbone, or in side chains grafted to the backbone (e.g. at the ends of the side chains). The conformation of isolated multi-block-copolymer chains with soluble and insoluble parts in a dilute solution (good solvent) has been studied by Halperin.[10] The typical conformation assumed in ref 10 for a large enough number, n, of blocks is a swollen chain of flowers. Since the flowers attract each other, we rather expect a collapsed chain of flowers forming a compact globule (with the structure of a reversible gel), the size of the globule being proportional to $n^{1/3}$.

The central results of the paper are the predictions for the elastic moduli and the zero-shear viscosity after the reversible gel formation, for concentrations $\phi > \phi^*$. It is worth noting here that *all* the results of the paper are applicable not only when the solvent is good for the central part of the copolymer but also when it is a Θ-solvent. The predictions for the Θ solvent are obtained by taking the swelling exponent ν equal to $1/2$.

The viscosity of the system sharply increases in the region $\phi \sim \phi^*$. Interestingly, it can then (for higher concentrations) decrease appreciably in a limited concentration range (see eq 51) if the aggregation number is high enough. This prediction is in qualitative agreement with experimental data for the viscosity of solutions of (oxyethylene)−urethane block copolymers with hydrophobic end groups.[31]

Our results are also relevant for a solution of star polymers with a high functionality $f = 2p$. The only important difference between a solution of telechelic micelles and a solution of stars is the absence of bridges between stars. However, bridges are not important for the elastic properties of the solution in the range $\phi^* < \phi < \phi_{\max}$. Therefore the elastic moduli given by eqs 30–35 are valid also for a star solution. The basic equation (eq 49) for the viscosity in the absence of bridges can be simplified as

$$\ln(\eta/\eta_s) \sim U$$

so that finally we get the following concentration behavior of the viscosity for a solution of stars (from eq 50):

$$\ln(\eta/\eta_s) =$$

$$p^{2-(4\nu/3)} \quad \text{for} \quad (\phi/\phi^*) - 1 \lesssim p^{-(1/2)+(\nu/3)} \quad (52a)$$

$$p^{3/2}[(\phi/\phi^*) - 1]^{(8\nu-3)/(3-2\nu)} \quad \text{for} \quad p^{-(1/2)+(\nu/3)} < (\phi/\phi^*) - 1 < 1 \quad (52b)$$

$$p^{3/2}(\phi/\phi^*)^{-(1/3)[1/(3\nu-1)]} \quad \text{for} \quad 2\phi^* \lesssim \phi < \phi_{\max} \quad (52c)$$

Note that the viscosity is exponentially large in all regimes a–c; it increases with concentration in the regime b, then decreases in the regime c.

The decrease of the viscosity in the regime c is expected both for stars and for telechelic micelles (if the aggregation number is high, $p > B^{2/3}$); it can be qualitatively explained as follows. The zero-shear viscosity is primarily governed by the activation energy for the jump of a micelle (star) to a new position (new "cell"). This process requires an appreciable deformation of the micelle (see Figure 10). The activation energy corresponding to this deformation is of order GR^3, where G is the elastic shear modulus, and R^3 is the volume per micelle. In the regime c the shear modulus is of the order of the elastic energy density due to the chain stretching. Therefore the activation energy is proportional to the total elastic energy per micelle. This energy, in turn, is proportional to the stretching energy of one chain (since the total number p of chains in a micelle is fixed), which obviously decreases with concentration (note that the spatial size of the micelles decreases as solvent is removed).

Several extensions of this work would be required. In the study of the viscoelasticity of the physical gel, we have neglected the entanglements. In the central part of the flowers the chains are stretched; a theory for the entanglements between stretched chains is not available and a full theory for the viscoelasticity of entangled telechelic chain is thus beyond the scope of this work. We also have only considered the case where a small fraction of the chains form bridges between flowers. In the higher concentration range where most of the chains form bridges, the physics is very different since a given chain does not connect nearest-neighbor micelles but far apart micelles. Finally, some other properties of the physical gel would also deserve a more detailed study such as the complex modulus or the nonlinear viscoelasticity.

