Swollen Conformations of Associating Polymer Chains

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ABSTRACT: Equilibrium statistics of a single associating polymer chain are studied by means of extensive Monte-Carlo computer simulations. The chain is treated as a self-avoiding random walk. Each associating group or sticker is constrained to be adjacent to one other sticker, though stickers are free to change partners. In three dimensions chains with alternating long and short intervals between the stickers have a swollen conformation for almost all sticker placements, with the predominant association occurring between chemically nearby groups. The observed swelling is consistent with a Flory picture with an excluded volume parameter that varies *linearly* with the placement asymmetry x, defined as the ratio of the short interval to the sum of the long and short intervals between the stickers. A scaling analysis of the simulations is used to estimate that a chain with $x = 0.496 \pm 0.004$ will behave as an ideal chain in the asymptotic limit. Since the maximum x equals 0.5, in which case the stickers are equally spaced, collapsed behavior is only possible for chains with almost equally spaced stickers. In two dimensions I find swollen conformations for all sticker placements. The single chain behavior is related to the solution properties of many-chain systems.

Introduction

Flexible polymers in a good solvent behave as self-avoiding random walks. Adding a few ionic neutralized acid groups to the polymer backbone might change this behavior drastically, though. When dissolved in a nonpolar solvent, the ionic groups tend to associate or stick together into small, long-lived multiplets,[1] which serve to attach chains to themselves and to one another. As a result these strongly associating ionomers form labile polymer networks. This network formation gives rise to their distinctive rheological properties.[2-4] Because of these rheological properties, e.g. shear thickening under proper conditions, associating polymers are currently of considerable interest.[2] The solutions show signs of phase instability, as well.[5,6] For example Lantman et al.[6] find that sulfonated polystyrene of molecular weight 10^6 is insoluble in tetrahydrofuran if the sulfonation level reaches 3.2 mol %. A mechanism has been proposed which suggests that this phase instability is intrinsic to the associating property.[7] Associations are a form of attraction of polymer chains to themselves and one another. Usually, such attraction, if strong, leads to a collapse of individual polymers and to phase separation of solutions. So the strong associations that give rise to good shear thickening properties might be inherently incompatible with good solvation properties.

Recently, Cates and Witten[7] suggested that this solubility problem could be solved by controlling the chain architecture. Here this mechanism is explored by means of extensive Monte-Carlo computer simulations. In the athermal model used, the associating property is treated as a geometric constraint. This simplification is justified by the fact that the distinctive molecular feature which gives rise to shear thickening and phase instability is essentially geometric and embodied in the strong tendency of the ionic groups to be together. Each configuration consists of a self-avoiding random walk, with a small number of ionic groups or "stickers" placed along side. Each sticker is constrained to be adjacent to one other sticker. Stickers are free to change partners, though. This freedom results in an entropic attraction and constitutes an attractive free energy. The entropic attraction competes with the excluded volume repulsion. The free energy of sticking is irrelevant, since all the configurations have the same number of sticker pairs, hence the same sticking energy. In previous work[8] it has been shown that indeed the net mutual interaction between polymer chains depends crucially on the placement of the stickers: The net interaction between two chains containing two stickers each changes from repulsive to attractive when the separation between the stickers is roughly 80% of the chain length.

In this paper I study the equilibrium behavior of a single long chain, made by joining our two sticker segments head to tail (see Figure 1). The resulting chain has alternating short and long intervals between the associating groups. A parameter x defines the chain architecture. x is defined as the length of the short interval divided by the sums of the lengths of the short and long intervals between the stickers. In the $x = 0$ limit the chain behaves as an ordinary polymer chain and has a swollen configuration. However, if x is increased, one might arrive at architectures for which the chain collapses. In that case there is also a critical placement, x_c for which a chain will show the statistical behavior of an ideal polymer chain in the asymptotic (large N) limit. For this architecture one might expect that in the asymptotic limit the net interaction (expressed as a second virial coefficient) of many chains in dilute solution vanishes.[9,10] For $x < x_c$ one expects such a solution to behave as an ordinary polymer solution, for $x > x_c$ however the attraction between the different chains might result in phase separation. So, when the equilibrium behavior of long chains is studied as function of their architecture, insight in their solution behavior is obtained as well.

Other studies on the equilibrium conformations of chain molecules containing several interactive sites have been done.[11-14] There many effects are studied simultaneously in an attempt to make realistic models, for either proteins or polyelectrolytes. Simulations on associating polymers using geometrical models similar to mine have likewise been done.[15,16] These two-dimensional studies explore cluster formation in many chain systems. Although in this case too a general dependence on the chain architecture was observed, this dependence has not yet been studied in detail.

