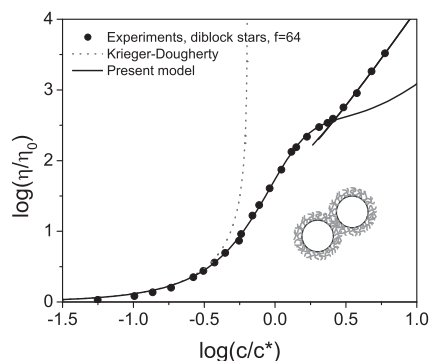


Model for the Shear Viscosity of Suspensions of Star Polymers and Other Soft Particles

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A model is proposed to describe the concentration dependence of the viscosity of soft particles. The softness of the particles is incorporated in a very simple way into expressions originally developed for rigid spheres. This is done by introducing a concentration-dependent critical packing, which is the packing at which the suspension loses fluidity. The resultant expression reproduces the experimental results for suspensions of star polymers in good solvents with high accuracy. The model allows the weak increase of the viscosity observed in the case of diblock copolymer stars to be explained, suggesting that the reason for this peculiar behavior is mainly a consequence of the softness of the particles. In the semi-dilute regime, suspensions of star polymers are modeled using the Daoud–Cotton picture to complete the description in the whole concentration regime.



It is of basic and applied importance to understand the flow behavior of fluids containing colloidal particles and macromolecules. The range of industrial applications of such complex fluids ranges from motor oils, coatings, drilling fluids, and food products among others. Many colloidal suspensions consist of hard particles whose rheological properties have been studied profusely. By contrast, much less attention has been paid to suspensions containing soft colloids. Representatives of soft colloids include deformable particles and particles that in addition may interpenetrate to some extent.

The interest in studying soft particles stems from the desire to explore the behavior of a number of complex fluids composed of nonrigid structures such as polymerically stabilized colloidal spheres,^[1] block copolymer micelles,^[2] star polymers,^[3] hard spheres with a grafted polymer brush,^[4] dendritically branched polymers,^[5] and others. In particular, star polymers, which are branched macromolecules with a small central core from where

f arms of identical linear polymer chains, each one containing N segments emerge is considered an important prototypical model of soft particle because their size and architecture can be tailored between that of linear polymers and ultrasoft colloids to nearly hard spheres.^[6]

Pioneering theoretical work to calculate the viscosity of dilute colloidal suspensions was initiated by Einstein who obtained an expression to calculate the viscosity as function of the concentration of dilute suspensions of spherical hard particles.^[7] Various models to calculate the viscosity of dilute suspensions of particles other than solid spheres have been proposed. Among them, we can mention the case of emulsions of spherical droplets,^[8] homogeneously porous rigid spheres,^[9–11] and uncharged spherical soft particles.^[12]

For non-dilute systems, the suspension rheology is determined by the interplay between the direct particle–particle interactions and the solvent-mediated hydrodynamic interactions (HIs).^[13] Their many body nature impose a formidable difficulty for the calculation of rheological quantities such as the shear viscosity of the system. The fact that many particles are soft complicates even more the calculation. Nonetheless, it is a common practice to correlate the concentration dependence of the viscosity of star polymers and other hairy

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particles using phenomenological models designed for solid hard spheres.^[14,15] In particular, experimental data are frequently compared with the expression proposed by Krieger and Dougherty for hard colloidal particles:^[16]

$$\eta(\phi) = \eta_0 \left[1 - \left(\frac{\phi}{\phi_{\max}} \right) \right]^{-[\eta]\phi_{\max}} \quad (1)$$

where $\eta(\phi)$ is the viscosity of the suspension, η_0 is the viscosity of the background solvent, ϕ is the volume fraction of the colloidal particles, ϕ_{\max} is the volume fraction at maximum packing and $[\eta] = 5/2$ is the intrinsic viscosity of hard spheres. Comparing experimental data for star polymers with this expression might be accurate for stars with a large number of short arms since they behave essentially as hard spheres. However, such comparisons do not give satisfactory results in the case of stars with larger arms because in this case the particles are much softer. In addition to this, it has been shown that the Krieger and Dougherty expression underestimates the viscosity of the suspension at large volume fractions even in the case of hard spheres, as explained thoroughly in ref.^[17]

