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Influence of Isotopic Labeling on Chain Dimensions in Polymer Solutions

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ABSTRACT: Using a recently established theory of ternary polymer solutions, I reconsider data on a mixture of deuterated and protonated polystyrene dissolved in cyclohexane. These data had been interpreted as showing the radius of a polymer chain in a binary semidilute solution. I find this interpretation to be wrong, the data showing pronounced ternary solution effects. Reasonable agreement between ternary theory and experiment is found; however a strong test of the theory needs more experimental work.

1. Introduction

Isotopic labeling has become a standard tool for measuring the size of a single polymer coil in the presence of many other polymer molecules of the same chemical species. The method exploits the large difference among the neutron scattering lengths of protons or deuterons. Scattering neutrons from a system containing a few deuterated probe chains among many protonated chains (or vice versa) and varying the concentration of the probe chains, one can extract the signal of a single probe chain. Thus the method yields the density autocorrelation function of a single polymer coil in the system, from which the radius of gyration can be determined. It widely has been used both in melts or other dense systems and in solutions of arbitrary concentrations.[1–4] The method rests on the assumption that deuteration does not change the thermodynamic or configurational properties of the polymer molecules, so that a probe chain is a true representative of all the macromolecules in the system. For dense systems this assumption recently has been criticized, and it has been shown that some thermodynamic quantities are sensitive to deuteration. (See ref 5 and references given therein.) Also for solutions close to their Θ-point, deuteration makes some effect,[6] which, however, generally is ignored in the analysis of the data.

In the present work I reanalyze data[2] on the radius of gyration of polystyrene (PS) molecules dissolved in cyclohexane, taken at temperatures near the Θ-point. In the original work these data were analyzed in the framework of scaling- and power-laws valid for binary solutions. Subsequent renormalization group analysis[7,8] did not confirm that interpretation, rather concluding that these data cannot properly be explained within the context of renormalization group or scaling theory of binary solutions. Here I treat the system as a ternary solution, taking into account the difference[6] among deuterated (PS(D)) or protonated (PS(H)) polystyrene. Renormalization group theory of ternary polymer solutions has been worked out during the last years (see ref 9 and references given therein), and recently Kappeler and the present author[10] have presented a calculation of the radius of gyration of a coil in ternary solution within the framework of first-order renormalized perturbation theory. Based on these results I find that the experimental data definitely cannot be understood in terms of simple scaling ideas, but allow for an explanation in terms of ternary solution theory, taking into account the surprisingly large difference among PS(D) or PS(H). Three-body interactions do not seem to play a decisive role, as judged from a simplistic discussion. While these qualitative results are firmly established, the quantitative fit still leaves some room for improvement. However, due to the large scatter of the data as well as to other ambiguities of the experiment, a more detailed analysis does not seem appropriate.

The organization of this article is as follows. In section 2, I give a short description of renormalization, and I analyze data on the binary subsystems PS(H)–C_6H_{12}, PS(D)–C_6H_{12} in order to determine some parameters of the theory. This also illustrates the degree of agreement between theory and experiment typical for binary solutions. Section 3 is devoted to the reanalysis of the PS(D)–PS(H)–C_6H_{12} experiment. Some equations necessary for the theoretical evaluation are collected in the Appendix. Section 4 contains a critical discussion of the experiment and its original interpretation, as well as suggestions for further experiments.

In closing this introduction, I want to stress that we here are concerned with polymers in moderate solvents, not in the good solvent excluded volume limit. In good solvents ternary effects are small,[9,10] and isotopic labeling presumably does not lead to observable changes in the configurational properties of macromolecules.

2. Binary Solutions

2.1. Basic Structure of Renormalization Group Theory. The theory has been discussed in detail in the literature. (See ref 11 or 9, and references given therein.) Here I only on a qualitative level recall some basic features necessary to understand the structure of the theoretical results.

The theory starts from a model of self-repelling Gaussian chains, parametrized by the mean segment size l, the number N of segments per chain, and the excluded volume constant β. The excluded volume vanishes at the Θ-temperature: $\beta \sim T - \Theta$. The (not normalized) statistical weight of the configuration $\{\mathbf{r}_0, \mathbf{r}_1, ..., \mathbf{r}_N\}$ of a single chain is taken as

$$e^{-\mathcal{H}/k_BT} = \exp\left\{-\frac{1}{4l^2}\sum_{j=1}^{N}(\mathbf{r}_j - \mathbf{r}_{j-1})^2\right\}\prod_{i<j}(1 - \beta l^3\delta^3(\mathbf{r}_i - \mathbf{r}_j)) \tag{2.1}$$

The extension to a solution of finite number concentration c_p of polymer chains is obvious.

