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Dynamics and Intrinsic Viscosity of Star Polymers in Poor Solvents

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Introduction

The dynamics of regular star polymers in a good solvent and in Θ conditions was recently studied in ref 1 (hereafter referred to as paper I) using the equilibrium results obtained through the configurational normal-mode description with self-consistent free-energy minimization.[2,3] This procedure yields the strain ratios of the normal modes, which permit the calculation of all the (quadratic) averages of interest. These equilibrium normal modes also form a first-order approximation to the *dynamical* normal modes.[1,4,5] In paper I the latter were obtained through diagonalization of a nonsymmetrical matrix formed by the product of two symmetrical matrices: these account for the intramolecular elasticity and for the preaveraged hydrodynamic interaction in terms of the actual polymer conformation through the strain ratios of the normal modes. These two matrices are first rendered quasi-diagonal through the equilibrium normal modes;[1,4] then the final diagonalization is performed numerically, taking advantage of the star symmetry. The eigenvalues, forming the reciprocals of the relaxation times, belong to two sets: one set, of unit multiplicity, is related to the concerted motion of the arms, the other one, having multiplicity $(f-1)$ (f is the arm number), to the independent motion of the arms. From the sum of the relaxation times, we eventually obtain the intrinsic viscosity $[\eta]$. The interested reader is referred to paper I for a full discussion and the computational details.

The regular star in a poor solvent was also studied within the same framework in ref 6 (paper II in the following). In this case, the two-body attractions shrink the star with respect to the phantom state, devoid of any intramolecular interaction (it shall be later indicated with a ph subscript). This contraction is resisted at small undercooling $\Theta - T$ by the intramolecular elasticity, and at large contraction by the long-range three-body repulsions and by the "screened interactions" arising from the intrinsic chain thickness.[7,8] A compact globular state is eventually reached at a large enough undercooling $\Theta - T$. Details of the transition to this collapsed state were discussed at length for linear[7,8] and star[6] polymers. A convenient and satisfactory approximation[7] is obtained by assuming that the interaction free energy at $T < \Theta$ depends only on the coil density, hence on the radius of gyration.[6,7] All the conformational properties, such as the strain ratios of the normal modes, the interatomic distances, and the contraction ratio of the mean-square radius of gyration $\alpha_S^2 = \langle S^2\rangle/\langle S^2\rangle_{\text{ph}}$ (see eqs 11−13 of paper II), are then simple functions of a suitable parameter univocally related to the reduced temperature $\tau = (T - \Theta)/T$ by the requirement of stationarity of the free energy. A link is thus established between α_S^2 and temperature (see Figure 5 of paper II). An important result of paper II, valid for the globular state, is

$$\alpha_S^{\ 2} \propto (|\tau|N^{1/2})^{-2/3} g_{S,\text{ph}}^{-1} \tag{1}$$

where N is the total number of bonds and

$$g_S = \langle S^2\rangle_{\text{star}}/\langle S^2\rangle_{\text{lin}} \tag{2}$$

Therefore, since $\langle S^2\rangle_{\text{ph,lin}} \propto N$, we find

$$\langle S^2\rangle \propto (N/|\tau|)^{2/3} \tag{3}$$

Thus, for a given N, $\langle S^2\rangle$ depends only on the undercooling $\Theta - T$, but not on the star functionality: this means that space-filling requirements dictate the chain conformation. Moreover, we get $g_S = 1$, while the average density ($\propto N/\langle S^2\rangle^{3/2}$) becomes independent of molecular weight.

In the present Note, we first use the results of paper II by choosing an arbitrary value of the parameter mentioned above to calculate α_S^2 and the strain ratios of the equilibrium normal modes (eqs 10 and 13 of paper II). Afterward, following the procedure of paper I, we calculate the relaxation times and the intrinsic viscosity of the star. We shall express $[\eta]$ as a function of $\langle S^2\rangle$, or equivalently the corresponding strain ratios $\alpha_\eta^3 = [\eta]/[\eta]_{\text{ph}}$ vs α_S^2, since the temperature dependence can be deduced from the results of paper II.

Results and Discussion

We performed calculations for linear chains ($f = 2$) and stars with $f = 6$, 12, and 18 having either the same arm length $N/f = 200$ or the same total number of bonds $N = 1200$.