Alternative expressions have been devised to predict the viscosity for concentrated suspensions including in a more accurate way hydrodynamic and excluded volume interactions. Using a differential effective medium technique based on a progressive addition of particles to the sample in which the new particles interact in an effective way with those added in previous stages, we have shown^[17–20] that the static and high-frequency viscosities of suspensions of colloidal particles can be correlated with the expression:

$$\eta(\phi) = \eta_0 \left(1 - \frac{\phi}{1 - k\phi} \right)^{-[\eta]} \quad (2)$$

where $[\eta]$ is the intrinsic viscosity and k is a fitting constant related to the critical volume fraction ϕ_c at which the suspension loses its fluidity and is given by:

$$k = \frac{1 - \phi_c}{\phi_c} \quad (3)$$

Expression (2) incorporates crowding effects and hydrodynamic interactions^[17–20] and has been applied successfully to suspensions of hard spheres,^[18] emulsions of spherical droplets,^[19] suspensions of arbitrarily shaped hard particles,^[17] suspensions of rigid core-shell permeable particles,^[20] and suspensions with power-law matrices^[21] with excellent results. However, as in the case of the Krieger and Dougherty model, when applied to soft (interpenetrable) particles, Equation 2 fails to reproduce the viscosity-concentration curves satisfactorily.

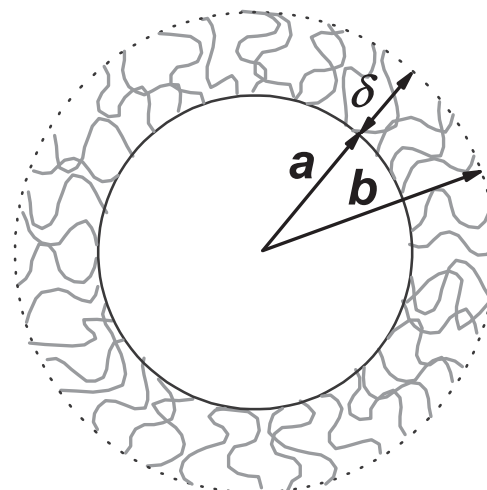


Figure 1. Schematics of a model for a suspension of core-shell spheres. A hard core of radius a covered by a porous layer of thickness δ . The total radius of the particle is $b = a + \delta$.

The purpose of the present work consists in propose a method to incorporate the softness of the particles in the above-mentioned expressions to obtain a model that better correlates with experimental results.

Since we have in mind to apply the model to suspensions of star-branched polymers, we have to take into account the possibility that the particles are permeable to some extent to the surrounding solvent. To do so, we consider a core-shell particle consisting of a spherical hard core of radius a coated with a surface soft layer of thickness δ . The soft layer may represent a grafted polymer brush^[22] or the outer sections of a star polymer, as represented in Figure 1. Thus, the polymer-coated particle or star polymer has a non-porous inner radius a and an permeable outer shell of radius $b = a + \delta$. The volume fraction ϕ is defined as the volume occupied by the particles including the shell, divided by the volume of the sample. To model the permeability of the outer shell, the polymer segments are regarded as resistance centers distributed in the permeable polymer layer, exerting frictional forces $-\gamma\mathbf{u}$ on the liquid flowing in the layer, where \mathbf{u} is the liquid velocity relative to the particle and γ is the frictional coefficient. The result of this model is:^[12] $[\eta] = (5/2)L_2(\lambda b, a/b)/L_1(\lambda b, a/b)$, where $\lambda = \sqrt{\gamma/\eta_0}$. Expressions for $L_1(\lambda b, a/b)$ and $L_2(\lambda b, a/b)$ can be found in ref.^[20] The quotient $L_2(\lambda b, a/b)/L_1(\lambda b, a/b)$ expresses the effect of the polymer layer coating the particle upon its intrinsic viscosity, it is an increasing function of λb and a/b , it takes the minimum value $L_2(\lambda b \rightarrow 0, a/b \rightarrow 0)/L_1(\lambda b \rightarrow 0, a/b \rightarrow 0) = 0$, and we recover the hard-sphere result, $L_2(\lambda b, a/b)/L_1(\lambda b, a/b) = 1$ when $\lambda b \rightarrow \infty$ or $a/b = 1$. In this way, the permeability of the outer shell is incorporated in the intrinsic viscosity $[\eta]$ of the core-shell spheres.

