1996 *Macromolecules* **1992,** *25,* 1996–2003

Quantitative Theory of the Globule-to-Coil Transition. 4. Comparison of Theoretical Results with Experimental Data

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Received July 20, 1991; Revised Manuscript Received December 9, 1991

ABSTRACT: In this series of papers new results and a brief review of the current state of mean-field theories of the condensed globular state and of the globule-to-coil transition in the Θ-region for a linear, homogeneous, noncharged macromolecule are presented. As a basis of our consideration, we use both Lifshitz's theory and interpolation Flory-type theory. Complete quantitative theoretical results are obtained and compared with experimental data. In this paper (the fourth in this series) we compare in detail our quantitative theoretical results with the available data of real experiments and computer simulations on single-chain gyration and hydrodynamic radii and on binodal and spinodal curves of a polymer solution phase diagram. The comparison manifests a rather good agreement of the mean-field theory with experiments. However, the question of the observation of equilibrium polystyrene–cyclohexane single-chain globules before solution precipitation remains to be discussed. Criterion of the globularity of an experimentally observed chain is discussed.

1. Introduction

There are a lot of various systems in which polymer transitions of the coil-to-globule type were observed using real experiments or computer simulations (see, for instance, reviews in refs 1 and 2). In this paper, as well as in the three previous ones,[3] we discuss only one type of such a transition—collapse of a linear uncharged long homopolymer chain, which can be considered as the basic model for more complicated systems.

This model is the simplest one theoretically but not experimentally: serious technical difficulties occur in real experiments on this type of globule-to-coil transition. The main problem is the necessity to use a polymer solution of an extremely small concentration; therefore macromolecule size measurement becomes a very complex problem. The use of such a low concentration is necessary to observe the collapse of separate chains until they aggregate and fall out in sediment upon a decrease of the solvent quality. This is why most of the real experiments deal with rather complex polymer chains (see the review in ref 2) such as mesogens (which form liquid-crystalline globules), heteropolymers (like proteins), polyelectrolytes, and others. In these systems there exist some physical reasons which delay or even prevent solution precipitation.

In the meantime, some interesting and important problems[3] require the investigation of just the basic model, mentioned above. Experimental investigations of this type have also been performed in a lot of works (see refs 2–21 in part 1 of this series[3]) with mainly the polystyrene–cyclohexane system. The question of whether separated equilibrium globules have been observed in this system is now, however, a matter of opinion.[4,5] In our minds, this question cannot be answered without a well-reasoned theoretical criterion of the globular state.

Unlike real experiments, in computer simulations (see refs 22–33 in part 1 of this series) there have not been difficulties with the sediment, but the simulations are considerably limited in the length of the polymer chains. This limitation, connected with the resources of modern computers, results in the fact that near the transition point globules become very dense. This means that their properties are determined not by the universal characteristics of globular state but by specific local details of the investigated model structure. These obstacles, unfortunately, restrict seriously the completeness of the data in most simulations.

This paper is organized as follows. In section 2 we present brief résumé of the theoretical results of the three previous papers of this series. In section 3 available experimental and computer simulation data, which can be compared with the theoretical predictions discussed in section 2, are considered. The adjustable parameters of the theory are described in section 4. Section 5 is devoted to comparison of theoretical and experimental results. In section 6, we discussed the criterion of the globular state. Our main conclusions are presented in section 7.

2. Brief Résumé of Theoretical Results

1. The three-parametric description of the polymer system in the Θ-region including the globule-to-coil transition region is a well-known theoretical concept (see, for example, the book in ref 6). Specifically, our quantitative results[3] have been formulated in terms of (i) the ideal Gaussian-coil-state size $\langle S^2\rangle_{\mathrm{id}} = Na^2/6$, (ii) the chain stiffness parameter $\sqrt{C}/a^3$, and (iii) the reduced temperature

$$t \equiv \frac{BN^{1/2}}{C^{1/4}}\left(\frac{6}{a^2}\right)^{3/4} \sim \tau N^{1/2} \qquad (1)$$

(We use the standard designations: N is the link number per chain, B and C are two- and three-body interaction constants of quasimonomers, a is the link size, and $\tau \equiv (T - \theta)/\theta$ is the dimensionless deviation from the Θ-point.)

More precisely, three parameters of the theory can be referred to as Na^2, $\sqrt{C}/a^3$, and $B\sqrt{N}/a^3$ in the framework of a polymer-chain modeling by the standard Gaussian beads-on-a-string system. When another persistent model is used, these three parameters are of the form Ll, d/l, and $BL^{1/2}/l^{7/2}$ (L is the polymer contour length, l is the persistent length, and d is the polymer thickness). We discuss the interpretation of the experimental data in terms of the persistent model in Appendix B.

2. Main observable characteristics of a polymer chain in the globular range obey the following dimensionless relations.[3] (a) expansion factor of the globule radius of

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gyration:

$$\alpha_{S_{\rm glob}} \equiv \left[\frac{\langle S^2\rangle_{\rm glob}}{\langle S^2\rangle_{\rm id}}\right]^{1/2} = \left(\frac{\sqrt{C}}{a^3}\right)^{1/2} \tilde{\alpha}(t) \qquad (2)$$

(a′) globule free energy:

$$F = -(a^3/\sqrt{C})T\tilde{F}(t) \qquad (3)$$

(b) fluctuations of the radius of gyration:

$$\frac{\langle S^4\rangle - \langle S^2\rangle^2}{\langle S^2\rangle^2} = \frac{\sqrt{C}}{a^3}s(t) \qquad (4)$$

(c) expansion factor of the globule hydrodynamic radius (calculated in the framework of the Kirkwood–Riseman approximation):

$$\alpha_{H_{\rm glob}}{}^{-1} \equiv \frac{\langle R_H{}^{-1}\rangle_{\rm glob}}{\langle R_H{}^{-1}\rangle_{\rm id}} = \left(\frac{\sqrt{C}}{a^3}\right)^{-1/2}\left[h_1(t) + \frac{\sqrt{C}}{a^3}h_2(t)\right] \qquad (5)$$

(d) pair virial constant A_2 of globule–globule interactions:

$$\frac{A_2}{\langle S^2\rangle_{\rm id}{}^{3/2}} = \left(\frac{\sqrt{C}}{a^3}\right)^{1/2}\tilde{A}_2(t, \sqrt{C}/a^3) \qquad (6)$$