Acknowledgment. This work was performed during the stay of one of the authors (A.N.S.) at Université Louis Pasteur in Strasbourg (Institut Charles Sadron). A.N.S. thanks the University and the Ministry of Higher Education of France for the opportunity to stay in Strasbourg. A.R.K. and A.N.S. also gratefully acknowledge the support of the E. I. DuPont de Nemours Company. We also thank N. Dan and I. A. Nyrkova for useful discussions.

References and Notes

(1) Williams, C. E. In *Multiphase Macromolecular Systems*; Culbertson, B. M., Ed.; Contemporary Topics in Polymer Science 6; Plenum Press: New York, 1989.
(2) Goethals, E. J., Ed. *Telechelic Polymers: Synthesis and Applications*; CRC Press: Boca Raton, FL, 1989.
(3) Pinery, M., Eisenberg, A., Eds. *Structure and Properties in Ionomers*; NATO Advanced Study Institute Series 198; D. Reidel Publishing Co.: Dordrecht, Holland, 1987.
(4) Tant, M. R.; Wilkes, G. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 1.
(5) *Developments in Block Copolymers*; Goodman, I., Ed.; Applied Science: New York, 1982 and 1985; Vols. 1 and 2.
(6) Stockmayer, W. *Macromolecules* **1991**, *24*, 6367. Tanaka, F.; Stockmayer, W. *Macromolecules* **1994**, *27*, 3943.
(7) Domszy, R.; Alamo, R.; Edwards, C.; Mandelkern, L. *Macromolecules* **1991**, *19*, 310.
(8) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 657.
(9) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1989**, *30*, 170.
(10) Halperin, A. *Macromolecules* **1991**, *24*, 1418.
(11) Daoud, M.; Cotton, J. P. *J. Phys.* **1982**, *43*, 531.
(12) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1983**, *16*, 214.
(13) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 1343.
(14) Witten, T. A.; Pincus, P. A. *Macromolecules* **1986**, *19*, 2509.
(15) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.
(16) Nyrkova, I. A.; Khokhlov, A. R.; Doi, M. *Macromolecules* **1993**, *26*, 3601.
(17) Broze, G.; Jerome, R.; Teyssie, P.; Marco, C. *Macromolecules* **1983**, *16*, 996.
(18) Gouin, J. P.; Williams, C. E.; Eisenberg, A. *Macromolecules* **1989**, *22*, 4573.
(19) Moore, R. B.; Bittencourt, D.; Gauthier, M.; Williams, C. E.; Eisenberg, A. *Macromolecules* **1991**, *24*, 1376.
(20) Williams, C. E.; Russel, T. P.; Jerome, R.; Horrion, J. *Macromolecules* **1986**, *19*, 2877.
(21) The aggregation number was observed to be rather insensitive to concentration, molecular weight of soluble parts, and other parameters.[20] (See ref 22 for a general discussion of the issue).
(22) Witten, T. A. *J. Phys.* **1988**, *49*, 1055.
(23) Milner, S. T.; Witten, T. A. *Macromolecules* **1992**, *25*, 5495.
(24) Leibler, L.; Rubinstein, M.; Colby, R. H. *Macromolecules* **1991**, *24*, 4701.
(25) Leibler, L.; Rubinstein, M.; Colby, R. H. *J. Phys. II* **1993**, *3*, 1581.
(26) Rubinstein, M.; Leibler, L.; Colby, R. H. *Polym. Prepr.* **1991**, *32*, 443.
(27) Tanaka, F.; Edwards, S. F. *Macromolecules* **1992**, *25*, 1516.
(28) Groot, R. D.; Agterof, W. G. M. *J. Chem. Phys.* **1994**, *100*, 1649.
(29) Groot, R. D.; Agterof, W. G. M. *J. Chem. Phys.* **1994**, *100*, 1657.
(30) Baljon, A. R. C. *Macromolecules* **1993**, *26*, 4339.
(31) Howard, P. R.; Leasure, E. L.; Rosier, S. T.; Schaller, E. J. *J. Coating Technol.* **1992**, *64*, (No. 804), 87.
(32) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.
(33) Zinn-Justin, J. *Quantum Field Theory and Critical Phenomena*; Oxford University Press: New York, 1989.
(34) Alexander, S. *J. Phys.* **1977**, *38*, 983.
(35) De Gennes, P. G. *J. Phys.* **1976**, *37*, 1443.
(36) De Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.
(37) Zhulina, E. B.; Borisov, O. V.; Pryamitsyn, V. A. *Polym. Sci. USSR* **1989**, *31*, 205.
(38) Zhulina, E. B.; Semenov, A. N. *Vysokomol. Soed. A* **1989**, *31*, 177.
(39) Witten, T. A.; Leibler, L.; Pincus, P. A. *Macromolecules* **1990**, *23*, 824.
(40) Joanny, J.-F. *Langmuir* **1992**, *8*, 989.
(41) Semenov, A. N. *Macromolecules* **1992**, *25*, 4967.
(42) This statement can be explained as follows. The excluded volume free energy is roughly proportional to the probability that two loops (which are end-grafted to different planes) have a contact near the midplane. This state implies that

