increased.

Conclusions

In the presence of added salt in the 0.01–0.15 M NaCl range, the dynamics of the polyelectrolyte sodium poly(styrenesulfonate) in dilute and semidilute solution are very similar to those of neutral polystyrene. The polyion concentration dependence of the cooperative diffusion coefficient in semidilute solutions is consistent with the predictions of both scaling and renormalization group theories. The dynamic quantity $D_c(C)/D_c(0)$ is a function only of A_2C for a given solvent quality parameterized by the interaction parameter (Z) but shifts to a curve characteristic of lower Z as salt increases and the solvent approaches a Θ solvent. In contrast, $D_c(C)/D_c(0)$ appears to be a universal function of KC, independent of molecular weight or salt concentration, following the curve predicted for $Z = \infty$. However, experimental uncertainties in K demand that this conclusion be regarded as preliminary.

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Influence of Chemical Disorder on the Statistics of a Semiflexible Chain

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ABSTRACT: The effects of quenched chemical disorder on the statistical properties of a semiflexible chain are investigated. A simple model with Gaussian fluctuations in the local persistence length is introduced, and its properties are studied to first order in the variance of the disorder. The polymer is found to be expanded relative to a (homopolymer) chain with the average persistence length. The model and results should be relevant to the phase behavior and characteristic dimensions of random copolymers with main-chain mesogens, such as those investigated by Stupp et al. [*Macromolecules* **1988**, *21*, 1217–1234].

1. Introduction

Stupp and colleagues have recently reported[1-3] the synthesis, characterization, and thermotropic phase behavior of a series of copolymers that contain two rigid (mesogenic) monomers (denoted A and B) and a flexible (spacer) monomer (denoted C). One copolymer possessed an ordered sequence of structural units (repeat unit CABCBA), while a second was a random copolymer with the same average composition, but the sequence of A, B, and C being statistically disordered. Among the interesting findings reported in ref 1–3 is the observation that the ordered copolymer exhibits a sharp nematic to isotropic transition over a narrow range of temperatures, while the chemically disordered copolymer shows a broad biphasic region separating the phases of different symmetry. Stupp et al.[3] interpreted this finding by modeling the disordered chains as thermotropic homopolymers, but with a distribution of persistence lengths ("polyflexibility"). By incorporating this distribution into an existing theory for the nematic to isotropic transition in main-chain homopolymers, they were able to reproduce various features of the experiments.

While the influence of chemical disorder on polymeric phase transitions is certainly a fascinating subject, the

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above experiments raise even more fundamental questions. One such question pertains to the configurational statistics of a single random copolymer chain. In particular, is the radius of gyration of a semiflexible random copolymer with equal proportions of A, B, and C larger or smaller (on average) than an ordered copolymer that is otherwise identical? Similarly, is such a random copolymer larger than a homopolymer with the same average flexibility? In the present paper I attempt to answer the latter question by means of a simple model calculation.

The classical model used to describe the configurational statistics of a semiflexible polymer is the wormlike chain,[4,5] defined by the partition function

$$Z = \int_C \delta\mathbf{r}\, \exp\left[-\frac{\kappa}{2}\int_{-L/2}^{L/2} \mathrm{d}s \left(\frac{\partial^2 \mathbf{r}}{\partial s^2}\right)^2\right] \qquad (1.1)$$

where L is the contour length of the chain, κ is a bending elastic constant with dimensions of length (the *persistence length*[4,5]), and $\mathbf{r}(s)$ is the position of the monomer at contour distance s along the chain. The notation $\int_C \delta\mathbf{r}$ denotes a functional (path) integration over all trajectories of the chain, subject to the finite-extensibility constraint $|\partial\mathbf{r}/\partial s| = 1$.

The statistical properties of the wormlike chain have been extensively studied;[5] of particular interest here is the expression for the mean-square end-to-end distance

$$\langle R^2 \rangle = 2\kappa[L - \kappa(1 - e^{-L/\kappa})] \qquad (1.2)$$

There are two interesting limits of eq 1.2. For long chains or small bending constants, $L/\kappa \gg 1$, eq 1.2 produces Gaussian (random flight) behavior $\langle R^2 \rangle \approx 2\kappa L$. In the opposite limit of short or stiff chains, $L/\kappa \ll 1$, rodlike behavior is obtained, $\langle R^2 \rangle \approx L^2$. The wormlike chain is thus a convenient model for describing semiflexible chains with stiffness intermediate between these limiting behaviors.