Evaluating the theory perturbatively in powers of β, we realize that the expansion parameter is $\beta N^{1/2}$ rather than β. This is problematic, since for long chains and $T > \Theta$ fixed, $\beta N^{1/2}$ becomes large and the expansion breaks down. Renormalization solves that problem by mapping the

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theory on its "renormalized" counterpart, defined for segments of size

$$l_R = 1/\lambda, \qquad \lambda \leq 1 \tag{2.2}$$

Thus

$$\beta \to f(\lambda)$$
$$N \to N_R(\lambda) \tag{2.3}$$
$$l^3 c_p \to l_R^{\,3}\, c_p = c_{pR} = l^3 c_p/\lambda^3$$

and the λ-dependence of f and N_R has to be chosen such that macroscopic observables calculated within the unrenormalized or the renormalized theories come out the same. (The existence of such functions $f(\lambda)$, $N_R(\lambda)$ is the highly nontrivial content of the theorem of renormalizability.) This condition yields the renormalization group equations, which give the change of $f(\lambda)$, $N_R(\lambda)$ under an infinitesimal change of the scaling parameter λ. To find f, N_R at a given scale $l_R = 1/\lambda$, we integrate these equations, starting from the unrenormalized model defined at $\lambda = 1$. The result is given in the Appendix, eqs A.1–3.

It turns out that the starting values can be given in terms of the parameters

$$R_\Theta^{\,2}(N) = l^2 N$$
$$\tilde{z} = \beta N^{1/2} = v_T \frac{T - \Theta}{\Theta} N^{1/2} \tag{2.4}$$

familiar from two-parameter theory. Here $R_\Theta(N)$ is the radius of the chain at the Θ-temperature and v_T is some chemistry dependent constant. (In using that form, we assume to work close to the Θ-temperature. We for instance neglect contributions to β quadratic in $(T - \Theta)/\Theta$.) It also is useful to introduce a concentration variable

$$\tilde{s} = \hat{u}\, c_p\, R_\Theta^{\,3}(N) \tag{2.5}$$

which will be addressed as "Θ-overlap" in the sequel. The numerical constant $\hat{u} = 5.756$ is of purely technical origin and is introduced for convenience. Since by accident $4\pi/3 \approx \hat{u}$, $\tilde{s}$ roughly measures the average number of chains found in a volume of the size of a Θ-chain.

Within renormalized theory the observables again have to be calculated perturbatively. The expansion orders in powers of $f(\lambda)N_R^{1/2}(\lambda)$. We now choose the free parameter λ such that the expansion is dominated by the zero-order terms, higher order corrections staying small. For an isolated chain the condition $N_R(\lambda) = O(1)$ results, implying $l_R \approx R_G(T,N)$, where $R_G(T,N)$ is the radius of an isolated self-repelling chain. For larger overlap excluded volume correlations persist only over a concentration-dependent range smaller than R_G. Beyond that "blob size" nontrivial correlations are destroyed by the interaction of many uncorrelated chains. This screening effect forms the basis of the blob model scaling theory[12] of semidilute solutions. In renormalization group theory it is incorporated[8] by choosing l_R to be of the order of the blob size. The resulting equation is given in the Appendix (eq A.9 with $c_R^{(2)} \equiv 0$). Together with the mapping from unrenormalized to renormalized parameters, this equation completely defines the renormalized theory.

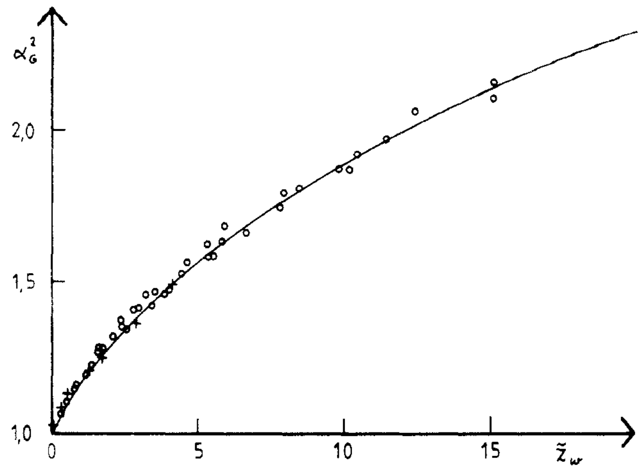

Figure 1. Swelling factor $\alpha_G^2(\tilde{z}_w)$ of an isolated polymer chain. Data points for the system PS(H)–C_6H_{12}: ○, ref 13 (9 chain lengths); +, ref 15.