At strong contraction, that is, for $\alpha_S^2 < 0.03$, say, the spectrum of relaxation times becomes flat for the most collective modes; in other words, the longest relaxation times are independent of the mode number, i.e., from the length of the chain portions that move in phase, since these are effectively confined within the globule. Thus, the polymer topology is irrelevant, the globular size being the only relevant quantity. Accordingly, the relaxation time of these modes, $\tau_{\max}$, depends only on the radius of gyration[9]

$$\sigma\tau_{\max} = (3.03 \pm 0.02)\langle S^2\rangle^{3/2} \tag{4}$$

where $\sigma = 3k_BT/\zeta l^2$ is the bond rate constant, ζ being the atomic friction coefficient and l^2 the mean-square bond length. (Here and in the following, $\langle S^2\rangle$ is in l^2 units.) Remembering eq 3, we get the interesting result that $\tau_{\max}$ is simply proportional to the molecular weight for any f.

Turning now to the intrinsic viscosity, in the poor-solvent regime $[\eta]$ is a unique function of the polymer radius of gyration irrespective of the arm number. This result is not surprising: using the linear-chain relationships $[\eta]_{\text{ph}} \propto \langle S^2\rangle_{\text{ph}}^{3/2}/N$ and $\langle S^2\rangle_{\text{ph}} \propto N$, together with eq 2, we have for the phantom star,

$$[\eta]_{\text{ph}} \propto g_{\eta,\text{ph}}(g_{S,\text{ph}})^{-1/2}\langle S^2\rangle_{\text{ph}}^{\ 1/2} \tag{5}$$

where

$$g_\eta = [\eta]_{\text{star}}/[\eta]_{\text{lin}} \tag{6}$$

In the phantom polymer,[1,5] we have $g_{\eta,\text{ph}} \cong (g_{S,\text{ph}})^{0.478}$, while $g_{S,\text{ph}} = (3f-2)/f^2$, and so the ratio $[\eta]_{\text{ph}}/\langle S^2\rangle_{\text{ph}}^{1/2}$ has a very weak dependence on f. The relationship in a poor solvent with $\alpha_S^2 \leq 0.5$ is shown in Figure 1. The universal asymptotic curve for linear and star polymers with either the same *total* molecular weight or the same

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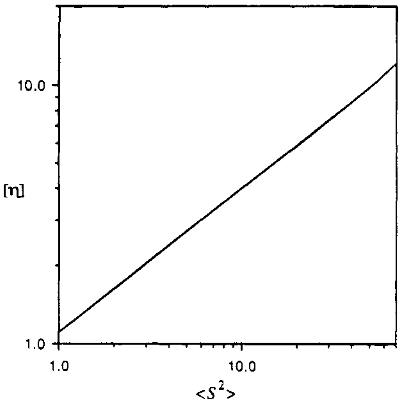

Figure 1. Universal plot of the intrinsic viscosity in units $\pi N_{Av} l^3/4M_0$ (see text) as a function of $\langle S^2\rangle$ in l^2 units for linear and star polymers in a poor solvent. Only polymers with $\alpha_S^2 \leq 0.5$ are included.

molecular weight *per arm* can be expressed as

$$[\eta] = \kappa\langle S^2\rangle^{\mu} \qquad (7)$$

with $\kappa = 1.11 \pm 0.01$ and $\mu = 0.56 \pm 0.01$ ($[\eta]$ is in units $\pi N_{Av} l^3/4M_0$, M_0 being the molar mass per chain atom). Since $g_S = 1$ for the collapsed globule, as said before, eq 7 yields $g_\eta = 1$ in the strong-contraction regime irrespective of f (g_η is defined for polymers with the same molecular weight at the same T). Furthermore, because of the relationship $\langle S^2\rangle \propto N^{2/3}$, eq 7 implies also that $[\eta] \propto N^{0.37}$. This exponent, though smaller than the 0.5 value of the unperturbed polymer, would suggest that we are still far from the limit of the compact sphere, where $[\eta]$ is independent of molecular weight.[10] On the other hand, in the globular state the ratio $R_H/\langle S^2\rangle^{1/2}$ was reported to be close to the $(5/3)^{1/2}$ value of the compact sphere,[12] whereas we get a ratio larger than the value 0.665 for the phantom state, but only close to unity. Moreover, our results[1,7] and the experimental data[11] indicate that the globular density can be up to some 40% of the bulk density.[11] These results make therefore questionable our treatment of the hydrodynamic interactions, which assumes that all the atoms are always bathed by the solvent.