Unfortunately, for a number of applications the wormlike chain is mathematically cumbersome due to the finite-extensibility constraint $|\partial\mathbf{r}/\partial s| = 1$. As a result, mean-spherical[6,8] and spherical[7] approximations have been introduced that simplify calculations with the model, yet still retain the essence of semiflexibility. In the present paper the following mean-spherical, Gaussian model[9] is employed:

$$Z = \int \delta\mathbf{r}\, \exp\left\{-\frac{3}{4}\int_{-L/2}^{L/2} \mathrm{d}s \left[\kappa^{-1}\left(\frac{\partial \mathbf{r}}{\partial s}\right)^2 + \kappa\left(\frac{\partial^2 \mathbf{r}}{\partial s^2}\right)^2\right]\right\} \qquad (1.3)$$

where the functional integral over $\mathbf{r}(s)$ is now unconstrained. It is easily demonstrated that the mean-square end-to-end distance obtained from eq 1.3 is *identical* with that given in eq 1.2 for the wormlike chain model. Higher order moments of the two models, however, will in general be different. It is important to keep in mind that the Gaussian model of eq 1.3 does not preserve constant chain length, so it is probably not very useful in situations with, e.g., strong hydrodynamic or nematic fields. However, for chains of intermediate flexibility in weak external fields and for the present purpose of investigating the effects of chemical disorder, eq 1.3 should be adequate.

2. A Semiflexible Random Copolymer

Equation 1.3 can be easily generalized to a random copolymer in which the constituent monomers have different flexibilities. In the following analysis, the effects of excluded-volume interactions among like or unlike monomers are not considered. Also, it is convenient to rescale the monomer positions by a constant, $\mathbf{c}(s) = (3/2)^{1/2}\mathbf{r}(s)$, to change the coefficient 3/4 in eq 1.3 to 1/2. The model that will be studied in the present paper is described by the following partition function:

$$Z = \int \delta\mathbf{c}\, \exp[-H(\mathbf{c})] \qquad (2.1)$$

with

$$H(\mathbf{c}) = H_0(\mathbf{c}) + H_1(\mathbf{c}) \qquad (2.2)$$

$$H_0(\mathbf{c}) = \frac{1}{2}\int_{-L/2}^{L/2} \mathrm{d}s \left[\kappa_2\left(\frac{\partial \mathbf{c}}{\partial s}\right)^2 + \kappa_4\left(\frac{\partial^2 \mathbf{c}}{\partial s^2}\right)^2 + \kappa_6\left(\frac{\partial^3 \mathbf{c}}{\partial s^3}\right)^2\right] \qquad (2.3)$$

$$H_1(\mathbf{c}) = \frac{1}{2}\int_{-L/2}^{L/2} \mathrm{d}s \left[\theta_2(s)\left(\frac{\partial \mathbf{c}}{\partial s}\right)^2 + \theta_4(s)\left(\frac{\partial^2 \mathbf{c}}{\partial s^2}\right)^2\right] \qquad (2.4)$$

The term $H_0(\mathbf{c})$ in the Hamiltonian describes a homopolymer chain with average elastic constants κ_2, κ_4, and κ_6. These phenomenological coefficients, κ_i, are assumed to be positive and have engineering dimensions of l^{i-3}, where l is a characteristic length. Note that to attain agreement with the wormlike chain, comparison of eq 1.3 and 2.3 yields the relations $\kappa_2 = \kappa^{-1}$ and $\kappa_4 = \kappa$. The term containing κ_6 is included in the model for the purpose of introducing a natural short-distance cutoff. However, κ_6 will consistently be taken to be small, i.e., $\kappa_6\kappa_2/\kappa_4^2 \ll 1$ is assumed throughout.