2.2. The System PS(H)–C_6H_{12}. For the system polystyrene–cyclohexane very precise data on the chain length and temperature-dependent swelling of an isolated chain are available.[13] The swelling factor of an isolated chain is defined as

$$\alpha_G^{\,2}(\tilde{z}) = \frac{R_G^{\,2}(T,N)}{R_G^{\,2}(\Theta,N)} \tag{2.6}$$

where of course $R_G^2(\Theta,N) \equiv R_\Theta^2(N)$ (eq 2.4). Both theory and experiment agree in that the swelling factor for long enough chains and $T \geq \Theta$ only depends on the scaling variable $\tilde{z}$. α_G^2 has been calculated in first-order renormalized perturbation theory (see, for instance, refs 8 and 11 and references given therein). Within the accuracy of the calculation the result can be parametrized as

$$\alpha_G^{\,2}(\tilde{z}) = (1 + 1.01\tilde{z} + 0.216\tilde{z}^2)^{0.18} \tag{2.7}$$

(This form is based on a new calculation, using a somewhat simpler renormalization scheme than employed in ref 8. After an appropriate readjustment of the nonuniversal parameter v_T (eq 2.4) the result is almost indistinguishable from our previous one.) α_G^2 has been calculated also to higher orders,[14] the result deviating from eq 2.7 by less than 1%.

Equation 2.7 holds for a monodisperse system, and in comparing to data we must take into account polydispersity effects. For polydisperse systems the variable N should be interpreted as the number average chain length. It turns out that a large part of the polydispersity dependence can be taken into account by replacing in eq 2.7 the variable $\tilde{z}$ by a variable

$$\tilde{z}_w = v_T \frac{T - \Theta}{\Theta} N_w^{\,1/2} \tag{2.8}$$

where N_w is the weight average chain length. For the fairly sharp fractions used in the experiment, the residual polydispersity dependence can be ignored.

According to ref 13 the Θ-temperature and the parameter l for PS(H)–C_6H_{12} are found as

$$\Theta_H = 307.7\ \text{K}, \qquad l_H = 2.95\ \text{Å} \tag{2.9}$$

where l_H is derived from the radius at the Θ-point. Fitting the data for $T > \Theta$ to our form of $\alpha_G^2(\tilde{z}_w)$ yields

$$v_{TH} = 0.41 \tag{2.10}$$

As shown in Figure 1 the fit is excellent.

I also considered the data of ref 15, where not only $\alpha_G^2(z)$ but also the second virial coefficient A_2 has been measured. The data for $\alpha_G^2(z)$ are included in Figure 1.

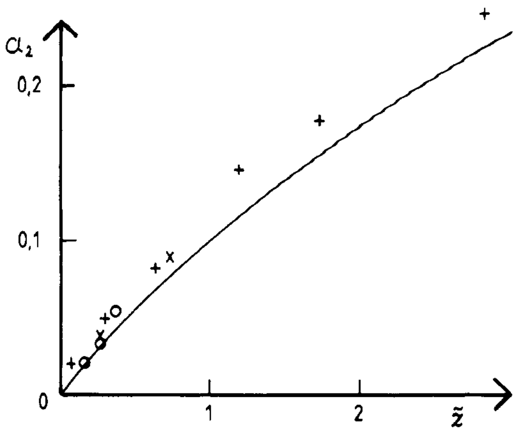

Figure 2. Reduced second virial coefficient $a_2(\tilde{z})$ (eqs 2.12 and 2.13): ○, PS(H)–C_6H_{12}, ref 15; +, PS(H)–C_6H_{12}, ref 6; ×, PS(D)–C_6H_{12}, ref 6.

From A_2 we can define a scaling function

$$a_2(\tilde{z}) = \frac{M_n^{\,2} A_2}{4\pi^{3/2} R_\Theta^{\,3}(N)} \tag{2.11}$$

where M_n is the number average molecular weight. First-order renormalized perturbation theory yields a result which can be parametrized as

$$a_2(\tilde{z}) = \frac{0.129\tilde{z}}{\left(1 + \left(3.014 - \frac{c}{0.23}\right)\tilde{z} + \frac{1.423\tilde{z}^2}{(1+c)^{0.435}}\right)^{0.23}} \tag{2.12}$$

Here c contains the polydispersity correction

$$c = \frac{0.541 - 0.183N_w/N}{0.763 + 0.237N_w/N} \tag{2.13}$$

This result is compared to the data in Figure 2. The agreement is fair, in particular if it is taken into account that I did not try to redetermine the chain length from these data. (As compared to ref 13, there is a slight inconsistency in the value assigned to $R_\Theta^2(N)$. If in reducing the data we would not use the measured value but the result of eqs 2.4 and 2.9, the data would fall right on top of the theoretical curve.) I also included three data points given in ref 6 for a system of comparable polydispersity.