Simulation Details

A configuration consists of a random walk chain on a simple cubic lattice. Each step of the random walk goes to a first, second, or third neighbor site (third neighbor

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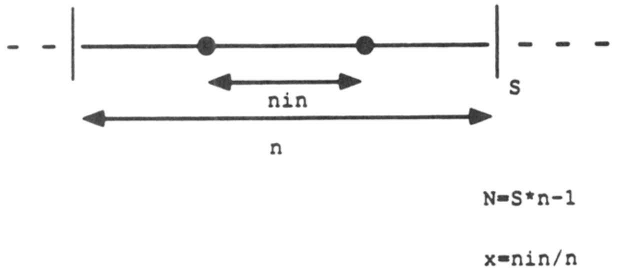

Figure 1. Chain architecture. Each chain consists of S equal segments. Each segment contains two symmetrically placed stickers. A parameter x defines the chain architecture. x is defined a the distance between the stickers over the segment length. The stickers are shown as black dots. Each segment consists of n monomers; the total number of bonds N equals $Sn - 1$.

sites are not allowed in two dimensions). No two steps of the walk occupy the same lattice site. A few monomers along the chain are designated as stickers. Figure 1 shows their placement. Each chain contains S identical segments. Each segment is n monomers long and contains two stickers. A parameter x specifies the sticker placement. x is defined as the distance between the stickers over the segment length. Each sticker is paired with one other sticker. Paired stickers occupy adjacent lattice sites. Parts a and b of Figure 2 show some typical configurations.

I will call a configuration as defined above an "allstuck" configuration. In the Monte-Carlo algorithm additional configurations in which not all stickers have a partner are allowed too. These "unstuck" configurations are intermediate configurations which take the system from one allstuck configuration to a new one, in which the stickers are paired differently. When averaging to obtain physical quantities, only the allstuck configurations are used. This strategy is based on the Metropolis importance sampling method.[17,18] In importance sampling methods each configuration X is sampled with a certain probability $w(X)$. When averaging to obtain physical quantities, one has to make adjustments for this probability. Usually, importance sampling techniques are used to explore preferentially those parts of the configuration space that contribute most to the physical quantities. I will explain how the technique is used. In a realistic (thermal) model of associating polymers one would allow the stickers to disconnect with a small probability $e^{-U/kT}$. Here U is the attractive energy between the associating groups and a typical value for strong associations is $10kT$. With such strong attraction and small probability for the stickers to disconnect, it is computationally almost impossible to sample enough statistically uncorrelated configurations. Instead, an importance sampling technique with weight function $w = e^{-p(W-U)/kT}$ is used. Here p is the number of disconnected sticker pairs and W is an adjustable parameter with $W \ll U$. This amounts to allowing the stickers to disconnect with a probability $e^{-W/kT}$ during the simulation. Since W is small, the stickers will have lots of opportunities "to explore" different partners and the configurational space is sampled much faster. In order to obtain physical quantities, e.g. the radius of gyration of the chain, a correction for the weight function has to be made. This amounts to multiplying each value with $e^{p(W-U)/kT}$. For strong associations (high U) one will find that only configurations with all stickers paired ($p = 0$) contribute to the weighted average. It is in this spirit that I call my model athermal.

Two kinds of moves are used in this Monte-Carlo algorithm. To sample chain configurations with fixed sticker positions, I use a bead jump algorithm, recently devised by Murat and Witten.[19] Local moves to nearby lattice sites change the positions of the stickers. The bead jump mechanism has been proven[19] to be a statistically unbiased sampling procedure and to produce well-known scaling results on single chains and loops. Each move is a bead jump in which a monomer (bead) is removed from one place on the chain and inserted at another. The details of the algorithm are described elsewhere.[7,8] The computational time for a single chain of molecular weight N to relax is empirically[19] of the order N^3. This time is defined, e.g., as the time for the chain to diffuse its own radius of gyration. Here I use the bead jump algorithm to relax the chain intervals between the stickers separately, so that the overall chain architecture does not change. In the sticker moves, an arbitrary sticker is chosen and moved to a lattice site less than the maximum bond length away from its predecessor on the chain. The move is accepted

