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Conformations of a Long Polymer in a Melt of Shorter Chains: Generalizations of the Flory Theorem

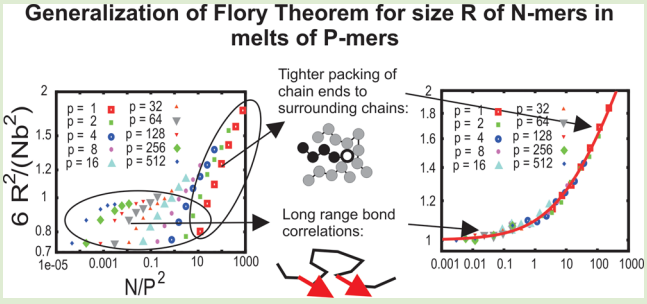
Michael Lang,*[,†] Michael Rubinstein,[‡] and Jens-Uwe Sommer[†,¶]

[†]Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany

[‡]Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290, United States

[¶]Institute of Theoretical Physics, Technische Universität Dresden, Zellescher Weg 17, 01062 Dresden, Germany

ABSTRACT: Large-scale simulations of the swelling of a long N-mer in a melt of chemically identical P-mers are used to investigate a discrepancy between theory and experiments. Classical theory predicts an increase of probe chain size $R \sim P^{-0.18}$ with decreasing degree of polymerization P of melt chains in the range of $1 < P < N^{1/2}$. However, both experiment and simulation data are more consistent with an apparently slower swelling $R \sim P^{-0.1}$ over a wider range of melt degrees of polymerization. This anomaly is explained by taking into account the recently discovered long-range bond correlations in polymer melts and corrections to excluded volume. We generalize the Flory theorem and demonstrate that it is in excellent agreement with experiments and simulations.



The description of macromolecular conformations in various environments is one of the cornerstones of polymer physics research. A fundamental test of standard models of polymer conformations is the problem of an N-mer immersed in a melt of chemically identical P-mers. This question has been addressed by numerous works in the past[1−6] and was considered to be well understood from the theoretical point of view. In all of these works it was argued that a scaling variable proportional to N/P^2 describes the crossover between ideal and swollen chain conformations.[5] However, the available experimental data[7−11] turned out to be in rather poor agreement with the theoretical predictions. Some studies even propose a significantly different scaling of the chain size[7,10,11] in its crossover between swollen and ideal chain conformations with increasing molecular weight of the matrix polymers. In this letter, we generalize the Flory theory by taking into account the recently proposed long-range bond correlations[12,13] and corrections to excluded volume in dense polymer systems. We demonstrate that the generalized Flory theorem is in excellent agreement with experimental and simulation data.

In the following, we use P and N to denote the number of Kuhn segments per matrix and guest chains, respectively. The Flory theorem is based upon the concept that the monomeric excluded volume parameter in a melt of P-mers is screened by a factor of $1/P$ and, thus, very small for large P. The root-mean-square radius of gyration R of dilute N-mers in a melt of P-mers can be estimated by minimizing free energy ΔF (dropping all coefficients on the order of unity)

$$\frac{\Delta F}{kT} \approx \frac{R^2}{R_0^2} + \frac{v}{P}\frac{N^2}{R^3} + \frac{R_0^2}{R^2} \tag{1}$$

where k is the Boltzmann constant; T is the absolute temperature; and v is the excluded volume in a liquid of Kuhn monomers. The first term of the free energy describes the entropic penalty for swelling a chain with N segments from its ideal size $R_0 \approx b(N/6)^{1/2}$ to R, whereby b is the length of a Kuhn segment. The second term is the mean field estimate of the interaction of N monomers with excluded volume parameter v/P randomly distributed over the chain volume R^3. The third term is the confinement free energy. Denoting the swelling ratio by $\alpha = R/R_0$, eq 1 can be rewritten as

$$\frac{\Delta F}{kT} \approx \alpha^2 + \frac{Z}{\alpha^3} + \frac{1}{\alpha^2} \tag{2}$$

where the interaction parameter

$$Z \simeq (v/b^3)N^{1/2}/P \tag{3}$$

determines the strength of the excluded volume interactions (Z^2 is proportional to the number of "thermal blobs"[14] per N-mer). Minimization of free energy ΔF (eq 2) leads to a swelling ratio as a function of the interaction parameter

$$\alpha = R/R_0 = f(Z) \tag{4}$$

For melt chains with $P \gg N^{1/2}$ this interaction parameter is small, $Z \ll 1$, and the size of an N-mer in the melt of relatively long P-mers (determined by balancing the first and third terms of eq 2) is almost ideal with swelling ratio $\alpha \approx f(0) = 1$.