To summarize, I conclude that the data on the system PS(H)–C_6H_{12} are in excellent agreement with the theory, yielding parameter values (2.9) and (2.10).

2.3. The System PS(D)–C_6H_{12}. For that system only very few data are available. The value of the Θ-temperature is well established[6,2]

$$\Theta_D = 303.7 \text{ K} \tag{2.14}$$

Strazielle and Benoit find a small increase of $R_\Theta^2(N)$ upon deuteration

$$l_D = 2.97 \text{ Å} \tag{2.15}$$

a change of l_D compared to l_H which clearly is within the error bars of the experiments. To determine v_{TD} only two data points for A_2 are available. These are included in Figure 2, yielding the estimate

$$v_{TD} = 1.5 \tag{2.16}$$

Compared to v_{TH} this is a surprisingly large difference, which however will be found to be supported by the measurements on the system PS(D)–PS(H)–C_6H_{12}. Still, more data allowing for a more reliable determination of l_D; v_{TD} clearly are needed. (Note that the dilute solution data of ref 4 suffer from a not well controlled concentration correction.)

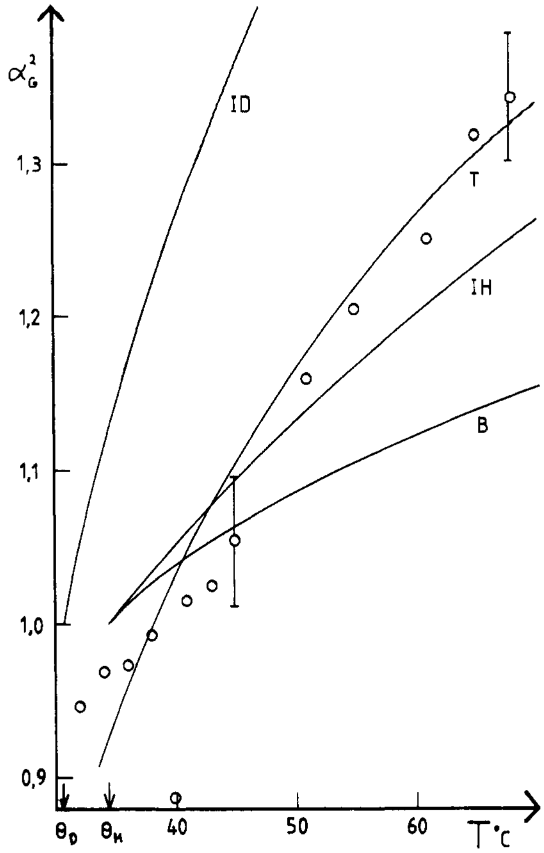

Figure 3. Swelling of a PS(D) chain in PS(H)–C_6H_{12} solution as a function of temperature, data of ref 2. Theoretical curves: T, ternary theory; B, radius of a PS(H) chain at the given concentration as predicted by the binary theory; IH, radius of an isolated PS(H) chain; ID, radius of an isolated PS(D) chain.

3. The System PS(D)–PS(H)–C_6H_{12}

3.1. Experimental Results in the Light of Binary Solution Theory. Reference 2 reports results of neutron scattering from a solution containing 10^{-2} g cm^{-3} PS(D), 14×10^{-2} g cm^{-3} PS(H). The temperature varies from 32 to 68 °C. The fractions are reasonably sharp, with number-averaged chain lengths $N_D \approx 1265$ and $N_H \approx 1375$. I analyze the experimental results in terms of a swelling factor α_G, which generalizes the definition (2.6) to arbitrary chain concentrations c_{PD}, c_{PH}

$$\alpha_G^{\,2} = \frac{R_{GD}^{\,2}(N_D,N_H,c_{PD},c_{PH})}{R_{\Theta D}^{\,2}(N_D)} \tag{3.1}$$

I use the Θ-radius resulting from l_D (eq 2.15), taking into account the polydispersity of the sample. The resulting data points are plotted in Figure 3, where for two points I indicated the statistical error as quoted by the authors. For a somewhat higher total concentration of polystyrene, similar results have been reported in ref 4. These data are consistent with those included here, as shown in Figure 15 of ref 8.