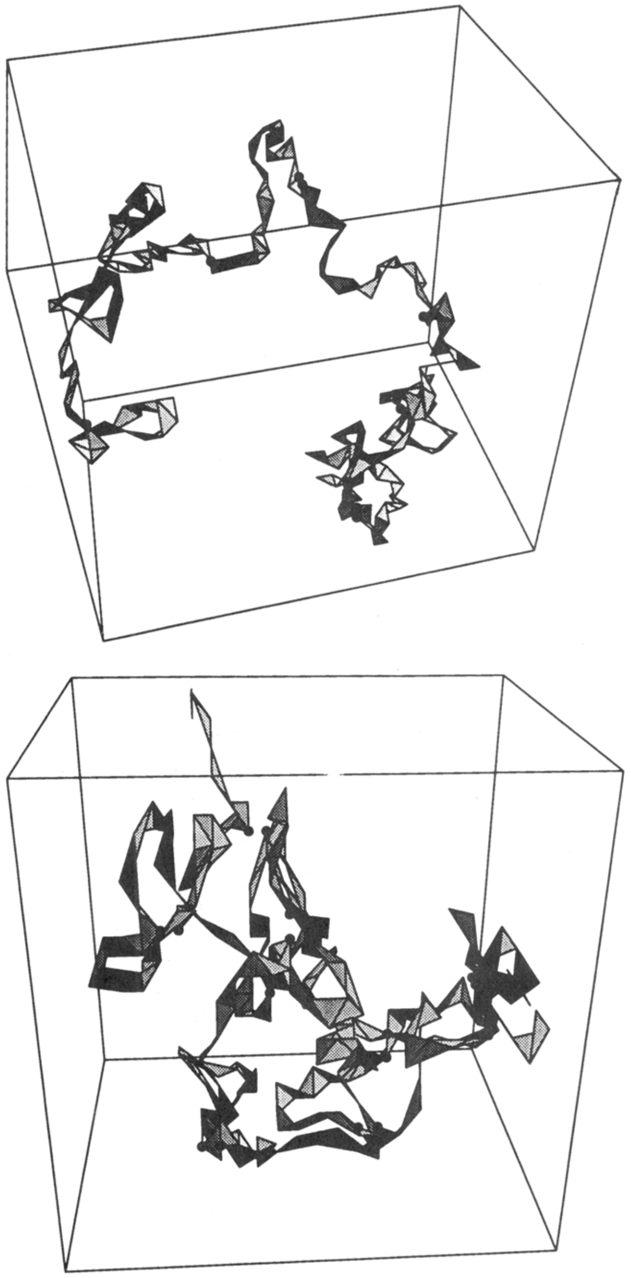

Figure 2. Typical chain configurations for $x = 0.147$ (a, top) and $x = 0.5$ (b, bottom). In the first case the sticking is predominantly between chemically nearby groups; in the second case sticking between distant groups can be observed. To show depth a polygon is plotted, for each three adjacent coordinates $\vec{r}_{i-1}$, $\vec{r}_i$, $\vec{r}_{i+1}$ of the chain if $i = 2$ to N. The stickers are shown as black dots.

when the picked site is empty and when the new bond length to its successor does not exceed the maximum bond length. In addition a paired sticker has to move to a site adjacent to its partners site. Moves that break the sticker pair are accepted with a small probability $e^{-W/kT}$. W has to be adjusted very carefully. Its sole purpose is to lower the energy barriers between the minima of the multidimensional energy surface. If W is too high, the energy barriers between the energy minima (that is allstuck configurations) prohibit the system to sample over configurations with different sticker combinations within a tractable amount of computational time. On the other hand, if W is too low too much time is used sampling unstuck configurations. The best value for W turns out to be the one for which the stickers are approximately 10% of the time allstuck. This value is found by maximizing the number of times that two sticker pairs dissociate and associate again with new or old partners. Each time that an unpaired sticker is moved, I check if a new pair is formed. This is the case if two unpaired stickers occupy adjacent lattice sites. Note that, when an unpaired sticker is adjacent to a sticker pair, it will not be connected to it. In case an unpaired sticker moves to a lattice site adjacent to two or more unpaired stickers, the moving sticker is paired with one of them at random. The ratio of sticker moves over monomer moves is adjusted so that there is approximately one successful sticker move for every $n/2$ successful monomer moves.

In the initial configuration all stickers are separate. Before sampling, the system is equilibrated. The equilibrium time τ, that is the number of bead jump moves it takes to get to an independent configuration, is estimated from the decay in the autocorrelations (C_{R_g}) in the radius of gyration (R_g):

$$C_{R_g}(t) = (\langle R_g(t)R_g(0)\rangle - \langle R_g\rangle^2)/(\langle R_g^2\rangle - \langle R_g\rangle^2) \qquad (1)$$

Figure 3a shows this decay for $S = 8$, $n = 34$, and $x = 0.441$. The decay time is 6×10^7 bead jumps. One might worry that during this time the chain has sampled over configurations with fixed sticker connections but that the stickers did not have enough time to find new partners. In that case one expects a second relaxation at much longer time scales, that is caused by the relaxation of the sticking configuration. I saw no signs of such relaxation, but then decided to check it differently. Consider the quantity F, defined as the distance along the chain backbone from one fixed sticker (in the middle of the chain) to its partner. The autocorrelations in F are given by

$$C_F(t) = (\langle F(t)F(0)\rangle - \langle F\rangle^2)/(\langle F^2\rangle - \langle F\rangle^2) \qquad (2)$$

Figure 3b shows the decay in the autocorrelations in F for $S = 8$, $n = 34$, and $x = 0.441$. In this case the decay time is 3×10^7 bead jumps, which is comparable to the decay time of the autocorrelations of the radius of gyration. So, for this chain configuration an estimate for the equilibration time is $\tau = 6 \times 10^7$. τ varies with the total chain length N approximately as N^3. Then I did a second check which confirms the conclusion that I am sampling over the total configuration space: I started from a different initial configuration, one in which each sticker was connected to a randomly chosen partner. For three different sticker placements I checked that my results were within error bars independent of the initial configuration.

In order to obtain enough statistically uncorrelated data each run lasts at least 1000τ. For the longest chain lengths ($N = 271$) this amounts to approximately 5×10^{10} bead jump moves or 100 h on an IBM560 Risc station.