(d′) concentrations of two coexistence phases (concentrated and diluted) of a polymer solution in the globular range:

$$\frac{c_{\rm conc}}{N}\langle S^2\rangle_{\rm id}{}^{3/2} \simeq \frac{-t}{(6^{9/4})(4)}\left(\frac{\sqrt{C}}{a^3}\right)^{-3/2} \times \left[1 + \left(1 - (6^{3/2})\,(8)\,\frac{\sqrt{C}}{a^3}t^{-2}\right)^{1/2}\right]$$

$$\frac{c_{\rm dil}}{N} \simeq \frac{c_{\rm conc}}{N}\exp\left[-\frac{a^3}{\sqrt{C}}\left(\frac{t^2}{(6^{3/2})(4)} - \tilde{F}(t)\right)\right] - 2A_2\left(\frac{c_{\rm conc}}{N}\right)^2\exp\left[-2\frac{a^3}{\sqrt{C}}\left(\frac{t^2}{(6^{3/2})(4)} - \tilde{F}(t)\right)\right] \qquad (7)$$

(d″) upper estimation of the spinodal conditions:

$$c_{\rm dil}^{\rm (spin.)}/N \leqslant -1/2A_2 \qquad (7a)$$

(Here concentrations are the numbers of links per unit volume in corresponding phases of solution. Besides, our definition of the A_2 value differs from usual one:[1] $A_2{}^{\rm (usual)} = (N_A/M^2)A_2$, where M is the molecular mass and N_A is Avogadro's number.)

3. The dimensionless functions $\tilde{\alpha}(t)$, $\tilde{F}(t)$, $s(t)$, $h_1(t)$, $h_2(t)$, and $\tilde{A}_2(t,\sqrt{C}/a^3)$ have been calculated numerically in previous papers of this series.[3]

3. On the Procedure of Theory–Experiment Comparison

Available experimental and computer simulation data, which can be compared with the theoretical predictions (a–d), are the following: (a) the results of measurements of the gyration radius of isolated chains suspended in dilute solution, depending on temperature and chain molecular mass, for, mainly, polystyrene–cyclohexane (PS/CYH) and polystyrene–dioctyl phthalate (PS/DOP) systems[4,5,7–13] and computer simulation;[14] (b) some qualitative observations concerning the magnitude of fluctuations of a single-chain radius in a polymer–solvent system[15] and in computer simulation;[16] (c) the results of single-chain hydrodynamic radius measurements for a PS/CYH system;[4,5,9,11,13,17] (d) coexistence curves for a PS/CYH system.[12,18–20]

As a first step we consider theoretical and experimental data in (a). From the comparison we are able to determine the values of all the parameters of the theory. At the following steps we compare the theory and the experiments concerning (b)–(d) without any additional adjustable parameters.

4. On the Adjustment of Theoretical Parameters

The value of Na^2 (one among three parameters of the theory, Na^2, t, and $\sqrt{C}/a^3$) does not play any role in our problems, since it determines absolute values of polymer chain sizes but not relative characteristics like the swelling ratio α_S or α_H, etc. The next parameter t (eq 1) depends on two experimentally measured variables (temperature T or $\tau \equiv (T - \Theta)/\Theta$ and chain molecular mass M) as $t = Q\tau M^{1/2}$, where Q = const.

Thus, two parameters should be considered as adjustable ones. They are $\sqrt{C}/a^3$ and Q. One of them (Q) can be easily determined as simply the scale of the $\tau M^{1/2}$ axis. So, the main empirical parameter of our approach is the chain stiffness $\sqrt{C}/a^3$.

As to the Θ-value, it is not an independent adjustable parameter. Indeed, the temperature point, where $\langle S^2\rangle$ is linear on M, can be found separately, and this very point should be identified with the Θ-point. For example, for a PS/CYH system according to the data in ref 21

$$(\langle S^2\rangle_\Theta/M)^{1/2} \cong 0.28 \div 0.31\ \text{Å}\cdot\text{mol}^{1/2}/\text{g}^{1/2} \qquad (8)$$

Using this value, we can define the Θ-point on the experimental dependence of $\langle S^2\rangle$ on temperature without any additional fitting.

However, it may be necessary to take into account the difference between the experimental and theoretical definitions of the expansion factor (this is the traditional terminology; in principle, the term "contraction factor" is preferable for the globular range): $\alpha_{S\rm(theor)}{}^2 = \langle S^2\rangle/\langle S^2\rangle_{\rm id} \neq \alpha_{S\rm(exper)}{}^2 = \langle S^2\rangle/\langle S^2\rangle_\Theta$, $\langle S^2\rangle_{\rm id}$ being the size of the ideal polymer without volume interactions. Although this last value cannot be measured, it is usually used as the reference size in the theoretical calculations and, in particular, in the perturbation theory. Indeed, according to eq 18 in paper 1 of ref 3

$$\alpha_S{}^2 \equiv \langle S^2\rangle/\langle S^2\rangle_{\rm id} = 1 + 0.2197t\,(\sqrt{C}/a^3)^{1/2} - 0.06168t^2\sqrt{C}a^3 - 6.668\,(\sqrt{C}/a^3)^2 \qquad (9)$$

The Θ-point is the $t = 0$ point, so that

$$\langle S^2\rangle_\Theta = \langle S^2\rangle_{\rm id}[1 - 6.668(\sqrt{C}/a^3)^2]$$

Therefore, as the reference for comparison of theoretical and experimental data the Θ-temperature should be used as the point where $\langle S^2\rangle$ is linear on M (for a PS/CYH system, it obeys the relation in eq 8), but the experimental data should be reformulated in terms of

$$\alpha_{S\rm(theor)}{}^2 = \alpha_{S\rm(exper)}{}^2\langle S^2\rangle_\Theta/\langle S^2\rangle_{\rm id} = \alpha_{S\rm(exper)}{}^2[1 - 6.668(\sqrt{C}/a^3)^2] \qquad (10)$$

According to our designations, we use the symbol $\alpha_S{}^2$ for the value of $\alpha_{S\rm(theor)}{}^2$.