To get a first feeling for these data I have calculated the theoretical prediction for the radius of a PS(H) chain in the solution, ignoring the difference among (PS(D) and PS(H). At the given chain length N_H a concentration of 15 10^{-2} g cm^{-3} PS(H) corresponds to a Θ-overlap

$$\tilde{s}_H = 4.75 \tag{3.2}$$

Using this value together with the other parameters of the

PS(H)–C_6H_{12} system I find curve B of Figure 3. The calculation is based on eqs 3.3 and 3.4 below, specialized to a binary system. Note that the experiment in fact aimed at a determination of R_G as calculated here, but clearly experiment and theory do not match.

The matter becomes worse if we recall the (experimentally verified) result (2.7) for the swelling of an isolated chain. Taking $N = 1265 = N_D$ together with the value (2.10) of υ_{TH}, I have plotted the isolated chain result as curve IH in Figure 3. For higher temperatures the experimentally found swelling is even stronger than for an isolated PS(H) chain. Since it is hardly conceivable that the swelling increases with increasing concentration, *this observation, based solely on experimental facts, rules out any interpretation of the data in terms of binary solution theory.*

3.2. Interpretation by Ternary Solution Theory. In solutions containing two different polymer species we have to distinguish three different excluded volume constants $\beta_{11}, \beta_{22}, \beta_{12} = \beta_{21}$, where two segments of species a or b respectively interact via the coupling β_{ab}. As a consequence there exist three different renormalized couplings denoted by f_1, f_2, $f_{12} = f_{21}$, respectively. The mapping from the unrenormalized to the renormalized couplings is given in the Appendix, together with the corresponding results for chain lengths and concentrations.

The radius of gyration of polymer chains in a ternary system has been calculated in ref 10 to first-order renormalized perturbation theory. Specializing the result to a single chain of species 1 in a solution of species 2, and taking both species as monodisperse, one finds (compare ref 10, eq 3.16)

$$R_{G1}{}^2(N_1,N_2,c_{p1} = 0,c_{p2}) = l_R{}^2 N_R{}^{(1)} \Bigg\{ 1 - 0.364 f_1 + 0.165 f_1 N_R{}^{(1)1/2} - 0.292 f_{12}{}^2 c_R{}^{(2)} N_R{}^{(2)} N_R{}^{(1)1/2} \int_0^\infty dz\, z^{-1/2} \times \frac{B(z) D(zN_R{}^{(2)}/N_R{}^{(1)})}{1 + f_2 c_R{}^{(2)} N_R{}^{(2)} D(zN_R{}^{(2)}/N_R{}^{(1)})} \Bigg\} \quad (3.3)$$

$$B(z) = \frac{1}{6} e^{-z} - 2D(z) + \frac{8}{z}(D(z) - 1) - \frac{10}{z^2}\left(D(z) - 1 + \frac{z}{3}\right) \quad (3.4)$$

Here $D(z) = 2(e^{-z} - 1 + z)/z^2$ is the Debye function, $N_R{}^{(a)}$ is the renormalized chain length of species a, and $c_R{}^{(a)} = \hat{u}\, c_{pR}{}^{(a)}\, N_R{}^{(a)}$.

It is easily checked that the integrand in eq 3.3 is always positive, so that the coupling of the chain considered to the background of other chains always decreases $R_{G1}{}^2$. It thus is of interest to calculate the radius of an isolated PS(D) chain of length $N_D \approx 1265$. With the parameter values 2.15 and 2.16, I find curve ID of Figure 3 showing that the measured values are lower than the results for an isolated PS(D) chain. It thus is no surprise that eq 3.3 can be used to fit the data by adjusting the initial value $f_{12,0}$ (corresponding to β_{12}) of f_{12} in the integration of the ternary renormalization group equation (A.4). For the binary parameters the previous results have to be taken, of course. (I identify species 1 with PS(D) or species 2 with PS(H), respectively.) Curve T of Figure 3, which gives a moderately good fit within the statistical uncertainty of the data, is found for

$$f_{12,0} = 0.04 + 0.55 \frac{T - \Theta_H}{\Theta_H} \quad (3.5)$$

Reasonably enough this value falls right between the parameters of the binary subsystems.