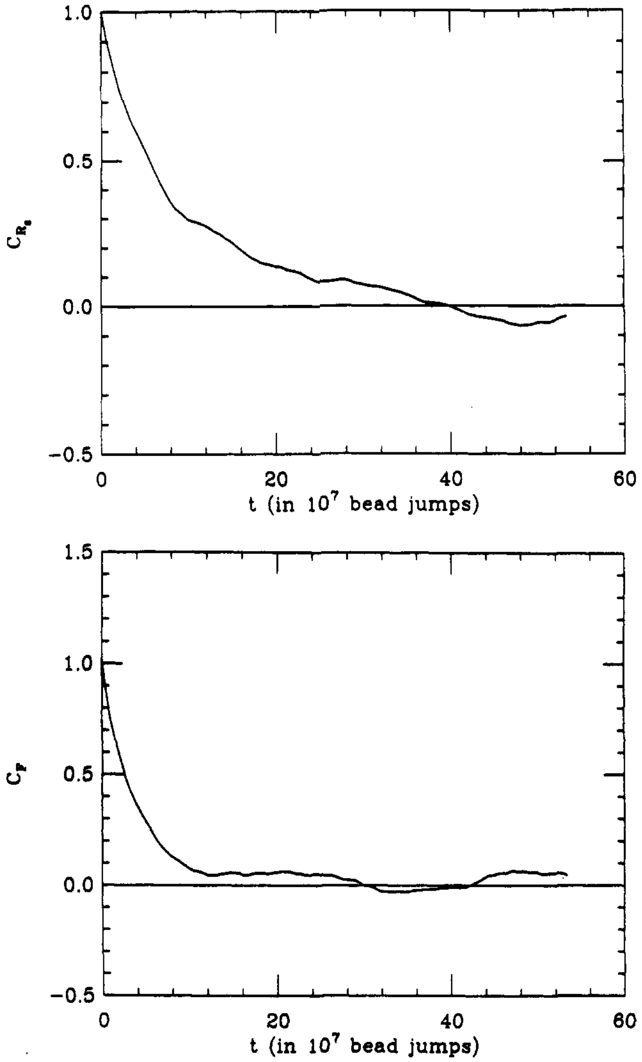

Figure 3. Decay of the autocorrelation of the radius of gyration (C_{R_g}) and the autocorrelation of the typical distance connected stickers (C_F). The time axis is in units of 10^7 bead jump moves. The data are in three dimensions: $x = 0.441$, $S = 8$, and $n = 34$.

Radius of Gyration

In three dimensions I obtain the radius of gyration R_g for $S = 2$, 4, 8 and $n = 34$. Since the total number of monomers equals the number of segments S times the number of monomers per segment n, the total number of bonds N varies from 67 to 271. Each run lasts at least 1000 equilibration times. The equilibrium value of the radius of gyration is obtained for each case as the average R_g of all allstuck configurations. Figure 4 shows the results for five different chain architectures. The swelling factor α is defined as the measured radius of gyration divided by the expected radius of gyration of an ideal Gaussian chain with the same number of monomers and average squared bond length.[20] The error bars shown are the statistical errors and are estimated by averaging over different parts of the run. The fits through the data are explained shortly. The dashed lines indicate the expected behavior for swollen and Θ chains (note the log–log scale). At first sight the data at small x seem in accordance with this swollen behavior, but for $x = 0.5$ the match is not as good: although the swelling factor incrases with N, clearly the asymptotic regime is not reached.

Predicting the scaling behavior of the chains at high N from the data at low N is a tricky business and is complicated by the fact that no theories for associating polymers are available on which to rely. For small x though, I expect the chains to behave similarly to ordinary

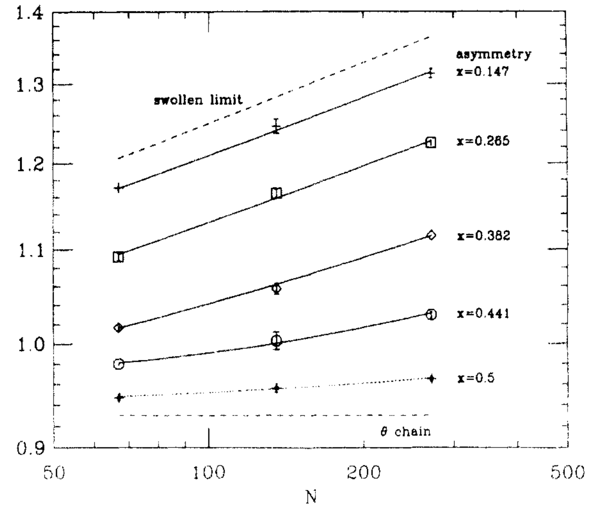

Figure 4. Log–log plot of the swelling factor α versus total chain length for different sticker placements in three dimensions. The swelling factor is defined as the average radius of gyration divided by the radius of gyration of an ideal Gaussian chain with the same length and average squared bond length. The solid lines are fits to eq 3. The dotted line is a fit to eq 6. The dashed lines indicate the expected behavior for swollen and θ chains.

Table I. Results for k and C from a Fit of the Three-Dimensional Radius of Gyration Data to Eq 3

x	k	C	χ^2
0.147	0.470 ± 0.004	0.08 ± 0.09	0.4
0.265	0.437 ± 0.003	0.13 ± 0.06	2
0.382	0.3873 ± 0.0012	0.47 ± 0.02	0.8
0.441	0.340 ± 0.002	1.22 ± 0.05	0.9
0.500	0.305 ± 0.002	1.86 ± 0.06	5

homopolymer chains. The asymptotic N dependence of the radius of gyration of a swollen homopolymer chain is

$$R_g \approx kN^{\nu}(1 + CN^{-\nu\omega}) \qquad (3)$$

The first term on the right hand side gives the expected scaling in the asymptotic limit. The second term is a correction for the fact that we deal with finite size chains. ν and ω are obtained from renormalization group theory:[21] $\nu = 0.5880 \pm 0.0010$ and $\omega = 0.850 \pm 0.015$. Fits to eq 3 are made for each architecture. They are drawn as solid lines in Figure 4. Table I shows the obtained values of k and C. Note that the value of C increases with increasing x. In fact $C = 0$ within error bars for the lowest x value. This means that for low x no scaling correction is necessary and the sampled chains exhibit asymptotic behavior. One might expect that this is the case if the excluded volume is much higher then the entropic attraction. This is in accordance with previous results on two sticker chains,[8] where it was found that the entropic attraction increases with increasing x. As a goodness of the fit measure the values of χ^2 are given in Table I.[22] Since there are three data points and two variables to fit, the fit is acceptable if $\chi^2 \approx 1$. Clearly, for $x = 0.5$ the data are not wholly in accordance with the swollen chain behavior, but for all other x values they are. In the latter case there is no clear indication that the chains will collapse on larger length scales. As will be shown in the next section, the sticking is predominantly local with associations between chemically nearby stickers.