5. Comparison of Theoretical and Experimental Results

5.1. Polystyrene–Cyclohexane System. Single-Chain Radius of Gyration. The most complete data on a PS/CYH system were obtained by the MIT group;[9] these data are presented on Figure 1 together with theoretical

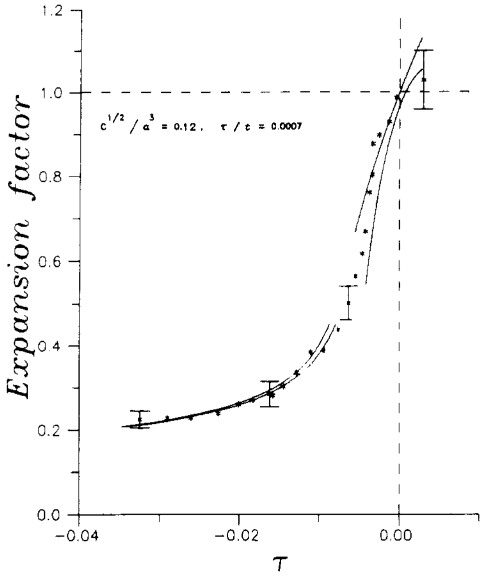

Figure 1. Experimental dependence of the expansion factor of the macromolecule radius of gyration on $\tau \equiv (T - \Theta)/\Theta$ in the globule–coil transition region for a PS/CYH system reported by the MIT group[9] and the corresponding theoretical results ($\sqrt{C}/a^3 = 0.12, \tau/t = 0.0007$), presented in the form of a "corridor", which characterizes both experimental and theoretical errors[3] caused by the finiteness of the width of the Θ-region.

results for the best fitted values of parameters

$$\sqrt{C}/a^3 \cong 0.12, \quad Q \cong 0.28\ (\mathrm{mol}^{1/2}/\mathrm{g}^{1/2}) \tag{11}$$

The Θ-point on Figure 1 was determined according to the expression in eq 8, and the data were rescaled according to eq 10. Theoretical results for these values of the parameters are presented as a corridor; this describes the imminent imperfections of the theory, which were discussed in detail in the first paper of this series (see paper 1 of ref 3); the borders of the corridor correspond approximately to the upper and lower estimations of the theoretical results.

Two parts of the theoretical curves, the globular and coil ones, cannot be interpolated in this case, because the value $\sqrt{C}/a^3 \cong 0.12$ corresponds to comparatively flexible chains.[3]

The experimental data were obtained using a slightly polydisperse mixture of chains of different lengths. Taking into account this polydispersity in the theory, we can show that the real value of the stiffness parameter $\sqrt{C}/a^3$ is slightly more than the estimation in eq 11; namely

$$\sqrt{C}/a^3)_{\text{improved estimation}} \cong 0.15 \pm 0.04 \tag{12}$$

The same data as in Figure 1 are plotted in Figure 2 as $\alpha_S{}^4(\alpha_S{}^2 - 1)$ versus $t\alpha_S{}^3$. We remind[3] everyone that simplified Flory-type theory predicts a linear dependence of the type

$$\alpha_S{}^4(\alpha_S{}^2 - 1) = \alpha_S{}^3 t_{\text{eff}} u + w \tag{13}$$

(eq 24 of the part 1 of this series[3]). Experimental points in Figure 2 do lie near a straight line. However, it is only a rough conclusion, because experimental errors for variables of Figure 2 are rather big, especially in the neighborhood of the Θ-point, where $\alpha_S \geqslant 0.8$. This is why a quantitative difference between t and t_{eff} cannot be established on the basis of data of ref 9 in Figure 2.

We note that the value of $\sqrt{C}/a^3 \cong 0.18 \pm 0.04$ was found in ref 22 for a PS/CYH system on the basis of surface tension measurement. This value is quite close to our result (eq 12).

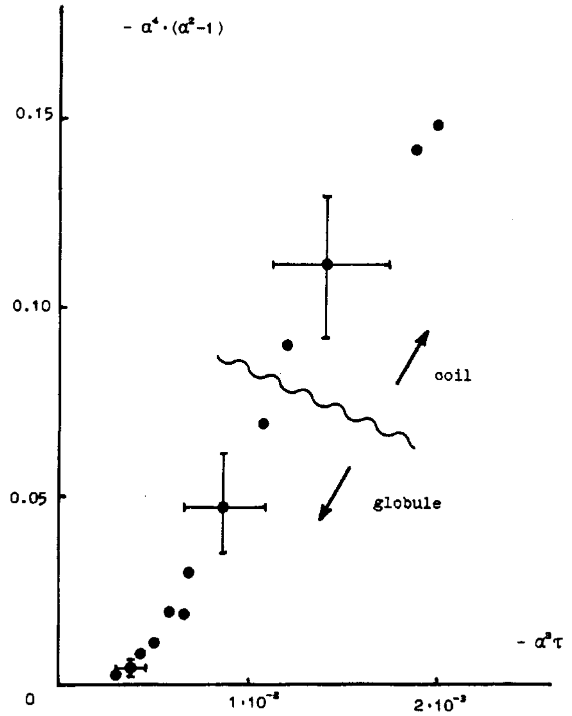

Figure 2. Experimental data of the MIT group[9] for the dependence of macromolecule expansion factor α_S of the radius of gyration on the solvent quality, characterized by the τ value, presented as $\alpha_S{}^4(\alpha_S{}^2 - 1)$ vs $\alpha_S{}^3\tau$.

There are a lot of papers where PS chain compression was observed in a PS/CYH solution below the Θ-point. Despite a great sparseness of molecular masses used in different works, the majority of the data can be included in Figure 1 because of the "corresponding states law", i.e., the dependence on the $\tau M^{1/2}$ combination only. Particularly, the data of ref 8 is included in Figure 1 by the τ-axis scale changing in $(M_{(\text{ref } 9)}/M_{(\text{ref } 8)})^{1/2} \cong 30$ times.

This corresponding states law is valid for polymers of different masses but in the same solvents. In reality the solvent purity is usually not better than 99%. However, 1% of the solvent exchange in some cases can be essential (see, for instance, ref 13). In these cases the "$\tau M^{1/2}$ rule" can seem to be broken down.

It is easy to see that all the data agree rather well with each other and with theoretical results for the same parameter values (eq 11) without any additional adjustment. However, comparison with the theory shows that most of the experimental works (refs 4, 5, 7, 8, and 10) deal with pretransitional coil compression only and not with a real coil-to-globule transition: all these data correspond to the $\alpha_S \geqslant 0.7$ region, i.e., to the coil state for real $\sqrt{C}/a^3$ values, as is clear from theoretical curves in Figure 1.