The term $H_1(\mathbf{c})$ describes the chemical disorder inherent in a random copolymer. The functions $\theta_i(s)$ are random variables with zero mean and represent fluctuations in the local elastic constants about the average constants κ_i at contour position s [i.e., $\kappa_i(s) = \kappa_i + \theta_i(s)$]. In general, the statistical properties of these random variables will depend on the details of the polymerization used to produce the random copolymer. For the illustrative purposes of the present paper, the $\theta_i(s)$ will be assumed to be independent Gaussian random variables with variances (i, j = 2 or 4)

$$\overline{\theta_i(s)\,\theta_j(s')} = \Delta_i\delta_{ij}\delta(s - s') \qquad (2.5)$$

where the overbar denotes a disorder average over the Gaussian distribution of $\theta_i(s)$. The variances Δ_2 and Δ_4 have engineering dimensions of l^{-1} and l^3, respectively, and are nonnegative, $\Delta_i \geq 0$. I anticipate that the qualitative results based on this model will be preserved for more complicated (or experimentally realistic) distributions of local flexibility.

3. Analysis of Chemical Disorder

The chemical disorder that characterizes random copolymers is a type of *quenched* randomness[10] because it is frozen-in at the time of synthesis. As a result, it is appropriate[10,11] to average the free energy, i.e., the logarithm of eq 2.1, over the chemical disorder. This is conveniently performed by means of the Edwards replica trick,[11] which relies on the identity

$$\overline{\ln Z} = \lim_{n\to 0}\, (\overline{Z^n} - 1)/n \qquad (3.1)$$

The procedure is thus to introduce n independent "replicas" of eq 2.1, forming Z^n, and then to average over the distribution of the $\theta_i(s)$. In the present case this can be done exactly because the $\theta_i(s)$ are Gaussian random variables. Evaluation of average chain properties then proceeds as in the case of no disorder. At the end of the calculations, all the results are analytically continued to $n = 0$.

By carrying out the above averaging procedure with eq 2.1–2.4, the following result is obtained:

$$\overline{Z^n} = \int \delta \mathbf{c}^n \exp\left\{-\sum_{i=1}^{n} H_0(\mathbf{c}_i) + \frac{1}{8}\sum_{i=1}^{n}\sum_{j=1}^{n}\int_{-L/2}^{L/2} \mathrm{d}s \times \left[\Delta_2\left(\frac{\partial \mathbf{c}_i}{\partial s}\right)^2\left(\frac{\partial \mathbf{c}_j}{\partial s}\right)^2 + \Delta_4\left(\frac{\partial^2 \mathbf{c}_i}{\partial s^2}\right)^2\left(\frac{\partial^2 \mathbf{c}_j}{\partial s^2}\right)^2\right]\right\} \tag{3.2}$$

where the indexes i and j label the n replicas and $\delta \mathbf{c}^n = \delta \mathbf{c}_1 \delta \mathbf{c}_2 ... \delta \mathbf{c}_n$. It is convenient to introduce a Fourier representation for the $\mathbf{c}_i(s)$:

$$c_{i\alpha}(s) = \frac{1}{L}\sum_k e^{-iks}\phi_{i\alpha}(k) \tag{3.3}$$

with $c_{i\alpha}(s)$ the αth component of the three-dimensional vector $\mathbf{c}_i(s)$. Employing a new vector notation in which $\vec{\phi}$ has the $3n$ components given in eq 3.3, eq 3.2 can be written

$$\overline{Z^n} = \int \delta\vec{\phi} \exp[-H_n(\vec{\phi})] \tag{3.4}$$

with the replica Hamiltonian

$$H_n(\vec{\phi}) = \frac{1}{2L}\sum_k(\kappa_2 k^2 + \kappa_4 k^4 + \kappa_6 k^6)\vec{\phi}(k)\cdot\vec{\phi}(-k) - \frac{1}{8L^3}\sum_{k_1 k_2 k_3}[\Delta_2 k_1 k_2 k_3(-k_1 - k_2 - k_3) + \Delta_4 k_1{}^2 k_2{}^2 k_3{}^2(-k_1 - k_2 - k_3)^2][\vec{\phi}(k_1)\cdot\vec{\phi}(k_2)][\vec{\phi}(k_3)\cdot\vec{\phi}(-k_1 - k_2 - k_3)] \tag{3.5}$$

Equations 3.4 and 3.5 define a particular $\mathcal{O}(3n)$ symmetric, ϕ^4 field theory in one spatial dimension and can be treated by the standard methods.[12] The quartic terms are proportional to the variance of the chemical disorder, so to investigate the effects of weak disorder it is logical to attempt a perturbation expansion in powers of Δ_2 and Δ_4. This will be carried out to leading order in the present section.