For shorter melt chains $P \ll N^{1/2}$, the interaction parameter is large, $Z \gg 1$, and the size of the polymer is determined by

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balancing the first two terms of the free energy eq 2 (since the confinement term is not important for swollen chains) with $f(Z) \sim Z^{1/5}$. In this case of $P \ll N^{1/2}$, one obtains[1,14] the size of a swollen N-mer

$$R \approx v^{1/5} b^{2/5} P^{-1/5} N^{3/5} \tag{5}$$

For monomeric solvent, $P = 1$, this leads to the well-known $R \approx bN^{1/2}(N^{1/2}vb^3)^{2\nu-1}$ with scaling exponent $\nu = 3/5$ close to the exponent $\nu = 0.588$ obtained by more accurate numerical methods.[15]

In order to test the above predictions and in order to explain the discrepancy between theoretical prediction and experimental data we simulated bidisperse melts of linear chains using the bond fluctuation model.[16] This simulation method was frequently used to study polymer melts and networks (see refs 12 and 17 and the references therein). To distinguish between Kuhn segments and degrees of polymerization of the simulated chains, we denote the latter by small letters p and n for melt and guest chains, respectively. We relate the degree of polymerization to the number of Kuhn segments via $p = C_\infty P$ and $n = C_\infty N$.[18] All samples of the present study contain 2^{17} monomers at a "lattice occupation density" of 50% of the maximum possible monomer occupation density, which refers to a monomer number density of 1/16 that is considered[19] as a concentrated solution with melt-like properties. As a starting point we used a well-equilibrated monodisperse melt of chains containing 512 monomers each. The degree of polymerization p of the bulk material and test chain degree of polymerization n were chosen as $p = 2^i$ with $i = 0, ..., 9$ and $n = 2^j$ with $j = 3, ..., 9$. A randomly selected fraction of 1/32 of the 512-mers was cut down to degree of polymerization n, while the 31/32 of all 512-mers were cut down to p. This volume fraction is sufficiently low that the n-mers in all samples are below their overlap volume fraction. Thereafter, the samples were relaxed for at least one more relaxation time of the longest chains in the sample. Furthermore, it was checked that the melt chains reached conformations with corrections to ideal behavior as described in ref 12. Afterward, conformations were sampled for a duration of 10^9 simulation steps for $n = 512$, which is roughly five relaxation times of the longest chains in a monodisperse melt. For shorter chains, the conformations were sampled for at least 20 relaxation times, as defined by the end-to-end vector autocorrelation time. Error bars for the root-mean-square radius of gyration R were computed from the mean fluctuations of the ensemble average of the R data as a function of time divided by the square root of the number of relaxation times of the chains in order to provide an accurate estimate of the statistical significance of each data point.

The classical works based on the Flory theorem[1−6] predict a universal plot for chain swelling ratio $\alpha = R/R_0$ as a function of $Z \propto N^{1/2}/P$. Figure 1, which is a naive plot of α^2 as a function of $N/P^2 \propto Z^2$ using $N/P^2 = nC_\infty/p^2$ with Flory's characteristic ratio $C_\infty = 1.52$ from ref 12, shows that this procedure does not lead to a collapse of the data. Thus, neither the experimental data[8−11] nor our simulation data agree with the classical prediction that the swelling ratio $\alpha = R/R_0$ is a universal function of the interaction parameter $Z \propto N^{1/2}/P$.