A scaling argument is used to predict the scaling behavior for $x > 0.441$. Table I indicates that the value of k decreases with increased x. x will reach its critical value, at which the chain behaves as an ideal chain, as k becomes 0. The functional dependence of k on x is obtained as follows: For homopolymers it is known from scaling theory[23] that

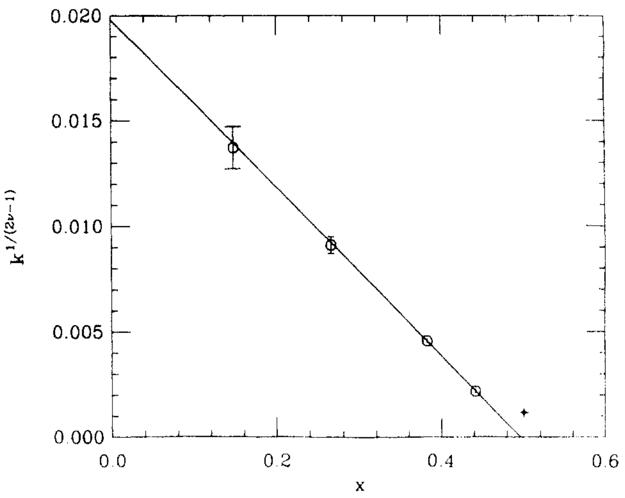

Figure 5. In order to test our scaling argument (in three dimensions) $k^{1/(2\nu-1)}$ is plotted versus x. From a linear least squares fit we obtain $x_c = 0.496 \pm 0.004$. Although the data point at $x = 0.5$ was not accepted (and not used for the fit), it is indicted for comparison.

$$R_g \sim N^{0.5}(\beta l^{-d}(N/l)(4-d)/2)(2\nu-1)/(4-d) \qquad (4)$$

Here β is the excluded volume parameter, d is the dimension of space, and l is the bond length. In my case the parameter β is the effective excluded volume between two chain segments. This effective excluded volume will contain the monomer repulsion as well as the sticker attraction. The parameter controlling the net effective excluded volume is x. Since β measures a local interaction, it is natural to expect that it varies smoothly with x as x passes through x_c. Thus near $x = x_c$, $\beta \sim (x - x_c)$. Then eq 4 results in

$$k \sim (x - x_c)^{2\nu-1} \qquad (5)$$

Figure 5 shows a plot of $k^{1/(2\nu-1)}$ versus x. For comparison the value of $x = 0.5$ is indicated, although in this case the fit is not accepted. The other data square with my expectation: remarkably, the anticipated linearity in x extends over the whole range of x studied. A linear least squares fit through these data gives $x_c = 0.496 \pm 0.004$ ($\chi^2 = 0.2$). This critical point is very close to $x = 0.5$. Would it be possible that the chain with equally spaced stickers is ideal in the asymptotic limit? If so, the first thing to expect is that this ideal behavior is related to the asymmetric sticker placement, that is to the fact that there is no distinction between long and short intervals. If this is the case I expect that these chains will show ideal behavior in two dimensions as well. As will be shown, the two-dimensional data do not confirm this hypothesis.

My scaling argument indicates that in three dimensions the chain with equally spaced stickers is marginally collapsed. The data in Figure 4 show marginally swollen behavior, though. Indeed if I try to treat the interaction as a small perturbation and fit the data to[24]

$$R_g \approx kN^{0.5}(1 + CN^{0.5}) \qquad (6)$$

the resulting fit, shown in Figure 4 as a dotted line, is quite good ($\chi^2 = 0.2$). For ordinary homopolymer chains this would indicate a swollen asymptotic conformation. For associating polymers, one cannot exclude the possibility that the data will decrease or become N independent at high N.

In the previous part the implicit assumption is made that the results are independent of the numbers of monomers per segment. We expect this to be the case when the number of monomers per segment is high enough.