The mean-square end-to-end distance, averaged over the chemical disorder, is obtained from the relation

$$\overline{\langle R^2 \rangle} = \lim_{n\to 0} \frac{2}{3}\langle[\mathbf{c}_i(-L/2) - \mathbf{c}_i(L/2)]^2\rangle = \frac{8}{3L^2}\lim_{n\to 0}\sum_\alpha\sum_k \sin^2(kL/2)\langle\phi_{i\alpha}(k)\,\phi_{i\alpha}(-k)\rangle \tag{3.6}$$

where angular brackets represent a Boltzmann-weighted average with the Hamiltonian of eq 3.5. Similarly, the mean-square radius of gyration is given by

$$\overline{\langle R_g{}^2 \rangle} = \frac{4}{3L^2}\lim_{n\to 0}\sum_\alpha\sum_{k\neq 0}\langle\phi_{i\alpha}(k)\,\phi_{i\alpha}(-k)\rangle \tag{3.7}$$

Thus, only the pair-correlation function $\langle\phi_{i\alpha}(k)\,\phi_{i\alpha}(-k)\rangle$ is required to calculate both quantities.

Case of No Disorder. In the case of no chemical disorder, $\Delta_2 = \Delta_4 = 0$, the quartic term in eq 3.5 vanishes and the correlation function of interest is obtained from the coefficient of the quadratic term:

$$\langle\phi_{i\alpha}(k)\,\phi_{i\alpha}(-k)\rangle = \frac{L}{\kappa_2 k^2 + \kappa_4 k^4 + \kappa_6 k^6} \tag{3.8}$$

To leading order in κ_6, the sum over k in eq 3.6 can be converted to an integral that can be performed analytically:

$$\langle R^2 \rangle_0 = \frac{2L}{\kappa_2}\left[1 - \left(\frac{\kappa_4}{\kappa_2 L^2}\right)^{1/2}(1 - e^{-(\kappa_2 L^2/\kappa_4)^{1/2}})\right] \tag{3.9}$$

which agrees with eq 1.2 for $\kappa_4 = \kappa_2{}^{-1} = \kappa$ as discussed above.

Using eq 3.7 and 3.8 for the case of no disorder, I find for the radius of gyration (to leading order in κ_6)

$$\langle R_g{}^2 \rangle_0 = \frac{2L}{\kappa_2 \pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2[1 + (\kappa_4/\kappa_2 L^2)(2\pi n)^2]} \tag{3.10}$$

For long or flexible chains, $\kappa_4/\kappa_2 L^2 \ll 1$, this gives the expected random flight result $\langle R_g{}^2 \rangle_0 \approx 2L/6\kappa_2 = \langle R^2 \rangle_0/6$.

Case of Weak Disorder. In the presence of chemical disorder, Δ_2 and $\Delta_4 > 0$, the pair-correlation function can be computed as a power series in the Δ_i. To first order in these variances, the correlation function can still be written in the form of eq 3.8, but with *renormalized elastic constants*, κ_{iR}:

$$\langle\phi_{i\alpha}(k)\,\phi_{i\alpha}(-k)\rangle = \frac{L}{\kappa_{2R} k^2 + \kappa_{4R} k^4 + \kappa_{6R} k^6} \tag{3.11}$$

where

$$\kappa_{2R} = \kappa_2 - \frac{\Delta_2}{2}(3n + 2)\int\frac{\mathrm{d}q}{2\pi}\,\frac{1}{\kappa_2 + \kappa_4 q^2 + \kappa_6 q^4} \tag{3.12}$$

$$\kappa_{4R} = \kappa_4 - \frac{\Delta_4}{2}(3n + 2)\int\frac{\mathrm{d}q}{2\pi}\,\frac{q^2}{\kappa_2 + \kappa_4 q^2 + \kappa_6 q^4} \tag{3.13}$$