5.2. Polystyrene–Cyclohexane System. Single-Chain Hydrodynamic Radius. MIT group data of ref 9 on a PS chain hydrodynamic radius are presented in Figure 3 together with our theoretical results.[3] Theoretical curves have been plotted without any additional adjustable parameters (solid curve); we have used the values of eq 11, determined above. (The dashed curve corresponds to the other best fitted values $\sqrt{C}/a^3 \simeq 0.14$ and $Q \simeq 0.25$.)

In Figure 4 the same data are presented in another form—as the ratio S/R_H dependence on the reduced temperature t. The fit is rather well in the broad interval of temperatures from the coil to the globular state, but the discrepancy increases and becomes essential with the globule's density growth. This means that the Kirkwood–

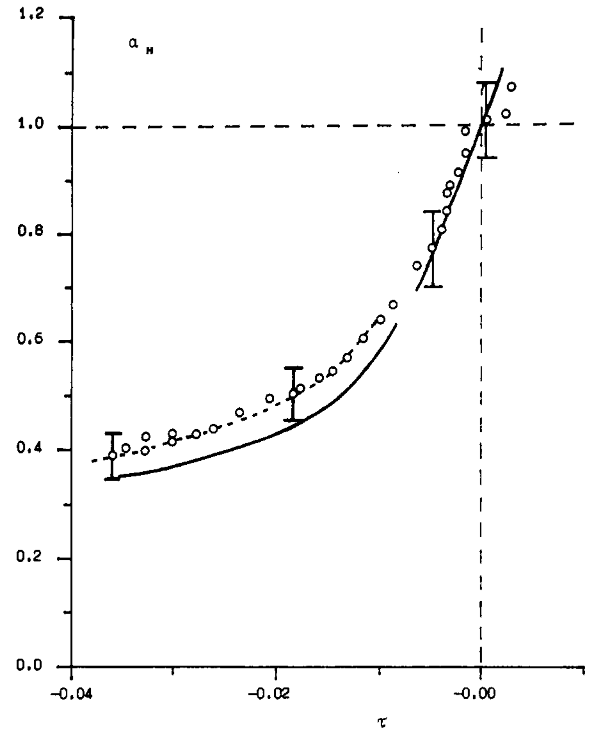

Figure 3. Experimental dependence of the expansion factor of a macromolecule hydrodynamic radius on τ for the very same PS/CYH system (ref 9) as in Figure 1 and the corresponding theoretical results, calculated with the same values of theoretical parameters $\sqrt{C}/a^3 = 0.12$ and $\tau/t = 0.0007$ (solid curve) and new best fitted values $\sqrt{C}/a^3 = 0.14$ and $\tau/t = 0.0008$ (dashed curve).

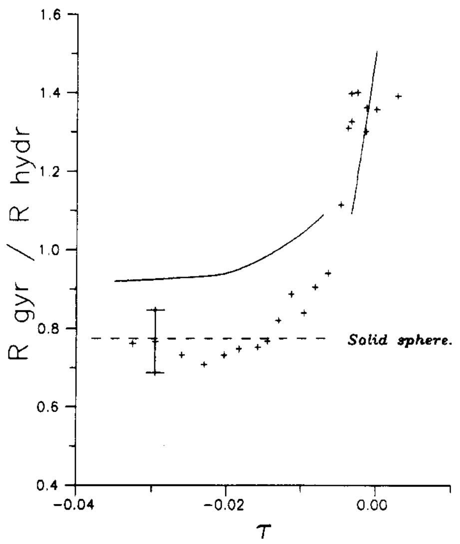

Figure 4. Experimental data of ref 9 for a PS/CYH system as the ratio of the radius of gyration to the hydrodynamic radius vs τ. Theoretical curves present the calculations based on perturbation and Kirkwood–Riseman approximations (solid curves) and a hard-sphere result (dashed line).

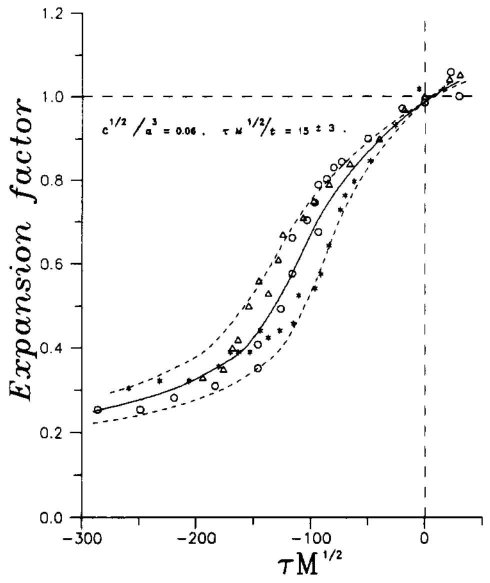

Figure 5. Experimental results of ref 12 for the expansion factor of the radius of gyration for various values of macromolecular masses in a PS/DOP system. Corresponding theoretical curves are shown for $\sqrt{C}/a^3 = 0.06$ and $Q = 0.07$ (central solid curve) and 0.06 and 0.08 (dashed curves).

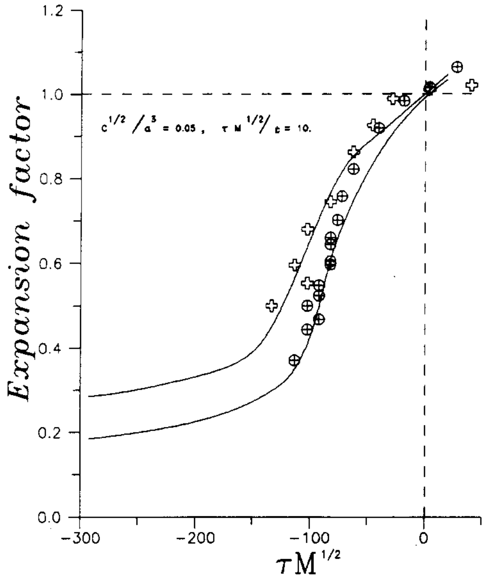

Figure 6. Experimental points for macromolecule expansion factors of gyration (⊕) and hydrodynamic (○) radii vs τ reported in ref 11 for a PS/DOP system and corresponding theoretical curves for $\sqrt{C}/a^3 = 0.05$ and $Q = 0.1$.

Riseman approximation, the basis of our calculation of the hydrodynamic radius (part 2 of ref 3), is invalid for the dense globular state.

The last conclusion seems to be quite justified physically. Really, the Kirkwood–Riseman approximation, i.e., the definition

$$\frac{1}{R_H} = \frac{1}{N^2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{14}$$

is based on the supposition that all the monomers are equally bathed by the solvent. It is quite clear that this supposition breaks down for the dense globular state. However, it is not so easy to estimate quantitatively the threshold density, which corresponds to the core creation inside the globule screened from a solvent.