If we consider that the outer core of the soft sphere do not exert frictional forces on the liquid flowing through it, that is, $\lambda = 0$, then the expression for $[\eta]$ simplifies considerably and one gets:

$$[\eta] = \frac{5}{2} \left(\frac{a}{b}\right)^3 \quad (4)$$

The present model Equation 2 together with Equation 4 allows the viscosity to be obtained as a function of the concentration of rigid porous core-shell particles and has been successfully applied to calculate the static viscosity of surfactant-coated particles and the high-frequency viscosity of homogeneous porous particles.^[20] However, it does not give satisfactory results for suspensions of star polymers.

As mentioned above, experimental results of the concentration-dependent viscosity of star polymers cannot be satisfactorily reproduced with models developed for hard colloids like the Krieger–Dougherty model, Equation 1 or the one given by Equation 2 even when the intrinsic viscosity for core-shell particles, Equation 4, is used. The problem with these expressions is that they assume that the particles are rigid. It is apparent that the softness of the stars must be taken into account to obtain better results. Here, we propose to model the softness of the particles by assuming that the critical volume fraction, ϕ_c , is larger than the random close packing value ϕ_{RCP} since soft particles can interpenetrate each other. Specifically, we propose the following ansatz:

$$\phi_c = \phi_{\text{RCP}} + \beta \phi^\alpha \quad (5)$$

where α and β are unknown constants that should be determined from the fitting to the experimental data. Equation 5 can be interpreted as follows, when the volume fraction is low, the soft particles are far apart from each other and therefore on average they do not overlap too much. In this situation, since the amount of overlap is small, their rheological behavior can be described in a manner similar to impenetrable spheres, that is to say, the critical packing can take the value $\phi_c \approx \phi_{\text{RCP}}$. As the volume fraction is increased, the particles are forced to collide more often increasing the average overlap, which, in turn, increases the value of ϕ_c since now the particles with that average overlapping can be more closely packed at maximum packing. Equation 5 then proposes that this increase follows a power law on the volume fraction.

To test the correctness of this proposal we compare the predictions of our model given by Equation 2 including the possibility that the outer sections of the star are solvent permeable, using the intrinsic viscosity (4). Finally and most importantly, we incorporate the softness of the particles substituting Equation 5 into Equation 3. This is done in Figure 2 where we compare the predictions of our

model with the experimental results of Roovers,^[15] for the relative viscosity of polybutadiene star polymers in the good solvent toluene. Typically, the viscosity versus concentration curves for star polymers are plotted in terms of the polymer concentration c/c^* , where c^* is the overlap concentration defined by $c^* = [(N_A/M)(4\pi/3)R_V^3]^{-1}$, where N_A is Avogadro's number, M is the molecular weight, and R_V is the viscosimetric equivalent hard-sphere radius of the polymer coil. On the other hand, models for the viscosity of colloidal suspensions like Equation 2 are written in terms of the particle volume fraction ϕ . In the dilute regime, these two quantities are related by:

$$\phi = c/c^* \quad (6)$$

which allows to plot our model in terms of the polymer concentration. In Figure 2, we perform such plot. Panel (a) shows the experimental results for stars with $f = 128$ arms. Notice that the viscosity-concentration curve is not very different from the hard-sphere result at low concentrations. However at large concentrations, a slight departure from the hard-sphere behavior is observed. Our model reproduces very well this departure with the fitting parameters shown in Table 1. If the number of arms is decreased, one expects a smaller steric repulsion between the arms of different stars allowing a larger overlap and therefore a larger departure from the hard-sphere behavior. This is shown in 2b where results for a star with 64 arms are shown. The softness of the star is larger than in the case of the star with 128 arms and the departure from the hard-sphere behavior is larger. Our model predicts correctly the experimental data and the increased softness of this case is reflected in a larger value of the parameter β , as shown in Table 1. Panel (c) shows the results for a star with 32 arms. The low number of arms of this case allows a much larger overlap allowing that concentrations above c^* can be reached. Experimental data show clearly a different behavior below and above c^* . The region below c^* can still be described with our model with an even larger value of β than in the previous cases. However, above c^* , the overlap is so large that the conformation of the star polymers should be described differently. Here, we use the Daoud and Cotton picture^[23] to describe the star conformation in this semi-dilute regime.