$$\kappa_{6R} = \kappa_6 + \mathcal{O}(\Delta^2) \tag{3.14}$$

and the continuum limit, $L^{-1}\sum_k \to (2\pi)^{-1}\int \mathrm{d}k$, has been taken. Thus, to first order in Δ_2 and Δ_4, κ_6 is not renormalized by the chemical disorder. The integrals on the right-hand sides of eq 3.12 and 3.13 can be evaluated in closed form, but for simplicity I provide the expressions only to leading order in $\kappa_6\kappa_2/\kappa_4{}^2$. For $n \to 0$:

$$\kappa_{2R} = \kappa_2 - \frac{\Delta_2(3n + 2)}{4(\kappa_2\kappa_4)^{1/2}} = \kappa_2 - \frac{\Delta_2}{2(\kappa_2\kappa_4)^{1/2}} \tag{3.15}$$

$$\kappa_{4R} = \kappa_4 - \frac{\Delta_4(3n + 2)}{4(\kappa_4\kappa_6)^{1/2}} = \kappa_4 - \frac{\Delta_4}{2(\kappa_4\kappa_6)^{1/2}} \tag{3.16}$$

Hence, to first order in the Δ_i, chemical disorder *reduces* the elastic constants κ_2 and κ_4.

It is readily apparent from the similarity of eq 3.8 and 3.11 that the mean-square end-to-end distance can be obtained from eq 3.9 by replacing the κ_i with the κ_{iR}:

$$\overline{\langle R^2 \rangle} = \frac{2L}{\kappa_{2R}}\left[1 - \left(\frac{\kappa_{4R}}{\kappa_{2R} L^2}\right)^{1/2}(1 - e^{-(\kappa_{2R} L^2/\kappa_{4R})^{1/2}})\right] \tag{3.17}$$

In the flexible limit, $\kappa_{2R} L^2/\kappa_{4R} \gg 1$, eq 3.17 leads to

$$\overline{\langle R^2 \rangle} \approx \frac{2L}{\kappa_{2R}} = \frac{2L}{\kappa_2}\left[1 + \frac{\Delta_2}{2\kappa_2(\kappa_2\kappa_4)^{1/2}} + ...\right] \tag{3.18}$$

or, relative to the (homopolymer) case of no chemical disorder

$$\frac{\overline{\langle R^2 \rangle}}{\langle R^2 \rangle_0} = 1 + \frac{\Delta_2}{2\kappa_2(\kappa_2\kappa_4)^{1/2}} + \mathcal{O}(\Delta^2) \tag{3.19}$$

Thus, the random copolymer is *expanded* with respect to a homopolymer with the same average elastic constants (persistence length). Note that for the wormlike chain parameters, $(\kappa_2\kappa_4)^{1/2} = 1$ and κ_2 is the reciprocal of the persistence length. In the same flexible limit, the mean-square radius of gyration, $\overline{\langle R_g{}^2 \rangle} \approx 2L/6\kappa_{2R}$, is expanded by the same factor as in eq 3.19.

For very short or stiff chains, $\kappa_{2R} L^2/\kappa_{4R} \ll 1$, eq 3.17 reduces to

$$\overline{\langle R^2\rangle} \approx \frac{L^2}{(\kappa_{2R}\kappa_{4R})^{1/2}} = \frac{L^2}{(\kappa_2\kappa_4)^{1/2}}\left[1 + \frac{\Delta_2}{4\kappa_2(\kappa_2\kappa_4)^{1/2}} + \frac{\Delta_4}{4\kappa_4(\kappa_4\kappa_6)^{1/2}} + ...\right] \quad (3.20)$$

which again implies chain *expansion* relative to the case of no disorder, where $\langle R^2\rangle_0 \approx L^2/(\kappa_2\kappa_4)^{1/2}$. Note that for the wormlike chain parameters $(\kappa_2\kappa_4)^{1/2} = 1$, so the polymer is actually extended beyond the contour length L. This is clearly a result of having lost the finite-extensibility constraint in our Gaussian model (cf. discussion after eq 1.3). Hence, eq 3.17 is probably useful only for large or intermediate [i.e., $\mathcal{O}(1)$] values of $\kappa_{2R}L^2/\kappa_{4R}$.