Several previous experimental studies proposed a significantly different scaling of the chain size[7,10,11] as a function of N/P instead of $N^{1/2}/P$. For this phenomenological scaling, we obtain a better but yet not satisfactory overlap of the simulation data in Figure 2. Notably, large deviations are found for $N/P < 10$ in Figure 2. This figure also contains a comparison[20] with the data

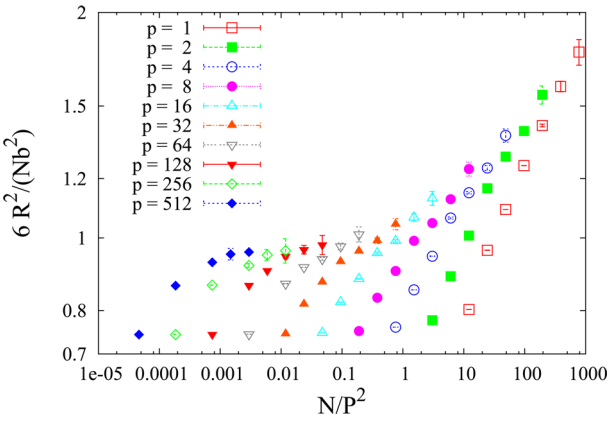

Figure 1. Lack of overlap of the simulation data of the ratios of the mean square radii of gyration R^2 of chains with N Kuhn segments in a melt of chains with P Kuhn segments to their ideal mean square radii of gyration $R_0^2 = b^2N/6$ using the classical scaling variable N/P^2.

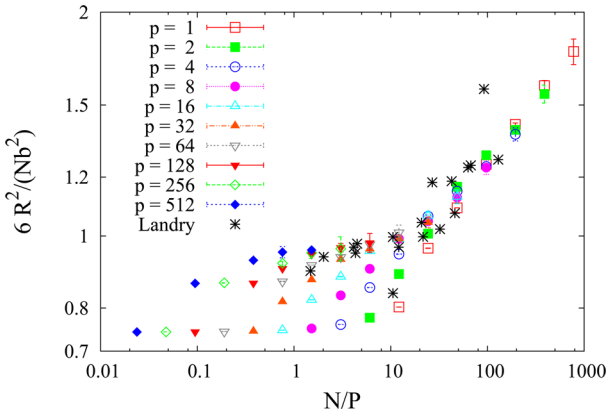

Figure 2. Partial overlap of the ratios of mean square radii of gyration R^2 of chains with N Kuhn segments in a melt of chains with P Kuhn segments to their ideal mean square radii of gyration $R_0^2 = b^2N/6$ using the nonclassical scaling variable N/P of Landry.[7] Same symbols for simulation data as in Figure 1; experimental data of ref 7 are depicted by black stars.

of Landry.[7] Both Figures 1 and 2 are suggesting that significant corrections for the unswollen regime are necessary.

Recently, it was emphasized[12,13] that the intramolecular bond correlation function in dense melts decays as a power law in contrast to an exponential decay for chains without long-range correlations. This leads to a partial swelling of polymer chains even in monodisperse melts with the mean square radius of gyration of a chain with n monomers approximated[12] by

$$\bar{R}_0^2 = \frac{C_n n l^2}{6} \tag{6}$$

with characteristic ratio

$$C_n = C_\infty\left(1 - \frac{c}{\sqrt{n}}\right) \tag{7}$$

The coefficient $c = 0.656$, root-mean-square bond length $l = 2.636$, and $C_\infty = 1.52$ were determined in ref 12 at simulation conditions identical to the present study. We expect that long n-mers dissolved in small p-mers start swelling from this new reference chain size $\bar{R}_0$. Thus, we define the expansion factor $\bar{\alpha} \equiv R/\bar{R}_0$ with this new reference size for the discussion below.

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To test this hypothesis quantitatively, we compute the new swelling ratio $\bar{\alpha}$ for all data and solve eq 2 numerically. Note that we return here to the original interaction parameter, eq 3, with the scaling variable $\propto N/P^2$ where N and P are numbers of Kuhn segments in test and melt chains, respectively. The excluded volume v is the only adjustable parameter. We obtain $v/b^3 = 0.17$ from a best fit to all simulation data. Figure 3 shows