5.3. Polystyrene–Dioctyl Phthalate System. Somewhat less complete results than in ref 9 are reported in refs 11 and 12, where the solution of polystyrene in dioctyl phthalate was investigated. In Figures 5 and 6 the experimental points of these papers for the macromolecule expansion factor of the radius of gyration and of the hydrodynamic radius are presented. Here the data were rescaled also according to eq 10. Unfortunately, the results of ref 11 with hydrodynamic data stop at the point just reaching the globular state (probably, due to the technique difficulties). Corresponding theoretical curves are also presented in Figures 5 and 6 for the following best fitted

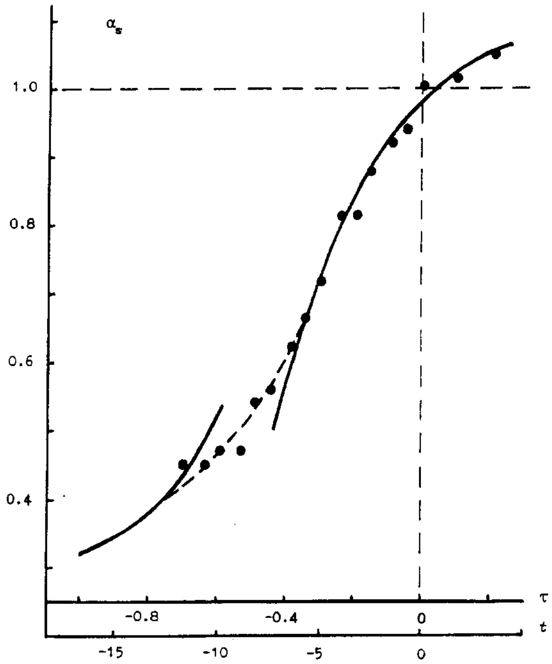

Figure 7. Computer simulation data of ref 14 for expansion factor α_S as a function of reduced temperature τ. The curve shows the corresponding theoretical results with $\sqrt{C}/a^3 = 0.08$ and $\tau/t = 0.06$.

values of adjustable parameters:

$$\sqrt{C}/a^3 \simeq 0.06 \pm 0.02, \quad Q \simeq 0.075 \pm 0.025\ (\mathrm{mol}^{1/2}/\mathrm{g}^{1/2}) \tag{15}$$

A relatively small value of $\sqrt{C}/a^3$ permitted the use of the two-level approximation[3] for the transition region and also turned the borders of the "corridor", essential in Figure 1, practically into one line. Here the theory also gives a good fit to the experiment within the experimental errors.

Thus, according to our results (eqs 11 and 15), a PS chain in a dioctyl phthalate medium is stiffer than one in cyclohexane. The coil-to-globule transition of a PS chain is of the first-order phase "bimodal" type in dioctyl phthalate and of the more smooth type in cyclohexane.

5.4. Computer Simulations. Chain Radius of Gyration. There are a lot of computer simulations on the coil-to-globule transition (refs 22–33 in part 1 of this series). As was already mentioned above, modern computer provides us with simulations on comparatively short chains only. The results for the longest chain from ref 14 are shown in Figure 7 together with the theoretical curve for the following best fitted values of the parameters:

$$\sqrt{C}/a^3 \simeq 0.08, \quad t/\tau \simeq 17$$

Unfortunately, the data of ref 14 is limited at the very beginning of the globular range—just like the real experimental data of ref 11.

5.5. Fluctuations of a Single-Chain Radius of Gyration. We remind everyone of our theoretical results (part 2) on the existence of a maximum of gyration radius fluctuations in the globule-to-coil transition region. This conclusion is in a good qualitative fit with computer simulation results[16] as well as with real experimental observation.[15]

5.6. Polystyrene–Cyclohexane System. Phase Diagram. We turn now to another group of experiments on the solutions with essential chain–chain interactions. There are a lot of experiments on a PS–CYH solution phase separation. The results of ref 19 for the coexistence curve of this solution are presented in Figure 8. Theoretical curves in this figure are plotted without any adjustable parameters; we have used the values determined above (eq 11). The part of these experimental data with the lowest molecular mass of polystyrene is in a good quantitative fit with our binodal results. For the longer polymers the experimental points are very close to the theoretical spinodal curve and, moreover, the empirical coexistence curve equation of ref 19 coincides with our spinodal eq 7a. In our opinion it means that for very long polymer chains in the solution of the same polymer weight concentration as for shorter chains the precipitation time is essentially more and therefore the experimental point moved to the spinodal conditions.

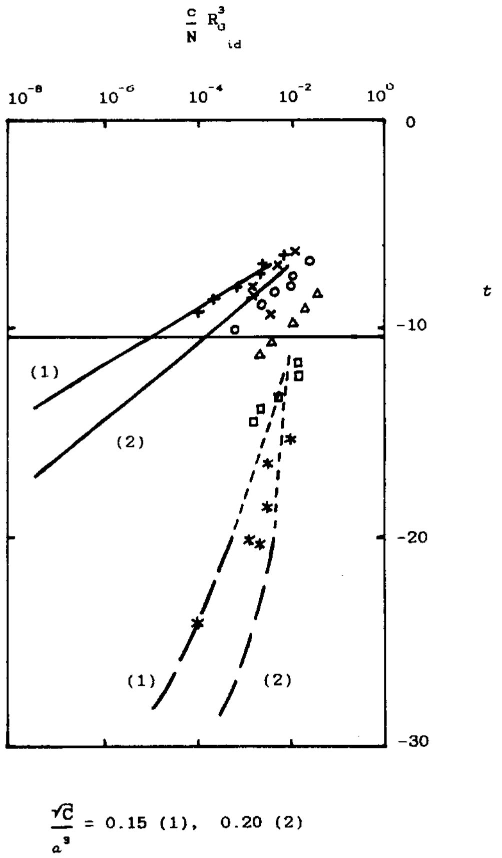

Figure 8. Coexistence curve experimental points (number of polymers in the volume, which corresponds to the Gaussian-coil one, vs the reduced temperature) of ref 19 for a PS/CYH system with molecular masses of 1.71×10^5 (+), 4.22×10^5 (×) 1.26×10^6 (○), 3.84×10^6 (△), 6.77×10^6 (□), and 2.06×10^7 (*) and corresponding theoretical binodal (solid) and spinodal (dashed) curves without any adjustable parameters. The above-determined values have been used. Here $\sqrt{C}/a^3 = 0.15$ (1) and 0.20 (2) and $Q \simeq 0.28$. The thin solid line shows the region of the coil-to-globule transition[3] ($t_{tr} \simeq -10.2$).