3.3. An Estimation of Three-Body Effects. Despite the large uncertainty of the data a critical view on Figure 3 might raise the suspicion that also the ternary theory does not catch all the relevant physics. In particular, close to the Θ-temperature three-body forces may be relevant. In fact, the concentration in the experiment is somewhat high, so that three-body forces should be taken into account. Such forces are known to be important for other quantities like the osmotic compressibility[10,17] or the screening length,[2,8] where they explicitely influence the lowest order approximation of the theory. For $R_G{}^2$ the lowest order approximation $R_G{}^2 = l_R{}^2 N_R$ is affected by the interactions only implicitely via eq A.7 fixing the renormalized theory. This suggests that three-body effects are weak, and indeed the coil radius in a Θ-solution is known to be not much different from the radius in a melt. The most important effect will be to shift the temperature $T_P < \Theta_H$, where the PS(H)–C_6H_{12} system undergoes a demixing transition. To lowest order renormalized theory this temperature is given by the vanishing of the denominator in the integral in eq 3.3, evaluated for $z = 0$.

$$1 + f_2\, c_R{}^{(2)} N_R{}^{(2)} = 0 \quad (3.6)$$

Evaluating this condition with the present set of parameters I find $T_P - \Theta_H \approx -3°$, to be compared to the experimental finding[2] $T_P - \Theta_H \approx -7°$. To cure this discrepancy we in the spirit of renormalized mean field theory may add to f_2 a contribution $\beta_3 c_R{}^{(2)}$, representing the dominant effect of three-body forces. To reproduce the experimental value of T_P, a value $\beta_3 \approx 0.03$ has to be chosen. In eq 3.6 an additional contribution $\beta_3\, (c_R{}^{(2)})^2\, N_R{}^{(2)}$ results, taking numerical values close to 0.5 in the temperature interval 300 K < T < 340 K. Note that not only this mean field type argument is in the same spirit as the modification[8] necessary to explain the data for the screening length but also the magnitude of the additional term is the same. This shows the internal consistency of this semiempirical argument.

If evaluating eq 3.3 with the thus modified integral, I find that curve T in Figure 3 essentially is shifted upward by a small amount. The main effect can be compensated by a small increase of the temperature-independent part of $f_{12,0}$ (eq 3.5). Neither the slope nor the curvature of the theoretical result is changed much, but for $T > 38$ °C a small effect bringing the theory closer to the experiment is seen.

I conclude that three-body interactions do not change the theoretical prediction for $R_G{}^2$ in an essential way. With the present experimental accuracy their (small) influence cannot be disentangled from ternary effects.

4. Discussion

In the original work[2] the data were interpreted as showing the cross over from the Θ-regime $R_G{}^2(T,N,c_p) \sim R_\Theta{}^2(N)$ to the semidilute excluded volume limit $R_G{}^2(T,N,c_p) \sim N((T-\Theta)/c_p N\Theta)^{1/4}$. This interpretation was supported by a double logarithmic plot (Figure 4 of ref 2), which I reproduce in Figure 4, correcting for the misplaced point $T = 38$ °C. For higher temperatures the data in fact seem to follow the predicted power law for half a decade of

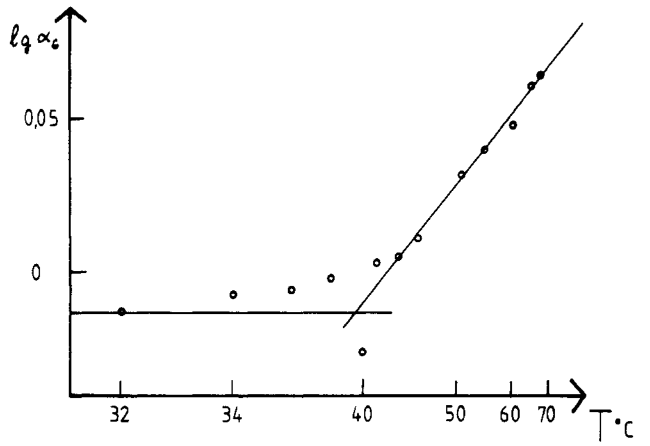

Figure 4. Doubly logarithmic plot log $\bar{R}$ versus log(T - Θ) as used in ref 2. The line with zero slope represents the "Θ-regime". The other line of slope 0.125 represents the asymptotic power law $\alpha_G \sim (T - \Theta)^{0.125}$ valid in the semidilute excluded volume regime.

($T - \Theta_D$), whereas a Θ-regime certainly cannot be identified, in particular if one ignores the point at T = 40 °C. This analysis shows that the high temperature data are consistent with binary solution theory, *provided one fits the nonuniversal binary parameters to these data only.* This was noted first in ref 7. As shown in section 2, this interpretation however is inconsistent with other very precise data on the PS(H)–C_6H_{12} system, which result in values of the nonuniversal parameters completely different from those found by naive analysis of the present data. Going into more detail, with the well-established parameter value v_{TH} = 0.41 (eq 2.10) I find that the renormalized coupling of the PS(H)–C_6H_{12} system in the parameter range discussed here obeys $f_H \lesssim 0.25$, and thus is far off the excluded volume limit $f_H \rightarrow 1$. This stresses the fact that an isolated scaling analysis of some set of data, without checking the consistency with other data, can be most misleading.