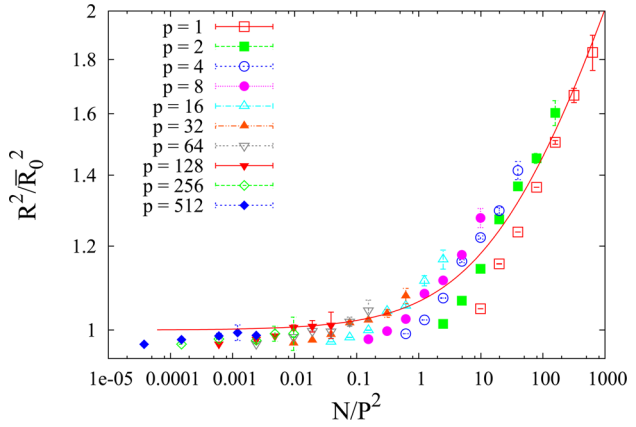

Figure 3. Ratios of mean square radii of gyration R^2 of chains with N Kuhn segments in a melt of chains with P Kuhn segments to their mean square radii of gyration $\bar{R}_0^2$ in monodisperse melt corrected for long-range bond correlations (eq 6). The line is the best fit of all data to the numerical solution of eq 2 for swelling ratio $\bar{\alpha} = R/\bar{R}_0$ with $v/b^3 = 0.17$.

that the above correction improves the overlap of the data at small $N/P^2 < 1$, but no unique crossover function of the data is obtained. Instead, the data show a systematic shift for small p.

For a lattice model with lattice constant smaller than monomer size or for off-lattice models, the excluded volume of a single monomer is larger than the bare volume of a monomer in contrast to regular lattice models including Flory–Huggins theory. Furthermore, denser packing with submonomer-size spacing between monomers becomes possible in models with a grid finer than monomer size. Thus, the gain in the net conformational entropy when placing chain ends in nearest positions next to inner monomers leads to a denser packing of chain ends next to other monomers similar to the enrichment of chain ends near a solid wall.[21] This is in accord with the fact that we detected a clearly larger fraction of p-mer chain ends as compared to inner monomers in nearest-neighbor positions of the monomers of n-mers.

An n-mer in a melt of p-mers is in contact with $\propto n/p$ ends of surrounding chains. Since the ends of p-mers pack closer to n-mers, the effective volume fraction $\bar{\phi}$ excluded by n-mers decreases with increasing concentration of ends of p-mers (with decreasing p). Similarly, the ends of n-mers contribute less to the total excluded volume of n-mers by a closer packing to surrounding monomers. In consequence, the inner monomers of the n-mers experience a different packing of ends of the surrounding p-mers. Such corrections to ϕ proportional to the concentration of chain ends of p-mers are expected to be

$$\bar{\phi} = \phi(1 - y/n)(1 - z_n/p) \tag{8}$$

with numerical constants y and an n-dependent z_n that can be determined directly from simulation data.

To detect whether there are indeed such corrections to the effective excluded volume fraction $\bar{\phi}_n$ (eq 8), we performed the following analysis: First, we calculated the number fraction of lattice sites that are accessible for inserting an additional monomer in all bidisperse blends. Next, we removed all n-mers (a number fraction of 1/32 of all monomers) from all snapshots of the bidisperse samples and repeated this analysis. The difference in the number fraction of accessible sites for bidisperse samples with n-mers removed and the original bidisperse samples measures the effective volume fraction $\bar{\phi}_n$ that is blocked by n-mers. The results of this analysis display a reasonable agreement with the correction proposed in eq 8 as shown in Figure 4. As we see from the fit, the effective excluded

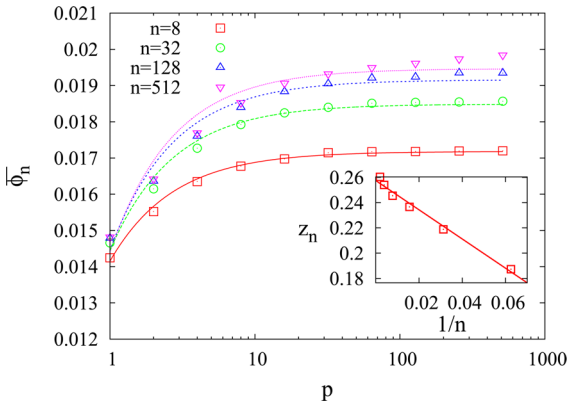

Figure 4. Corrections to the volume fraction of n-mers in binary blends with p-mers (eq 8), with $\phi = 0.0194 \pm 0.001$, $y = 1.3 \pm 0.1$, and $z_n \approx 0.26(1-1.2/n)$ approaching $z_\infty = 0.26 \pm 0.01$ for large n (inset).