In Figure 9 we presented the coexistence curve experimental points of ref 18 for a PS/CYH system and of ref 12 for a PS/DOP system. The rectangles I and II, respectively, correspond to the regions that were used for the coil-to-globule transition investigation by the same authors.[9,12] The region of the similar experimental investigation for a PS/CYH system in ref 4 is shown by rectangle III; the corresponding coexistence curve points[20] are in Figure 10. Our theoretical binodal and spinodal curves are presented for realistic values of the chain stiffness parameter. Here we have used the above-determined values of the scaling adjustable parameter Q (eqs 11 and 15). The coil-to-globule transition point[3] ($t_{tr} \simeq -10.2$) is shown by the thin line. In Figure 10 the scaling

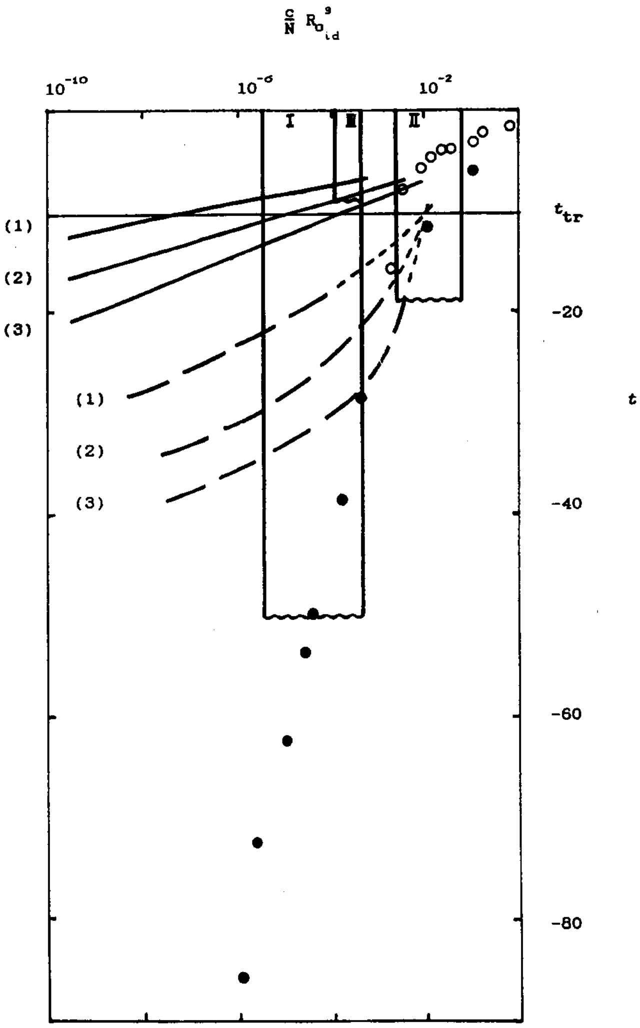

Figure 9. Experimental coexistence curve points of the MIT group[18] for a PS/CYH system (●) and of the Prague group[12] for a PS/DOP system (○). The rectangles correspond to the regions that were used for experimental investigations of the coil-to-globule transition by (I) the MIT group[9], (II) the Prague group,[12] and (III) the Stony Brook group[4] (PS/CYH system). Theoretical binodal (solid) and spinodal (dashed) curves are shown for three realistic values of the chain stiffness parameter $\sqrt{C}/a^3$ = 0.10 (1), 0.15 (2), and 0.20 (3). For the scaling adjustable parameter Q we have used the above-determined values (eqs 11 and 15) for these polymer–solvent systems. The thin solid line ($t \simeq -10.2$) corresponds to the coil-to-globule transition region.

theoretical coexistence curve[24,25] for a critical point neighborhood is presented also.

In Figures 9 and 10 the good agreement of our theoretical results[3] with the experiments of the Stony Brook group[4,20] and of the Prague group[12] is seen. At the same time the essential part of the MIT group's measurements is behind the spinodal conditions.

6. On the Criterion of the Globular State

Did anybody observe the condensed globular phase for a single PS chain suspended in a dilute solution? This phase can be observed easily for a much more complex system,[2,6] such as proteins, DNA, mesogens, etc., but what about the simplest uncharged homopolymers? To us, it is an important question not about PS only—see the introduction to our first paper of this series.[3]

As is clear from the consideration above, only the MIT group's experiments[9] and partially one of the Prague group[12] can be discussed on PS globule observation. However, the experiment interpretation has great difficulties in connection with the precipitation problem:[4] accordingly to theoretical results in Figure 9, the MIT group's measurements in ref 9 have been done with a far more concentrated solution than a stable or even metastable one. Of course, this does not mean that this experiment was wrong (even if our theory is right): the characteristic time of instability development is at least on the order of a collision interval, i.e., $\sim c^{-1/3}/D \sim 1$ min for the experimental conditions of ref 9. However, we do not know if this experiment was fast enough.

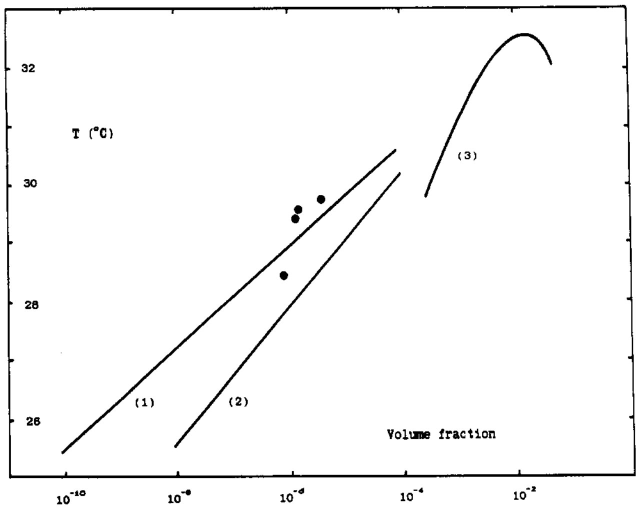

Figure 10. Experimental coexistence curve points of ref 20 for a PS/CYH system presented as the temperature dependence of a polymer volume fraction. Our theoretical binodal curves are shown for $\sqrt{C}/a^3$ = 0.15 (1) and 0.20 (2), with $Q \simeq 0.28$. Curve 3 is the scaling theoretical coexistence for a critical point neighborhood (refs 24 and 25).