My analysis clearly has shown that the data have to be interpreted in terms of ternary solution theory. On the quantitative level the fit may not be fully satisfactory, but it is hard to say whether this is due to a deficiency of the theory or to the large statistical error of the data. There also are several sources for systematic deviations. In particular, the parameter v_{TD} of the PS(D)–C_6H_{12} system is only purely known. A change of that parameter clearly will influence the starting value $f_{12,0}$ of the ternary coupling and also might change the shape of the theoretical result. Furthermore, in view of the large statistical error of the data, in the ternary calculation I ignored polydispersity effects, which also might change the optimal value of $f_{12,0}$ by several percent. Furthermore, there are sources of systematic error in the experiment itself. In the experiment the concentration of PS(D) was kept fixed at a value corresponding to a Θ-overlap $\tilde{s}_D \sim 0.3$. In view of the fact that for temperatures well above $T = \Theta$ a rapid decrease of R_G with increasing $\tilde{s}$ starts right at $\tilde{s} = 0$ (there is no "isolated chain region" in the sense of a plateau for R_G), this value of $\tilde{s}_D$ is not really small. As a consequence the true value of R_G will be above the measured values, the effect increasing with increasing T. The consequences of an improper extrapolation to infinite dilution of the labeled polymer species recently in detail have been discussed by Kent et al.,[18] who also analyze another source of systematic error: The residual scattering of the PS(H)–C_6H_{12} system interferes with the PS(D)–C_6H_{12} signal and cannot be simply subtracted off. Furthermore recent work[19] suggests that for polystyrene chains of the length used in ref 2, chain stiffness is not completely negligible. Though this is not established beyond all doubt,[20] it in principle could be another source of systematic deviations among our theory and experiment. In view of all these problems I conclude (i) that the parameter value $f_{12,0}$ extracted here should not be taken too literally and (ii) a more involved theoretical analysis, for instance properly including three body interactions, is not appropriate with the present data.

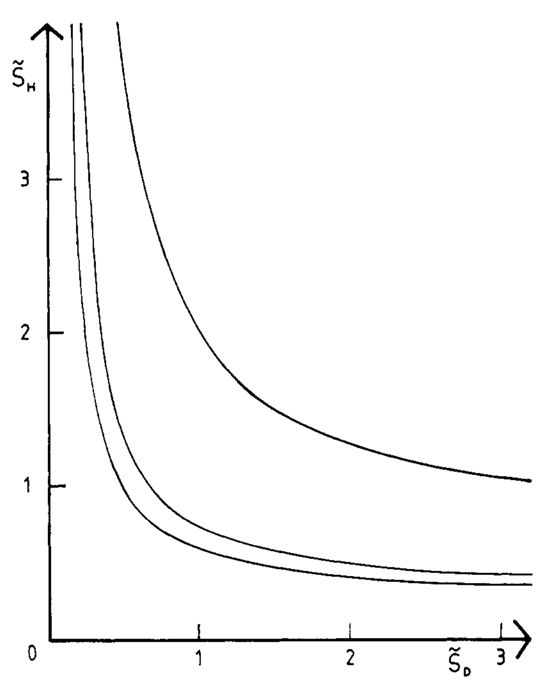

Figure 5. Spinodals of the system PS(D)–PS(H)–C_6H_{12} as calculated by renormalized Flory–Huggins theory. The chain lengths were taken to be equal: $N_D = N$. Parameter values of the curves (from top): $N = 10^3$, T = 40 °C; $N = 10^4$, T = 50 °C; $N = 10^4$, T = 40 °C.