volume fraction for long matrix chains $p \gg 1$ increases with degree of polymerization of test chains n as $\bar{\phi} \propto \phi(1 - y/n)$, due to the smaller excluded volume of chain ends. The asymptotic value $\phi = 0.0194$ for n, $p \gg 1$, corresponds to an average of 9.93 lattice sites excluded per test chain monomer. The effect of the ends of p-mers described by parameter $z_n \approx 0.26(1 - 1.2/n)$ (see Figure 4 inset) increases roughly with the fraction of inner monomer sections $1 - 1/n$ at which the ends of p-mers prefer to pack. In this work we consider relatively long[22] test chains; therefore, we neglect the y/n correction to $\bar{\phi}$ in eq 8. For similar reasons, we use the limiting value of z_∞ in our analysis below.[23] This reduces the expression for the effective volume fraction to

$$\bar{\phi} \approx \phi(1 - z_\infty/p) \tag{9}$$

with $\phi = 0.0194$ and $z_\infty = 0.26 \pm 0.01$.

In the framework of the Flory–Huggins model, the excluded volume interaction is[14] $\propto (v/P)\bar{\phi}^2$, and the p-dependence of the volume available for n-mers is considered by replacing P by $P/(1 - z_\infty/(PC_\infty))^2$ with $z_\infty = 0.26$ in the expression for the interaction parameter.

This leads to a modified interaction parameter

$$\hat{Z} \simeq (v/b^3)N^{1/2}(1 - z_\infty/(PC_\infty))^2/P \tag{10}$$

In Figure 5, we plot the normalized mean square radius of gyration of chains with N Kuhn segments, $\bar{\alpha}^2 = R^2/\bar{R}_0^2$, as a function of $N(1 - z_\infty/(PC_\infty))^4/P^2 \propto \hat{Z}^2$. The parameter c in the expression for mean square reference size of chains, $\bar{R}_0^2$, (eq 6 and 7) is varied to optimize the collapse of the data along the y-axis. Optimum overlap is obtained for $c = 0.86 \pm 0.03$, if data for $N < P$ are ignored (see Figure 5). Next, we fit the minimum of

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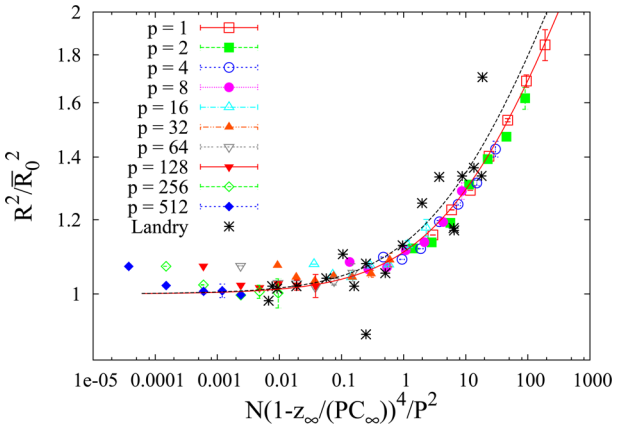

Figure 5. Ratio of mean square radius of gyration R^2 of chains with N Kuhn segments in a melt of chains with P Kuhn segments to their mean square radius of gyration $\bar{R}_0^2$ corrected for long-range bond correlations (eq 6). Abscissa is proportional to the square of the interaction parameter $\hat{Z}^2$ corrected for the effective volume fraction of test chains (eq 10). Red solid line is best fit of the numerical solution of eq 11 to simulation data, and dashed line is the fit of solution of eq 11 to experimental data.

$$\frac{\Delta F}{kT} \approx \bar{\alpha}^2 + \frac{\hat{Z}}{\bar{\alpha}^3} + \frac{1}{\bar{\alpha}^2} \tag{11}$$

to the data in Figure 5 resulting in a best fit for the excluded volume parameter $v/b^3 = 0.30 \pm 0.01$ (see red solid line in Figure 5). Our optimum value of parameter $c = 0.86$ is larger than $c = 0.656$ of refs 12 and 13 which was obtained for monodisperse melt data ignoring the contribution of excluded volume interactions. Our slightly larger value of c corresponds to a smaller size of test chains in a melt of infinitely long matrix chains in comparison to weakly swollen chains in monodispersed melt. The increase of the excluded volume parameter from $v/b^3 = 0.17$ in Figure 3 to $v/b^3 = 0.30$ in Figure 5 results from the corrections to the interaction parameter (eq 10).