In the Daoud and Cotton model,^[23] a single star polymer is regarded as a spherical region of a semi-dilute polymer solution with a local, position-dependent screening length $\xi(r)$, where r is the distance from the center. This is represented pictorially by associating with each arm a string of blobs of increasing size $\xi(r)$ as shown in Figure 3. The blob size varies as $\xi(r) \approx rf^{-1/2}$ and the corresponding local polymer volume fraction as $c_s(r) \approx f^{2/3}(b/r)^{4/3}$. The size of the star can be obtained from monomer conservation^[24,25]

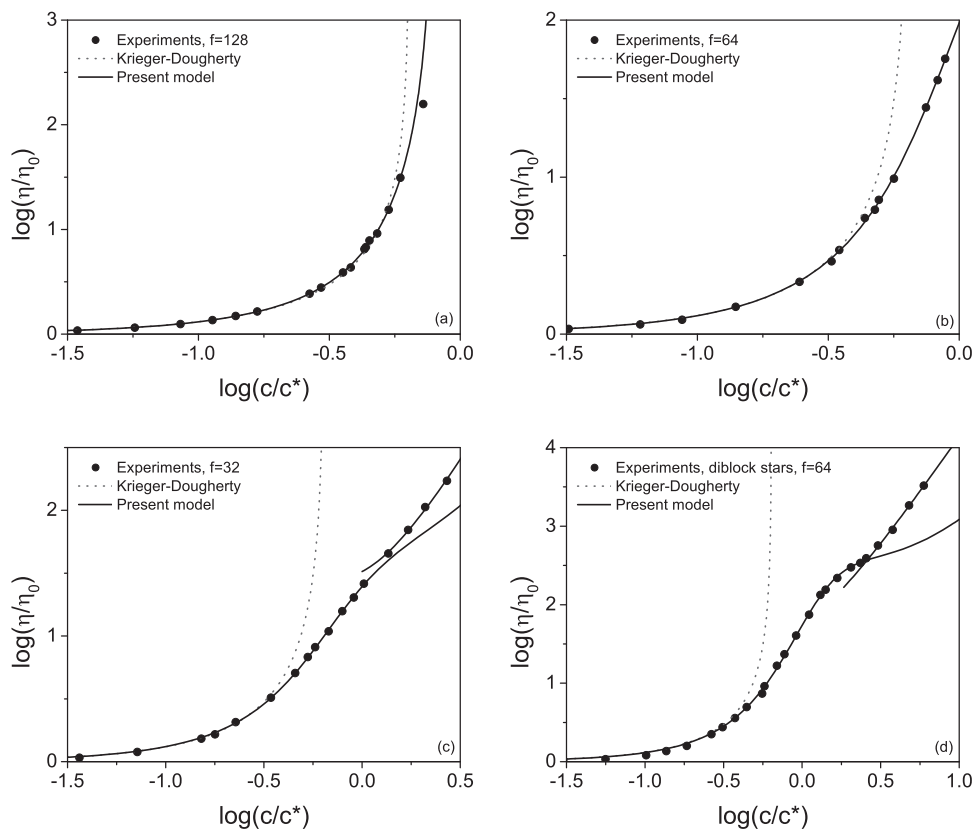


Figure 2. Relative viscosity $\eta(\phi)/\eta_0$ as a function of the particle volume fraction ϕ for star polymers with (a) 128, (b) 64, and (c) 32 arms and (d) diblock copolymer micelle with 64 arms in the good solvent toluene. While in panels (a) and (b) only the dilute regime appears, in panels (c) and (d) a second regime, the semi-dilute regime, is apparent and modeled using the Daoud–Cotton picture as explained in the text. The experimental data are from ref.^[15]

to obtain $R \approx \beta \xi_p N f^{A/5}$, where ξ_p is the Kuhn length. Above the overlapping concentration $c^* = f N \xi_p^3 / R^3$, the outer sections of the arms overlap and build a semi-dilute solution, often called the sea of blobs, where the inner parts of the actual stars are embedded and where the polymer concentration of the sea of blobs levels off (see Figure 3). The stars embedded in the sea of blobs occupy a volume fraction ϕ and the sea of blobs the remaining fraction $1 - \phi$. Above the overlapping concentration c^* , the values of the polymer concentration in the sea of blobs c_p , of the fraction occupied by the stars ϕ , and of the radius

of the embedded stars R_{sd} can be calculated from mass conservation:^[25]

$$\phi = k_1 \left(\frac{c^*}{c} \right)^{5/4} \quad (7)$$

$$c_p \simeq c \quad (8)$$

and

$$R_{sd} = R k_2 \left(\frac{c^*}{c} \right)^{3/4} \quad (9)$$

Table 1. Fitting parameters of the model for the systems of Figure 2.