Equation 7 indicates also that $[\eta]$ decreases with chain contraction much less than $\langle S^2\rangle$, as already found for the linear chain.[9] For a given molecular weight *per arm*, α_η^3 turns out to be a unique function of α_S^2, independent of the number of arms, throughout the poor-solvent regime, as shown in Figure 2. Conversely, some slight differences are present if we consider stars with the same *total* molecular weight. In fact, from eq 7 we get

$$\alpha_\eta^{\ 3} = \kappa(\alpha_S^{\ 2})^{\mu}\frac{(g_{S,\mathrm{ph}})^{1/2}}{g_{\eta,\mathrm{ph}}}\langle S^2\rangle_{\mathrm{ph}}^{\ \mu-1/2} \qquad (8)$$

According to what was said after eq 5 and due to the value of μ, some weak residual dependence on the arm number f and an even weaker dependence on N are still present. The differences due to the different functionalities for a fixed N are best seen in a logarithmic plot (see Figure 3). Equation 8 is well verified for $\alpha_S^2 \leq 0.5$ and is roughly valid up to the unperturbed state with $\alpha_S^2 = 1$.

Concluding Remarks

In the poor-solvent regime at $T < \Theta$ the star polymers eventually achieve a compact globular state where space-filling requirements are essential. Both the globule's size and its intrinsic viscosity become independent of the arm number, but change only with molecular weight and/or temperature. The dynamical results reported here use the approach of paper I, which needs some comment. In a poor solvent, the *dynamical* normal modes are even closer to the equilibrium ones than in a good solvent,[1] and the intrinsic viscosity is unaffected to better than 0.5% by the full diagonalization, which therefore is not necessary (Zimm−Hearst approximation;[4,13] see also paper I). On the other hand, the preaveraging approximation leads to large errors in unperturbed star polymers with many arms,[14] leading to overestimation of the intrinsic viscosity. The preaveraging errors are difficult to assess in the present case, but we may qualitatively expect that they are larger in a globule because of the increased compactness. However, a basic result is that *the presence of the branch point becomes largely irrelevant at strong collapse*, so that stars and linear polymers behave more and more in the same way. This suggests that in the globular state the preaveraging error should be basically the same for any topology, so that we can still expect $g_\eta = 1$, whereas $[\eta]$ should actually be smaller, and indeed closer to the compact sphere limit.

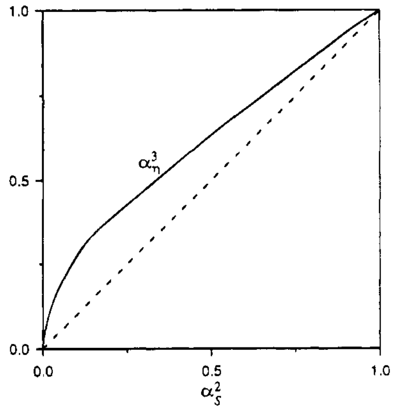

Figure 2. Contraction ratio α_η^3 plotted as a function of α_S^2 for polymers with $N/f = 200$ and $f = 2$, 6, 12, and 18. The dashed line corresponds to α_S^2 itself.

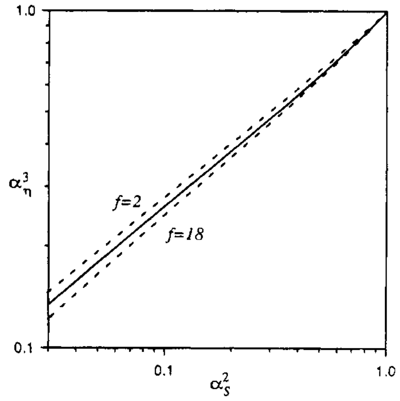

Figure 3. α_η^3 plotted as a function of α_S^2 for polymers with the same *total* number of atoms $N = 1200$ and $f = 2$, 6, 12, and 18. The solid curve corresponds to $f = 6$ and is the same as that reported in Figure 2, the two dashed curves are for $f = 2$ (upper curve) and for $f = 18$ (lower curve).

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