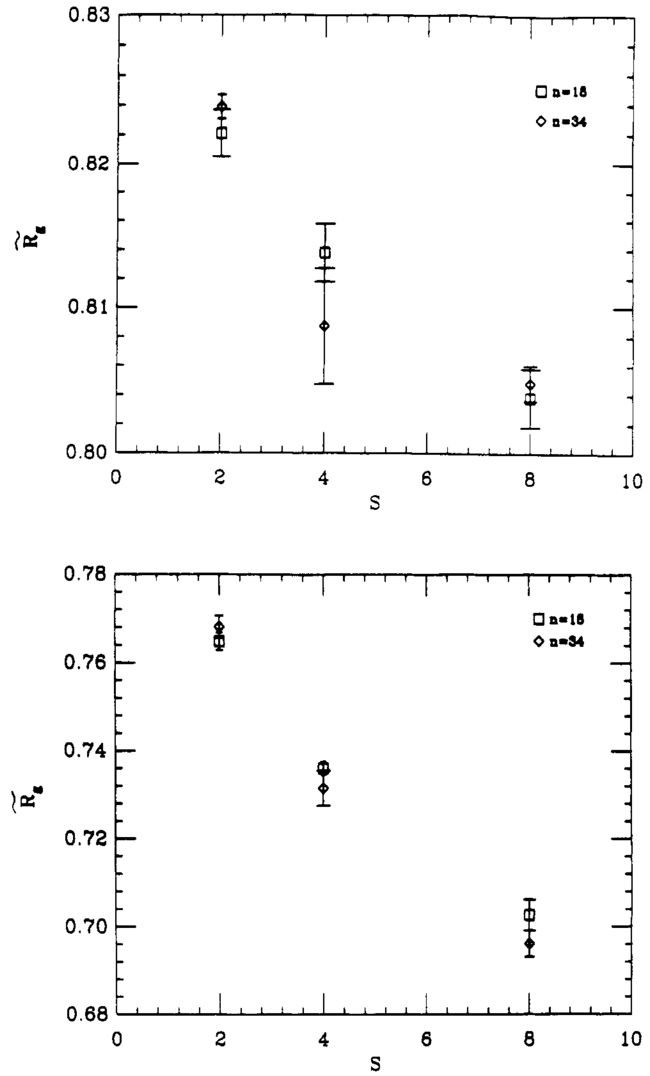

Figure 6. Test of the influence of segment length for two different sticker placements: x = 0.383 (a, top) and x = 0.5 (b, bottom). For two different lengths, n = 34 and n = 18, the measured radius of gyration over the radius of gyration of a swollen chain with no stickers of the same total length is shown. Within error bars the data are independent of n, indicating that the used segment lengths were high enough.

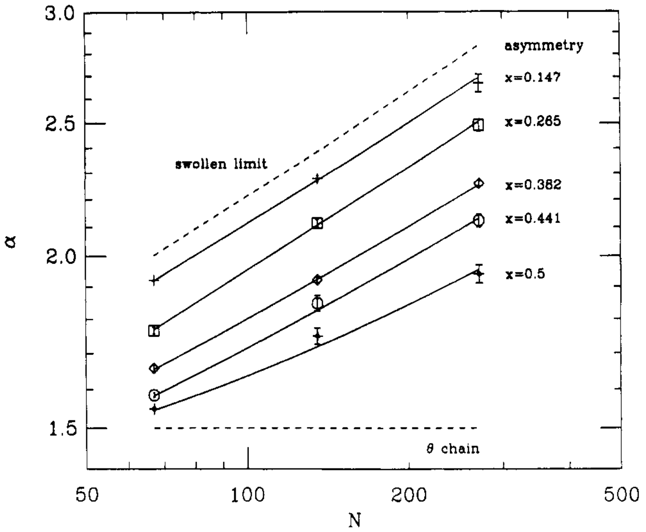

Figure 7. Swelling factor α for different sticker placements in two dimensions. The solid lines are fits to eq 3. The dashed lines indicate the expected scaling behavior for swollen and θ chains.

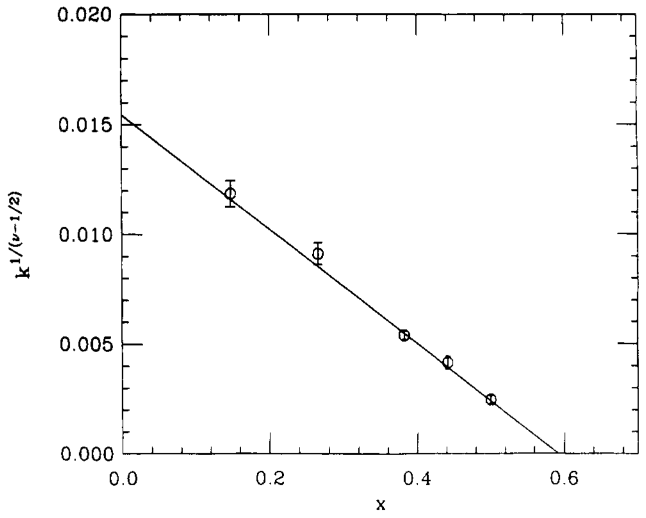

Figure 8. Test of scaling argument in two dimensions. A linear least squares fit gives x_c = 0.593 ± 0.007.

Table II. Results for k and C from a Fit of the Two-Dimensional Radius of Gyration Data to Eq 3

x	k	C	χ^2
0.147	0.330 ± 0.004	0.3 ± 0.2	0.4
0.265	0.309 ± 0.004	0.0 ± 0.3	0.6
0.382	0.271 ± 0.002	1.2 ± 0.2	0.2
0.441	0.254 ± 0.004	1.6 ± 0.3	0.9
0.500	0.223 ± 0.004	3.8 ± 0.4	1.8

This assumption must be checked. For two sticker placements results for n = 18 and n = 34 are compared. To this end the ratio of the radius of gyration of the chain with stickers over the radius of gyration of a chain of equal length with no stickers is calculated. When there are stickers present the radius of gyration will be reduced. The reduction factor should depend only on the number of segments per chain and not on the segment length in the asymptotic chain length limit. Parts a and b of Figure 6 show the results. These confirm indeed that the used segments are long enough: the data for different segment lengths agree within error bars.

