Length of Subchains and Chain Ends in Cross-Linked Polymer Networks

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ABSTRACT: A general theory is presented for computing the distributions and averages of the lengths of subchains and chain ends in cross-linked polymer networks. This theory was tested by computer simulations, and we show the results of both theory and simulations, for a better comparison. We find a significant difference between the values of chain ends and subchains depending on the extent of the reaction. As a consequence, the fraction of elastically active or effective material was clearly overestimated in previous works. We show how the different length distributions of intramolecular loops or cycles, subchains, and chain ends influence each other and how they can be combined into one general distribution. The influence of the spatial density or homogeneity of the chains, the functionality of the cross-links, the length distribution of the initial polymer chains, and other deviations from an idealized system are discussed briefly.

1. Introduction

The elastic properties of polymer networks can only be understood completely if constitution, occurrence and effect of each structural unit that influences the deformation behavior is known. The most important structural units of polymer networks are the cross-links and the subchains in between. For this reason attempts were started long ago to describe the length of chains and subchains formed by different cross-linking reactions or polymerizations.[1−4] In the case of cross-linking of existing polymer chains, the work of Scanlan and Case[5,6] laid another foundation stone for the beginning of the theoretical investigations. Defects, flaws, dangling chains, and the determination of elastically active material were the topics of discussion. They derived their equations for initially uniformly or geometrically distributed lengths of the molecules and determined, for example, the weight fraction of elastically active material. However, the effects of the formation of inactive short intramolecular loops (often called "cycles") were totally neglected in their work. Case furthermore[6] distinguished between elastically active and inactive subchains and calculated the mean length of the elastically active chains for both cases.

Some years later Miller and Macosko[7,8] determined inter alia the average molecular weights for the cross-linking of polymer chains without specifying the distribution function of the molecular weight between the junctions or considering cycle formation. To facilitate their calculations, they assumed that chain ends are half as long as subchains.[9] Dusek et al.[12] applied their spanning-tree approximation of the cascade theory to the calculation of the number of elastically active network chains and to the calculation of elastically inactive cycles for a better description of the evolving network during cross-linking. Up until now the formation of cycles has been a frequent topic of research,[13−16] and it is still discussed with regard to its influence on the properties of polymeric materials. The additional point of its influence on distribution and average of the molecular weight between the cross-links of the network is still barely considered, although Tonelli and Helfand[17,18] recognized in the early 1970s that this influence is of particular importance.

Almost every theoretical publication on the structure of polymers tries to describe the elastic properties of the system. In this respect, a special point of interest is the behavior at or just above the gel point and the further development by increasing the extent of reaction. This is still a frequent topic of research; for instance, see the work of Stepto and co-workers during the last few years.[19−22] At this critical point it is very hard to compare any theory with experimental data, because the system is very sensitive to small deviations of the spatially homogeneous case and thus precise quantification of the sol−gel transition is hardly possible.

In recent years, this problem has been tackled and partly solved by the use of computer simulations. Homogeneity can be ensured during the simulation and the amount and effect of cycles can be controlled easily or even suppressed by simple procedures. Regarding the simulation of cross-linked networks, different approaches and results are found in the literature. Shy et al.[23] and subsequent work of Eichinger et al.[24,25] used a static simulation of phantom chains obeying a Gaussian statistic or rotational isomeric state models to model the radiation-curing of polymer networks. Although their simulation method is static, they were able to verify some of the results of Tonelli and Helfand.[17,18] To get more realistic results, dynamic simulations of self-avoiding chains[10,11] are more suitable. Grest and Kremer[10] were the first to find a difference between the average lengths of chain ends and subchains depending on the extent of reaction. Because of the lack of a theoretical description, they were not able to explain all the effects recognized, and approximated the distributions by simple exponentials. Lay et al.[11] found relations

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for the distributions of subchains and chain ends, which were close to our results for the idealized networks, but they could only give a proportionality for both. On the basis of these distributions, they calculated the average value of the length of the subchains. They assumed that the distribution of the lengths of the chain ends is shifted toward somewhat higher values because of the relatively high number of short strands generated by the formation of cycles.

The aim of this work is to formulate one general theory to describe the lengths of subchains and chain ends. Thus, first of all we focus on the statistical distribution of chain lengths between arbitrary junction points and derive distributions for the dangling ends of the chains and the subchains in between. These equations hold for random cross-linking reactions forming (almost) no cycles. Then we discuss an additional approach in general for the cycle forming cross-links and show that addition of both leads to the complete distribution. Incidentally this allows us to discern geometrical and statistical aspects of the formation of the networks via cross-linking. The results are not calculated in respect of elastically active or effective chains because of the controversial discussion[26] about this topic. Nevertheless, the determination of the lengths of the elastically active chains or effective chains requires as a first step the determination of the complete distribution of the lengths of the subchains. We developed our theory in a way that can easily be applied to the determination of active or effective chains.