The PS(D)–PS(H)–C_6H_{12} system is a most interesting example of a ternary solution not close to a scaling limit but deep in the cross-over regime. It thus allows for a critical test of the recently established theory. However, the situation clearly longs for more experimental information. In particular, the characterization of the binary PS(D)–C_6H_{12} system is insufficient. Light scattering experiments on dilute solutions measuring $R_G{}^2$ of A_2 to a precision comparable to that reached for the PS(H)–C_6H_{12} system would allow for an unambiguous determination of the nonuniversal parameters l_D, v_{TD}. Independent information on the ternary parameter $f_{12,0}$ could be gained by localizing the spinodal of the two fluid phase separation of the PS(D)–PS(H)–C_6H_{12} system. Such experiments should be carried out through sufficiently far above Θ_H, so that the effects of three-body forces, which certainly will influence the spinodal for $T \sim \Theta$, can be neglegted. Using the parameter values as determined here, I for some temperatures and chain lengths evaluated the spinodal using renormalized Flory–Huggins theory,[9,21] which is the lowest order approximation of renormalized perturbation theory. The analytical expressions are given in the Appendix. Numerical results are shown in Figure 5. Being based on a lowest order calculation and using parameter values of unknown reliability, the results of Figure 5 should be viewed as order of magnitude estimates rather than as quantitative predictions. Still we may conclude that for reasonably long chains ($N \gtrsim 5000$) the spinodal should extend into the region of low concentrations: $c \lesssim 10^{-1}$ g/cm^3. A precise determination, including the temperature dependence, would allow for a more reliable determination of the ternary parameters.

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Appendix A: The Renormalization Group Mapping

I here summarize the equations[10] used for mapping the unrenormalized theory to its renormalized counterpart. For the binary variables of species a I use

$$\tilde{z}_a = N_R^{(a)1/2} f_a (1-f_a)^{-1.059} (1 + 0.824 f_a)^{0.25} \qquad \text{(A1)}$$

$$c_R^{(a)} = N_R^{(a)-1/2} (1-f_a)^{-0.572} \tilde{s}_a \qquad \text{(A2)}$$

$$l_R^2 = N_R^{(a)-1} (1-f_a)^{-0.381} R_{\Theta,a}^2 \qquad \text{(A3)}$$

The renormalized length scale l_R is independent of the species. The physical variables $\tilde{z}_a$, $\tilde{s}_a$, and $R_{\Theta,a}^2$ have been defined in eqs 2.4 and 2.5.

The ternary coupling obeys the differential equation

$$l_R \frac{d}{dl_R} f_{12} = f_{12}\left(1 - \frac{f_{12}}{f_{12}^*(f_1,f_2)}\right)\left[w_{12}^{(0)}(f_1,f_2) \times \left(\frac{f_{12}}{f_{12}^*(f_1,f_2)} - 1\right) + w_{12}^*(f_1,f_2)\frac{f_{12}}{f_{12}^*(f_1,f_2)}\right] \qquad \text{(A4)}$$

$$f_{12}^*(f_1,f_2) = 2 - \frac{1}{2}(f_1+f_2) - (0.133 + 0.128(f_1+f_2)) \times \left(1 - \frac{f_1+f_2}{2}\right)^2 + \frac{0.1575(f_1-f_2)^2}{1 + 0.1125(f_1+f_2)} \qquad \text{(A5)}$$

$$w_{12}^{(0)}(f_1,f_2) = \sum_{a=1}^{2} 0.305 f_a \left(1 + \frac{0.220(1-f_a)}{1 + 0.978 f_a}\right) - 1 \qquad \text{(A6)}$$

$$w_{12}^*(f_1,f_2) = 0.820 - 0.140(f_1 + f_2 + f_1 f_2) \qquad \text{(A7)}$$

Equation A.4 is to be integrated with the initial condition

$$f_{12}(l_R = l_H) = f_{12,0} \qquad \text{(A8)}$$

The structure of these equations has been explained in the Appendix of ref 10.

These equations define renormalized parameters as functions of the renormalized length scale l_R, where a priory is a free parameter. This freedom is fixed by imposing the condition[10]

$$1 = \frac{1}{N_R^{(1)}} + 2 f_1 c_R^{(1)} + 2 f_{12} c_R^{(2)} \qquad \text{(A9)}$$

I finally recall the equation[9,21] for the spinodal. Renormalized Flory–Huggins theory yields

$$0 = 1 + f_1 c_R^{(1)} N_R^{(1)} + f_2 c_R^{(2)} N_R^{(2)} + (f_1 f_2 - f_{12}^2) c_R^{(1)} c_R^{(2)} N_R^{(1)} N_R^{(2)} \qquad \text{(A10)}$$

This equation has to be evaluated with the RG-mapping as given above. l_R, however, has to be determined by a condition symmetric in the two species:

$$1 = \frac{1}{2N_R^{(1)}} + \frac{1}{2N_R^{(2)}} + f_1 c_R^{(1)} + f_2 c_R^{(2)} + \left[\left(\frac{1}{2N_R^{(1)}} - \frac{1}{2N_R^{(2)}} + f_1 c_R^{(1)} - f_2 c_R^{(2)}\right)^2 + 4 f_{12}^2 c_R^{(1)} c_R^{(2)}\right]^{1/2} \qquad \text{(A11)}$$

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