System	128 arms	64 arms	32 arms	Diblock star 64 arms
a/b	0.988	0.989	0.993	0.984
α	1.90	1.60	1.74	1.50
β	0.244	0.580	0.966	0.662
η_{sb}^0	–	–	9.28	17.4
γ	–	–	2.67	2.88

The constant k_1 can be obtained from continuity of the volume fraction at $\phi = \phi_{RCP} = 0.637$ from Equations 6 and 7 to get $k_1 = 0.3625$, while the constant k_2 is obtained by continuity from Equations 6 and 9 since $R_{sd} = R$ at the same point, to get $k_2 = 0.7130$. Notice that an increase of the polymer concentration c leads to an increase of the fraction of space occupied by the sea of blobs and a shrinkage of the inner star dimensions. Additionally, the stars are embedded in a solvent with viscosity η_{sb} formed by the sea of blobs and from Equations 4 and 9 the intrinsic viscosity of the embedded stars is:

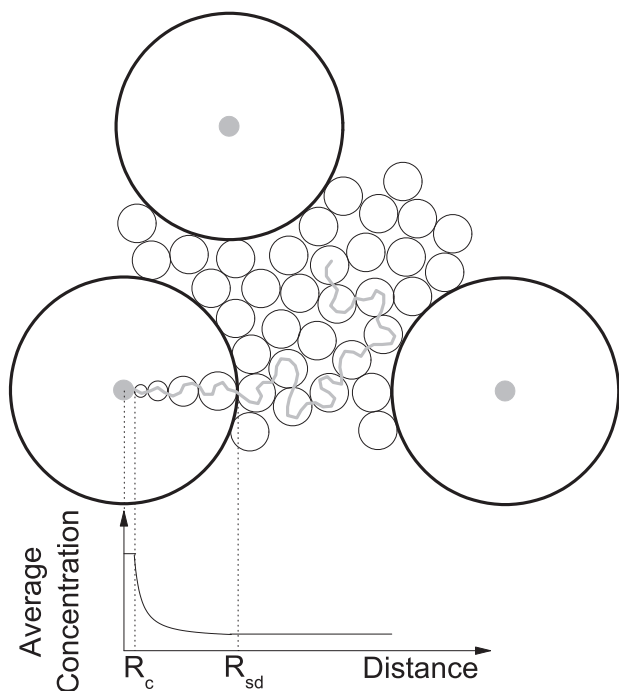


Figure 3. Daoud and Cotton model for a semi-dilute suspension of star polymers.

$$[\eta] = \frac{5}{2} \left[\frac{a}{b} k_2^{-1} \left(\frac{c}{c^*} \right)^{3/4} \right]^3 \quad (10)$$

The sea of blobs exerts a strong opposition to flow because movement proceeds through a disentanglement of the stars from their neighbors^[26] and since they consist of a semi-dilute polymer suspension we suggest to model the viscosity of the sea of blobs using the scaling relation:

$$\eta_{sb} = \eta_{sb}^0 \left(\frac{c}{c^*} \right)^\gamma \quad (11)$$

where η_{sb}^0 and γ are additional fitting constants that allow to model the large viscosity of the sea of blobs.

Finally, substituting Equations 7 and 10 and replacing the viscosity of the solvent η_0 in Equation 2 with the viscosity of the sea of blobs η_{sb} , we obtain the viscosity for c above c^* .

Using this approach, we can reproduce the viscosity-concentration curve of the star with $f = 32$ above c^* as shown in Figure 2c. Notice that in this regime, the volume fraction occupied by the stars decreases with concentration and this effect alone would produce a decrease of the viscosity with concentration. However, this decrease is offset by the increase of the viscosity of the sea of blobs with concentration. The parameters α and β used in this region are the ones obtained in the dilute regime and η_{sb}^0 and γ are also shown in Table 1. Finally, in panel (d), we show the case of a diblock copolymer star with 64 arms,

an inner core composed of polybutadiene arms with $N_{\text{inner}} = 20\,000$ and an outer shell of polystyrene arms with $N_{\text{outer}} = 10\,000$. The viscosity data were collected in toluene, which is a good solvent for both blocks. Again, two different regions are apparent and additionally a shoulder appears at a concentration near c^* . Surprisingly, our model reproduces correctly this shoulder. Therefore, our model suggests that the origin of this characteristic is an intrinsic feature of the softness of the particles. The semi-dilute region is again well described by the Daoud–Cotton picture. The reason why the shoulder is visible in the case of the copolymer and not in the case of the star polymer is because in the last case the semi-dilute regime appears before the shoulder can be observed. This is shown in Figure 2c, where the theoretical curve corresponding to the dilute regime is plotted to values $c/c^* > 1$. If it were not by the appearance of the semi-dilute regime, the shoulder would be visible. Notice that in all the cases considered the thickness of the porous layer is very small as compared with the core size (see the values of the parameter a/b in Table 1). In other words, for any practical purpose, the star polymers behave as nonporous particles and the value $[\eta] = 5/2$ can be used.