For intermediate flexibilities, eq 3.17 also predicts chain expansion, as is easily demonstrated. The ratio of eq 3.17 for the random copolymer to eq 3.9 for the homopolymer can be written

$$\frac{\overline{\langle R^2\rangle}}{\langle R^2\rangle_0} = \frac{\kappa_2}{\kappa_{2R}}\left\{\frac{f[(\kappa_{2R}L^2/\kappa_{4R})^{1/2}]}{f[(\kappa_2L^2/\kappa_4)^{1/2}]}\right\} \quad (3.21)$$

where

$$f[x] = 1 - x^{-1}(1 - e^{-x}) \quad (3.22)$$

is a monotonically increasing function of x. From eq 3.15, the first factor in eq 3.21 is greater than unity for weak disorder. The second factor is also greater than unity because (for $\kappa_6\kappa_2/\kappa_4^2 \ll 1$)

$$\frac{\kappa_{2R}}{\kappa_{4R}} \approx \frac{\kappa_2}{\kappa_4}\left[1 + \frac{\Delta_4}{2\kappa_4(\kappa_4\kappa_6)^{1/2}} + ...\right] > \frac{\kappa_2}{\kappa_4} \quad (3.23)$$

and because of the monotonicity of $f[x]$. Hence, the random copolymer is expanded in relation to the homopolymer for any amount of flexibility.

It is a straightforward matter to continue the perturbation expansion to higher order in the Δ_i. At second order, there are finite renormalizations of κ_6, as well as additional corrections to κ_{2R} and κ_{4R}. The variance of the disorder is also modified at second order to

$$\Delta_{2R} = \Delta_2 + 4\Delta_2^2\int\frac{dq}{2\pi}\,\frac{1}{(\kappa_2 + \kappa_4q^2 + \kappa_6q^4)^2} \quad (3.24)$$

$$\Delta_{4R} = \Delta_4 + 4\Delta_4^2\int\frac{dq}{2\pi}\,\frac{q^4}{(\kappa_2 + \kappa_4q^2 + \kappa_6q^4)^2} \quad (3.25)$$

and a new wavevector-dependent quartic interaction is generated in eq 3.5.

4. Summary and Discussion

In the present paper a simple model of a semiflexible random copolymer was introduced. The most characteristic feature of the model is that the bending elastic constants (which determine the persistence length and other measures of chain flexibility) are random variables that can assume different values along the contour of the polymer. For this initial study, the elastic constants were assumed to be independent Gaussian random variables and δ function correlated along the chain contour. By employing replica methods, I demonstrated that to first order in the variance of the chemical disorder the random copolymer is expanded in relation to a homopolymer with the average elastic constants. Although the physical mechanism responsible for the expansion is not entirely clear, it appears that fluctuations involving a local excess of stiff monomers are more effective at expanding the coil than fluctuations involving more flexible units are in contracting it.

The model can be easily extended to more experimentally relevant distributions of the chemical disorder. In particular, correlations could be introduced between the θ_i and θ_j with $j \neq i$ and between $\theta_i(s)$ and $\theta_i(s')$, where s and s' do not necessarily point to neighboring monomers along the chain. I expect that, except for highly pathological types of disorder, the conclusions of the present paper will remain intact.

A difficulty with the present model is that the finite-extensibility constraint of real chains (and the wormlike chain model) is violated. This is not a major concern unless the chain is very extended, for example, in strong nematic, magnetic, or hydrodynamic flow fields. Under such conditions a model that preserves contour length should be employed. The spherical model of Ronca and Yoon,[7] for example, should not be too difficult to implement in situations with quenched chemical disorder.

Ultimately one would like to use the model presented here, or a variant thereof, to explain the broad biphasic region found by Stupp et al.[1-3] for their random copolymers at the isotropic to nematic transition. At present, it is not clear what role the chain extension found here plays in this phase transition. However, there is one experimental observation that appears to be in agreement with the present results. Stupp et al.[3] found a biphasic region for their disordered copolymer that extends from 250 to 400 °C, while the corresponding ordered copolymer exhibited a sharp nematic to isotropic transition at 275 °C. If the ordered polymer had a size and persistence length comparable to the average of all the random copolymers in the sample, it would be expected to have a transition temperature that falls in the middle of the biphasic region. The fact that the transition temperature of the ordered polymer falls on the low-temperature side of the biphasic region is consistent with the random copolymer being larger (and stiffer) on average.[13] We intend to address these issues in more detail in the near future.[14]

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