Figure 7 shows the two-dimensional results. Again n = 34 and S = 2, 4, 8. The radius of gyration data are divided by those expected for an ideal Gaussian chain with the same average squared bond length. The data in Figure 7 ar qualitatively similar to those found in three dimensions. The same method is used to analyze them. Table II gives the results of fits to eq 3. These fits are drawn in Figure 7 as solid lines. This time the data for x = 0.5 show swollen behavior and the fit to eq 3 is accepted, since χ^2 is small. Here the results from conformal field theory are used:[25] ν = 0.75 and ω = 11/12. Figure 8 shows a fit to eq 4. A linear least squares fit to all five data points gives x_c = 0.592 ± 0.007 ($\chi^2 = 2$). We conclude that in two dimensions swollen chain conformations exist for all x values. In two dimensions many configurations in which the sticking is not local are prohibited because the chain is not allowed to cross itself. This fact could explain the swollen behavior in two dimensions. If a lattice with two layers in the third direction as in earlier work[8] is used, the configurations that are forbidden in the strict two-dimensional case are allowed with a small probability. Swollen configurations are found for all sticker placements in this two-layer model as well.

Locality of Sticking

Figure 2 shows two typical configurations. In case x = 0.147, the sticking is predominantly local: the associations occur between chemically nearby stickers. However, for

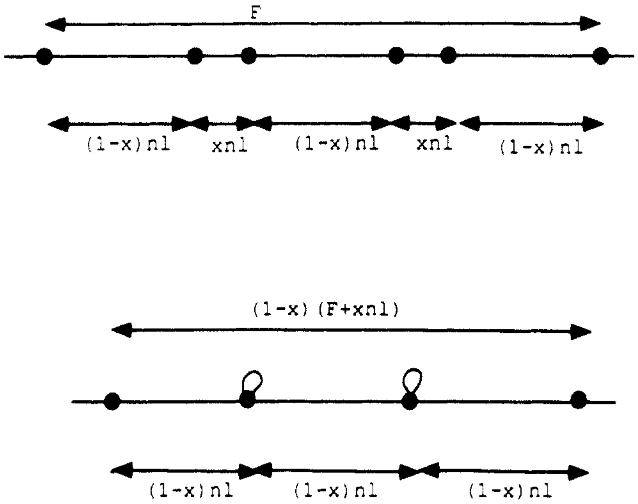

Figure 9. Two stickers separated by one additional long interval, as compared to short ones (a, top), and the resulting configuration if the sticking between the other stickers is local (b, bottom). The stickers are shown as black dots.

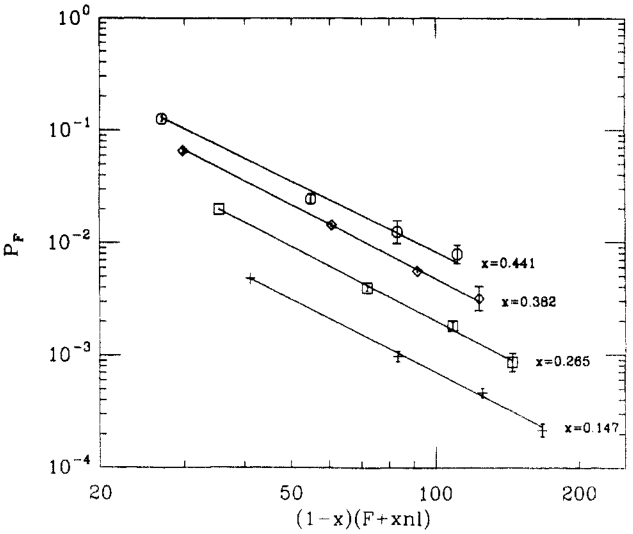

Figure 10. Probability P_F that a sticker in the middle of the chain is connected to a sticker a chemical distance F separated. The solid lines are fits to eq 7. The data show clearly the expected power law behavior.

Table III. Results for the Power Law Coefficient s from a Fit of the Three-Dimensional Data to Eq 7

x	s	χ^2	x	s	χ^2
0.147	−2.16 ± 0.06	1.3	0.382	−2.20 ± 0.04	1.4
0.265	−2.21 ± 0.05	2	0.441	−2.10 ± 0.10	4

$x = 0.5$ global associations between chemically distant groups seem to be important. To study this effect I look again at the quantity F, defined as the distance along the chain backbone from one fixed sticker (in the middle of the chain) to its partner. A histogram for F shows for all architectures a decay in the probability of finding a certain F with increasing F, as expected. I would like to know how the data decay and how this decay depends on x. To this end the following observation is made: The chance that in a random self-avoiding walk two points a chemical distance L separated are adjacent in space is proportional to $L^{-\nu(d+\theta)}$. Here θ is an exponent describing certain interior correlations within a self-avoiding chain. Its value depends on the placement of the two correlated points. For one point well within the chain and the other either in the middle or at the end of the chain however the measured values are indistinguishable and equal to $\theta = 0.67 \pm 0.34$ or $\nu(d+\theta) = 2.16 \pm 0.2$.[26] I have to deal with multiple correlations, though. The reduction factor in conformatinal space of a single chain due to many self contacts is exactly known for an ideal random walk.[24] Excluded volume interaction between the different loops make the self-avoiding case almost untractable. Chan and Dill studied loop formation in chains containing up to three contacts in the context of protein folding.[13] In the case at hand there are up to eight contact points, and I can only hope to obtain insight into the data using a simplified model: I look at two stickers separated along the chain by one-additional long interval, as compared to short ones, as rendered in Figure 9a. What is the probability P_F that these stickers are connected? I will assume that when these stickers are connected, all other stickers along the chain are sticking to the stickers that are chemically closest to them, as in Figure 9b. Moreover, the assumption is made that the probability for the two stickers to connect depends only on the distance between the stickers, given the fact that all other stickers are connected so as to form small loops. This distance equals the total length of all long intervals between the stickers, and expressed in F, x, n and l it equals $(1 - x)(F + xnl)$. It follows that