four half-chains are strongly stretched (the end-to-end distance of each of these half-chains must be nearly $D/2$). On the other hand a bridge implies only two strongly stretched half-chains. Therefore the average number of bridges must be much larger than the number of loop contacts. Thus bridging attraction must dominate over repulsion due to excluded volume between the two brushes.

(43) In fact the edge of a corona can be roughly considered as a slightly curved planar "brush", the height of the brush being smaller than the radius of curvature. Thus in zero's approximation the curvature can be neglected. This has already been suggested by Wijmans and Zhulina (Wijmans, C. M.; Zhulina, E. B. *Macromolecules* **1993**, *26*, 7214).

(44) Of course there is another possibility that the micelles would crystallize in a superstructure. Here we simply assume that this is not the case, i.e. that the system of micelles is amorphous (like a liquid or a glass).

(45) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1970.

(46) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164.

(47) Turnbull, D.; Cohen, M. H. *J. Chem. Phys.* **1961**, *34*, 120.

(48) Macedo, P. B.; Litovitz, T. A. *J. Chem. Phys.* **1965**, *42*, 245.

(49) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.

(50) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell Univ. Press: Ithaca, NY, 1979.

(51) Doi, M. D.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford Univ. Press: Oxford, U.K., 1986.

(52) As was mentioned above the equilibrium system in the regime $\phi < \phi^*$ is separated into two macrophases: a dilute phase and the gel phase. The separation process must be very slow however. It starts with formation of finite clusters of the gel phase immersed in the dilute solution, the size of clusters increasing with time. The final time of formation of a gel macrophase must be extremely long since rearrangements of clusters are restricted by high potential barriers. Thus it is the viscosity of the cluster system that is usually probed in experiments (if the experimental time is not too long). Since the volume fraction of clusters is nearly time independent, the apparent viscosity of the cluster system must be also nearly constant (during the intermediate stage), being of order of the viscosity of a dilute solution.

(53) Layton, L. H.; Jackson, E. G.; Strauss, U. P. *J. Polym. Sci.* **1952**, *9*, 309.

(54) Balsara, N. P.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1992**, *24*, 1975.

(55) Plestil, J.; Hlavata, D.; Hrouz, J.; Tuzar, Z. *Polymer* **1990**, *31*, 2112. Tuzar, Z.; Konak, C.; Stepanek, P.; Plestil, J.; Kratochvil, P.; Prochazka, K. *Polymer* **1990**, *31*, 2118.

MA941100Q