The experimental data of ref 7 are added to Figure 5 using the optimal value of parameter $c \approx 5 \pm 3$ to ensure $R^2/\bar{R}_0^2 = 1$ for small N/P^2. The best fit of experimental data to the solution of eq 11 is shown by the dashed curve in Figure 5 with excluded volume parameter $v/b^3 = 0.38 \pm 0.03$.[24] We observe a clearly better collapse of the experimental data as a function of the corrected interaction parameter $\propto \hat{Z}^2$ with a chain expansion that follows the classical prediction instead of a scaling $\propto N/P$ as suggested in ref 7.

Interestingly, it is not possible to fully collapse the simulation data in Figure 5 at small $N(1 - z_\infty/(PC_\infty))^4/P^2$, if $N < P$. The Flory approach seems to break down for $N < P$, possibly because the surrounding p-mers no longer fit into the pervaded volume of an n-mer. Instead, only sections of $\approx n$ monomers of the larger p-mers are overlapping with the n-mer. In consequence, the excluded volume contribution (but not the correction due to packing of ends) becomes similar to the contribution in monodisperse melts $\propto v/N$ instead of $\propto v/P$ for $N < P$. This can be taken into account by using a new interaction parameter

$$\tilde{Z} \simeq (v/b^3)N^{1/2}(1 - z_\infty/(PC_\infty))^2/\min(P, N) \tag{12}$$

The resulting plot in Figure 6 leads to an overlap of all data[25] confirming that these three corrections are necessary to understand the conformations of n-mers in a melt of p-mers:

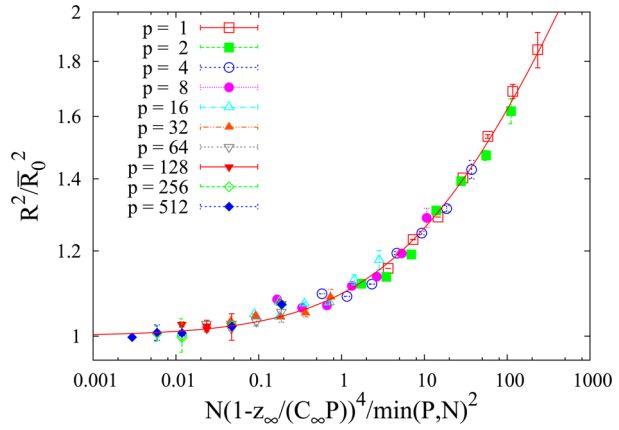

Figure 6. Computer simulation data[23] from Figure 5 with overlap correction to excluded volume (eq 12).

(a) long-range correlations due to intramolecular contacts, (b) p-dependence of the volume fraction $\bar{\phi}_n$ occupied by n-mers, and (c) the correction to the excluded volume for long matrix chains $p > n$.

Our analysis demonstrates that the swelling of n-mers approaches the classical prediction for sufficiently large p and n. Less than 10% shift from the limiting case is obtained for our simulation data, if $n > 100c \approx 86$ (shift along y-axis) or $p \gtrsim 38z_\infty \approx 10$ (shift along x-axis), when plotting the data as a function of $\tilde{Z}^2$. It is also evident from our discussions that the effect of correlations in bond orientations modify predominantly the unswollen regime $N/P^2 < 1$, while the corrections to excluded volume are most important for small p and, thus, predominantly for $N/P^2 > 1$. Furthermore, data with $P > N$ can be collapsed, if the excluded volume is computed as a function of $\min(P, N)$. Previous observations[7,10,11] of the data scaling with N/P rather than N/P^2 can be understood from the combined effect of these corrections.

AUTHOR INFORMATION

Corresponding Author

*E-mail: lang@ipfdd.de.

Notes

The authors declare no competing financial interest.

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(22) Short chains of $n \approx 10$ hardly swell; a 10% correction to $\overline{\phi}$ for $n \approx 10$, for instance, leads to less than 2% swelling of chain size, which is about the symbol size in Figure 5.
(23) When using z_∞ instead of z_n a maximum error of about 1% is found for estimating chain size of $n = 10$.
(24) The smallest p are ≥ 24 and thus too large for a reliable determination of z_∞. Therefore, we used $z_\infty = 0.26$ from the simulation data as a first estimate. Additional data at small N and P are required for a better determination of c and z_∞.
(25) Data of Landry[7] were not included because no blends with test chains shorter than matrix polymers, $N < P$, were reported.

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