We again stress the good agreement of our theoretical results[3] and the experiments[4,20] of Chu et al. on coexistence curve determination (see Figures 9 and 10). The characteristic relaxation time in this experiment was on the order of 1 week.

Nevertheless, our theory does not confirm the assumption about globule observation in the experiments of refs 4, 5, 13, 17, and 20 before precipitation. We remind everyone that this assumption was based on the data presentation in the form like Figure 11 ($\alpha_S^3\, t$ vs t). The nonmonotonic behavior of the data in these variables was interpreted in the above-mentioned papers in the following way: data approaching the maximum was supposed to be the manifestation of asymptotic globular scaling law $\alpha_S^3\, t \simeq$ const, i.e., $R_S \sim \tau^{-1/3}$; data decrease after the maximum was construed as a preseparation phenomenon. However, the theory also predicts nonmonotonic behavior (see the curve in Figure 11). Moreover, a globular asymptote is reached at far larger values of t than the maximum ones.

Generally speaking, asymptotic behavior of the type $R_S \sim \tau^{-1/3}$, to us, cannot be considered as an adequate criterion of the globular state. Unfortunately, due to accidental reasons, for the chain with $\sqrt{C}/a^3 \simeq 0.15$ this scaling law $R_S \sim \tau^{-1/3}$ gives a uniform approximation of the theoretical dependence of $R_S(\tau)$ in a broad temperature interval in the slightly compressed coil region, the transition region, and the low-density globule region to the well-formed globule regime. This is the case for a PS/CYH system, and this is why a globular asymptote seems to be reached in many experiments. Of course, this chance does not take place for the chains with all other values of the stiffness parameter.

To us, the criterion of the globular state cannot be formulated universally, independent of the $\sqrt{C}/a^3$ value.

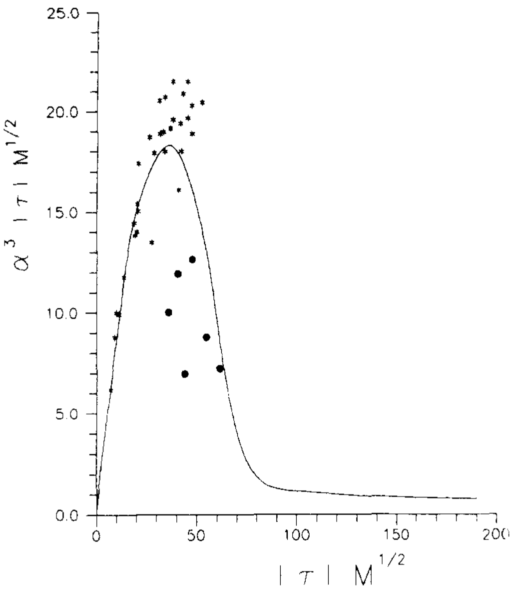

Figure 11. Experimental dependence of the expansion factor α_S of the polymer radius of gyration vs the reduced temperature for a PS/CYH system of ref 4 presented as $|\tau|M^{1/2}$ dependence on a $\alpha_S^3|\tau|M^{1/2}$ value. In accordance with ref 4, the points, marked as ●, correspond to metastable states. The theoretical curve demonstrates that the experimental data approaching the maximum value cannot be considered as the manifestation of the asymptotic globular scaling law, i.e., $R_S \sim \tau^{-1/3}$. This scaling law is not an adequate criterion of the globular state.

However, for many real polymers with $\sqrt{C}/a^3 < 0.2$, according to our theory, a state can be interpreted as the globular one in the region $\alpha_S < 0.3$ only. In the general case, for an unknown polymer without any a priori estimation of the $\sqrt{C}/a^3$ value, the question can be solved by detailed theory–experiment comparison only.

7. Conclusion

A brief résumé of the main results of this series of papers[3] is as follows:

(1) The mean-field theory provides us with a satisfactory description of the whole mass of experimental information on the coil-to-globule transition.

(2) Experiments do not indicate surely any effects beyond the mean-field approach.

(3) The classical Kirkwood–Riseman approximation is not valid quantitatively for a dense enough globular chain.

(4) As to the possibility of observation of single-chain globules in a fast enough experiment before precipitation, we need some additional theoretical investigations: mainly due to the topological constraints,[23] it is unclear whether it will be equilibrium globules and whether they will aggregate in an equilibrium way.

(5) The experimental situation for the concrete example of a polystyrene–cyclohexane system seems to be rather complicated from the point of view of theoretical results: observation of the dissolved equilibrium globules without precipitation as well as observation of equilibrium precipitation (which includes the entangling between chains) remains a difficult problem; more subtle properties of globules beyond the mean-field ideas are, probably, out of the experimental possibilities at present.

(6) Only the simplest type of coil-to-globule transition slightly below the Θ-point was the subject of this series of papers. The following aspects are out of this consideration: another type of first-order collapse transition above or below the critical point[1]; deviations from universality due to the restricted chain length, such as small,[1] toruslike,[26,27] and liquid-crystalline[27] globule formation; ψ-condensation of DNA;[28] the role of polyelectrolyte effects;[29] the role of heterogeneous frozen[30] or an annealed[31] sequence of different types of links; globules confined at the interface or in the hole;[32,33] the globular state of the chain without knots,[23] etc.

Appendix A: Effect of Polydispersity on Macromolecular Size Determination in the Globule-to-Coil Transition Region

The above-discussed theory of the globule-to-coil transition deals with isolated macromolecules of the same molecular mass. For comparison of the theory with experimental data it is desirable, naturally, to take into account the effect of inevitable polydispersity on measuring values of macromolecular sizes. However, here we do not plan a detailed consideration of this problem. We will estimate the effect of polydispersity on the determination of the polymer stiffness parameter $\sqrt{C}/a^3$ in comparison of the theory with experiments in the case of a very narrow molecular weight distribution.