At this point, we would like to emphasize that the *ansatz*, Equation 5 does not preclude the existence of a critical packing where the viscosity diverges. This is shown in Figure 4, where we plot ϕ_c versus ϕ . The solid lines correspond to ϕ_c as given by Equation 5 with the parameters α and β used to fit the data of Figure 2 and given in Table 1. Each curve is labeled with the letter of the panel of Figure 2 where the parameters were extracted.

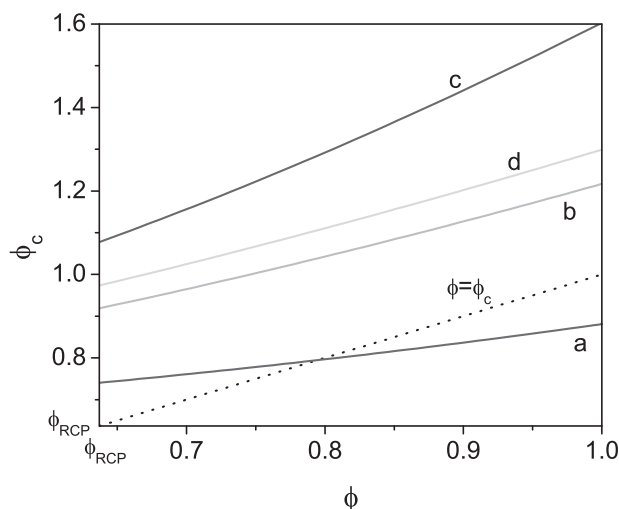


Figure 4. ϕ_c versus ϕ as given by Equation 5. The values of the parameters α and β used in each curve are given in Table 1. Each curve is labeled with the letter corresponding to the panel in Figure 2 where the parameters were obtained. Only the curve labeled *a* satisfies the condition $\phi = \phi_c$, at $\phi \approx 0.795$, where the viscosity diverges.

The divergence of the viscosity occurs when $\varphi = \varphi_c$. It is clear that only in the case of the star with $f = 128$ arms (curve labeled a) this condition is satisfied and the viscosity diverges at a value $\varphi \approx 0.795$. The other cases do not satisfy the condition $\varphi = \varphi_c$ since φ always lies behind φ_c and thus no divergence in the viscosity is expected. It is in these cases where the shoulder appears and it represents the transition onset from a regime where φ_c is dominated by φ_{RCP} (when φ is small) to a regime where $\varphi_c \approx \beta\varphi^\alpha$ (for larger values of φ). Finally, let us mention that a somewhat related way to treat the softness of the particles, has been proposed in the context of the glass transition of dense fluids of compressible spheres in ref.^[27]

Summarizing, in this work, we have presented a simple model for the calculation of the concentration dependence of the viscosity for suspensions of soft spherical particles consisting of a hard core of radius a covered with a porous shell of thickness $\delta = b - a$. The model contains three main ingredients, the first one consists in using an accurate model for the viscosity originally developed for rigid particles (Equation 2). Secondly, we use a simple expression for the intrinsic viscosity of permeable core-shell particles (Equation 4) to allow the possibility that the outer region of the particle is solvent permeable. Thirdly and most importantly, we incorporated in a very simple way the effects of the softness of the particles through Equation 5. Using this model, we were able to reproduce the experimental results for the viscosity of star-branched polymers and explained the appearance of a shoulder seen in the viscosity–concentration curves of the diblock star near the overlap concentration. We conclude that this peculiar behavior is an intrinsic feature of the softness of the particles and there is no need to invoke alternative mechanisms as a shrinking of the polybutadiene block^[15] when the total polymer concentration increases. Additionally, in the semi-dilute regime $c/c^* > 1$, the suspension is modeled using the Daoud–Cotton picture, which completes the description of the viscosity in the whole concentration regime. We have tested our model comparing with experimental results finding an excellent agreement in spite of the numerous simplifications used in the obtention of our model.

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