$$P_F \sim ((1 - x)(F + xnl))^{-s} \tag{7}$$

where $s = 2.16 \pm 0.2$. The assumptions are exact in the $x = 0$ limit. One might expect that they break down if x increases. This model is a simplification, and it should be regarded as a first attempt to get insight into the decay of the data. Interactions between the different loops in particular are neglected. Figure 10 shows however that the data are within errors in accordance with eq 7 for all sticker placements except $x = 0.5$. Here we used the data for the longest chains ($S = 8$ and $n = 34$). The errors are estimated from the differences in P_C for the two middle stickers. Table III lists the calculated s values, which are equal to the expected value within error bars. When $x = 0.5$ we are not able to distinguish long and short intervals, and there is no reason for the chain to behave as assumed above.

Chain Collapse and Loops

In none of the simulations described above is a collapsed state found. Obviously, such a state is obtained when the excluded volume is turned off, that is if the condition that no two steps of the random walk are allowed to go to the same lattice site is dropped. Results are shown in Figure 11 for three sticker placements. The data are again divided by the radius of gyration of an ideal Gaussian chain with the same average squared bond length. Moreover they are plotted versus $\sqrt{N}$. The observed linearity indicates marginally collapsed behavior. Equation 6 (with negative C) fits the data well. These fits are shown as dotted lines.

One might wonder what happens for $x > 0.5$. Studies at $x = 0.735$ show that the configurations are similar to those at $x = 0.265$: local sticker interactions dominate. The difference is that the two stickers at the chain ends tend to be connected if $x = 0.735$ so as to form a big loop. This loop behavior seems to result from our athermal model and is in that sense not realistic. A better way to study loops is to study associating polymer rings. In this case the architecture x is indistinguishable from the architecture $1 - x$.

Summary and Conclusion

I used an athermal model to study the equilibrium behavior of associating polymers of different architecture. In this model the associations are treated as geometric constraints. For chains with alternating long and short

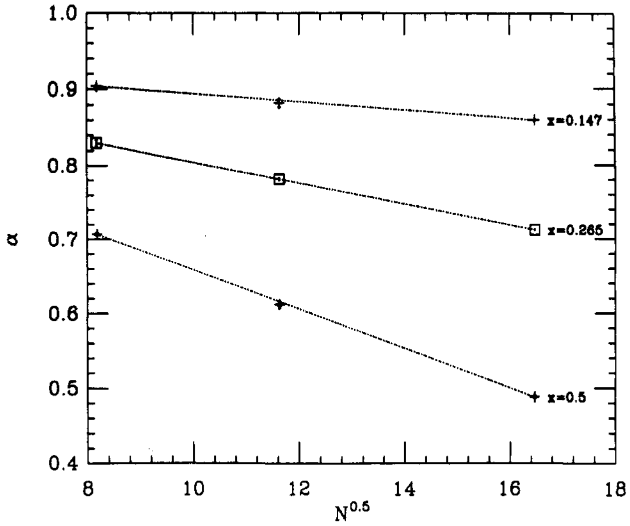

Figure 11. Swelling factor α versus the square root of the chain length if there is no excluded volume. The linearity indicates marginally collapsed behavior. The dotted lines are fits to eq 6. The simulations are done in three dimensions.

intervals between the associating groups or stickers and pairwise associations, swollen behavior is found for almost all sticker placements. In these swollen conformations the dominant sticking is between groups chemically nearby. The decay in the probability for two stickers to connect as a function of their chemical distance confirms this observation. Small chains with equally spaced stickers show marginally swollen behavior in three dimensions. We were not able to predict their asymptotic behavior yet. A scaling argument predicts marginally collapsed behavior. Ideal behavior should not be excluded, though. In two dimensions the chains with evenly spaced stickers are swollen.

The simulations give quantitative predictions for real associating polymers with strong pairwise sticker attraction (e.g. hydrogen bonding[8]). Moreover, from the asymptotic scaling behavior for single chains I predict that for almost all architectures studied the second virial coefficient of many chains in solution is positive, indicating good solubility at low concentrations. For chains with associating groups that stick in bigger multiplets (as the sulfonated polystyrene mentioned in the Introduction) collapsed conformations and phase instability are expected for more architectures. The simulations suggest that in that case the solubility can likewise be controlled by sticker placement.

Phase instability could also be present at higher concentrations if the higher virial coefficients are negative, due to the fact that the entropic attraction is not pairwise additive. Although for ordinary polymer chains, when the second virial coefficient is positive, so is the third one, analytical work[27] on polyelectrolytes shows that for these strongly interacting polymers the situation can be different. I intend to investigate this novel aspect of the thermodynamics of multichain solutions in future work.

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