Let $S(M)$ be the root-mean-square radius of a macromolecule with mass M in a monodisperse solution. This may be the radius of gyration, hydrodynamic radius, etc. The same variable for a polydisperse solution can be written as

$$\bar{S}_k^{\,2} = \frac{\sum_i S^2(M_i)\, M_i^k n_i}{\sum_i M_i^k n_i} \qquad \text{(A1)}$$

where M_i is the mass of a macromolecule consisting of i links, and n_i is the total number of such macromolecules in a solution. Index k shows the kind of averaging. $\bar{S}_k^2$ is the number-average value at $k = 0$; at $k = 1$ or $k = 2$ it is the weight-average or the z-average value, respectively. Due to the narrow mass distribution and the large number-average value M_0, it is possible to expand the $S^2(M)$ function near the M_0 point in a power series of $M - M_0$ and to restrict the series by the first terms. Taking into account that $M_k \equiv \sum_i M_i^{k+1}n_i/\sum_i M_i^k n_i$, we can write

$$\bar{S}_k^{\,2} = S^2(M_0) + (M_k - M_0)\frac{\mathrm{d}S^2(M)}{\mathrm{d}M}\bigg|_{M=M_0} + \dots \qquad \text{(A2)}$$

Under ideal coil conditions, $S_{\rm id}^2(M) \sim M$; therefore

$$\bar{S}_{k_{\rm id}}^{\,2} = (M_k/M_0)S_{\rm id}^{\,2}(M_0) \qquad \text{(A3)}$$

We are usually interested in the expansion factor value $\alpha_k^2 \equiv \bar{S}_k^2/\bar{S}_{k_{\rm id}}^2$, which with account of eqs A2 and A3 can be presented now in the following form:

$$\alpha_k^{\,2} \simeq \alpha^2(M_0)\,\frac{M_0}{M_k}\left[1 + \frac{M_k - M_0}{S^2(M_0)}\,\frac{\mathrm{d}S^2(M)}{\mathrm{d}M}\bigg|_{M=M_0}\right] \qquad \text{(A4)}$$

In the volume approximation[3] ($|t| \gg 1$)

$$\alpha^2(M) \sim |t|^{-2/3}(\sqrt{C}/a^3) \sim M^{-1/3} \qquad \text{(A5)}$$

and $S^2(M) \sim M^{2/3}$, so

$$\alpha_k^{\,2} \simeq \alpha^2(M_0)\left[1 - \frac{M_k - M_0}{3M_k}\right] \qquad \text{(A6)}$$

As is seen here, in this approximation weight-average ($k = 1$, $M_k = M_w$), z-average ($k = 2$, $M_k \equiv M_z$), etc. ($k \geqslant 1$), values of α_k for a polydisperse solution are smaller than those for a monodisperse solution, since $M_0 \leqslant M_w \leqslant M_z$

$\leqslant$ .... It is necessary to note that negligible terms in the square brackets of eqs A4 and A6 do not vanish, generally speaking, in the case of $k = 0$ and therefore $\alpha_0^2 \neq \alpha^2(M_0)$ usually too.

Corresponding to the state of a well-formed globule, the correction in eq A6 for the expansion factor of a macromolecule in a polydisperse solution is expressed in the form of a scaling factor to the monodisperse result. At the same time, as follows from eq A5, the scale of a $\alpha^2(M_0)$ value in the globular region is determined by the $\sqrt{C}/a^3$ factor. If we did not take the correction in eq A6 into account, we could determine from the experimental data the apparent $\sqrt{C}/a^3$ value. The real value is slightly larger than the apparent one:

$$\left(\frac{\sqrt{C}}{a^3}\right)_{\text{real}} \simeq \left(\frac{\sqrt{C}}{a^3}\right)_{\text{appar}} \left[1 - \frac{M_k - M_0}{3M_k}\right]^{-1}$$

Appendix B: Interpretation of the Experimental Data in Terms of the Persistent Model

To make the interpretation of the experiments on the coil-to-globule transition more obvious, it is useful to treat a macromolecule like a homogeneous persistent chain. Let us remind everyone that in the region of the globule–coil transition macroscopic properties of a polymer does not depend on the details of its microscopic structure, and in this sense different models of the macromolecule are equivalent.[1,34] Here we discuss the determination of the parameters of a polymer–solvent system in terms of the persistent chain.

If the contour length of a chain is L, the effective Kuhn segment length is $2l$, then in the Θ-conditions the mean-square end-to-end distance equals $2lL = Na^2$. We call the chain part with length $2l$ a link; then $N = L/2l$ and, consequently, $a = (2lL/N)^{1/2} = 2l$. For interacting straight rods with length $2l$ and thickness d the third virial coefficient is $\sim l^3d^3 \ln (2l/d)$. It is clear that, for segments of the persistent chains, the power dependence on l and d when $l \gg d$ must be the same. It is natural, therefore, to write the following:

$$\sqrt{C}/a^3 = (d/2l)^{3/2} \tag{B1}$$

Really, as the d value has no simple stereochemical meaning but characterizes the effective polymer thickness taking into account interactions of the van der Waals type, the role of the solvent, and so on, we may consider this expression as an exact one and use it as a definition of d. This definition is applicable not only when $l \gg d$ but also in the general case when $l \geqslant d$. We outline the fact that d, introduced by this way and defined by the parameters of the equivalent beads on a string model, does not depend on the freedom in links dividing the chain, i.e., on the choice of N.

The second virial coefficient of sterical interactions of rigid rods with length $2l$ and diameter d equals $\pi l^2 d$; then the second virial coefficient of interactions of persistent chain segments near the Θ-point may be expressed as

$$B = \pi l^2 d\beta\tau \tag{B2}$$

Phenomenological coefficient β characterizes several effects at once: first, the flexibility of the chain segments and the difference between quasimonomers and monomers; second, the influence of the solvent and other factors on the effective polymer thickness d, defined by the expression in eq B1; third, the sharpness of the temperature dependence of B. Now we can write

$$Q \equiv t/\tau M^{1/2} = (N/M)^{1/2}\,(d/2l)^{1/4}\beta(6^{3/4}\pi)/4 \tag{B3}$$

We discuss briefly the above-obtained result (eq 12) on the value of the polymer stiffness parameter for a PS/CYH system in terms of the persistent model. In accordance with eqs B1 and 12 the ratio of the Kuhn segment length to the effective thickness of the polymer chain is $2l/d \simeq 3.5 \pm 0.6$. The mass of the elementary polystyrene link $m_0 \simeq 104$ and its length along the chain $a_0 \simeq 2.4$ Å; then using the expression $\langle S^2\rangle/M = a_0l/3m_0$ and eq 10, we can calculate $l \simeq 12 \pm 2$ Å. This means that $d \simeq 7 \pm 2$ Å.

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Registry No. PS (copolymer), 9003-53-6.