To test the theoretical results, we apply two kinds of simulations. The first aims to verify the theoretical results for the idealized cross-linking reaction not forming any cycle by use of a random array approach without any geometrical information on the system. In the second case, including cycle formation, all the geometric and spatially available information is needed and the whole network has to be constructed step by step. For a reasonable compromise between the accuracy of the picture of the network and the available resources for computing, we chose the bond fluctuation method (BFM) of Binder et al.[27,28] as simulation algorithm.

2. Theory

2.1. Basic Assumptions and Definition of the Terms Used. The derivation of the theory starts with six basic assumptions in order to obtain a concise and general formulation. We confine ourselves in this basic approach to the discussion of chemical cross-links[29] connecting only two chains and monomers which can react only once. The following set of statements summarizes our assumptions:

1. Polymer chains and cross-links are arranged homogeneously and statistically in space.
2. Each monomer of any chain reacts with the same probability.
3. Cross-links react twice to connect chains.
4. Monomers of chains react at most once.
5. The reactions are independent.
6. Monomers and cross-links have to be in close contact to react.

How these assumptions can be generalized is discussed at the end of the Theory section.

When dealing with chemical cross-links, we have to keep in mind that only cross-links connecting parts of chains can contribute to the elastic behavior. Thus, the extent of reaction is expressed in our approach by the percentage of completely reacted cross-links.[30] This definition serves for a better comparability of different cross-linking reactions and the elastic properties obtained. After reaction each monomer of a reacted chain is called "branching point". The length of a subchain n_s is defined as the number of monomers between branching points (cf. Figure 1). The length of a dangling end n_e is determined by the number of monomers ahead of the first branching point or beyond the last one of each chain. The number of monomers of the primary chain is denoted by n_p.

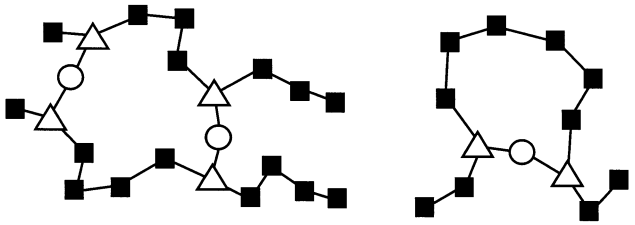

Figure 1. Schematic sketch of cross-linking reactions: Each symbol represents a reactive unit. The chemical cross-links (circles) act as a bridge between the chains; the branching points (triangles) are placed on the chains and determine the length of the subchains in between. Unreacted monomers are presented as squares. Direct coupling of chains directly connects branching points.

In the first step of generalization, we study cycles formed by one chain and one cross-link. The length of such a cycle[31] is defined by the complete number of monomers which form this cycle and differs from the length of the subchain generated by the cycle. These cycles are divided into two different types: primary cycles (all cycles obtained by double reaction of the same cross-link and the same chain) and remaining cycles (all cycles without any further reaction of at least one monomer of that cycle). The latter are usually assumed to be mostly inactive during the deformation of a polymer network. The results for these special cases are generalized at the end of the theoretical part to a higher number of chains and cross-links forming a cycle and we call these generalized cases cycles of higher order. Since the cross-links act as a bridge between two branching points, they should also be treated in effect as subchains and should be added to our statistics, but due to the small length of this bridge and the trivial addition of this distribution we left this point aside.

Note that each distribution function or probability obtained is normalized with respect to the proportion of chains or cross-links which satisfy the preconditions. We consider this in our notation: $P(...|...)$, for example, denotes a probability P that is a function of the terms before the upright line | and is normalized in respect of the conditions behind this line.

2.2. Idealized Networks. In this paragraph we use assumptions 1 to 5 and neglect everything concerning the spatial arrangement of the polymer. We call this kind of network "idealized" and develop equations for the lengths of subchains and chain ends in the case of purely statistical cross-linking for the whole system, not differenciating between sol or gel. The theory is constructed in order to specialize easily in sol or gel or to calculate elastically active or effective material afterward.

2.2.1. Number of Branching Points of a Chain. First we consider the case of uniform chains. If the system consists of k chains of uniform chain length of n_p monomers and ν completely reacted cross-links, we

can define the density ρ of branching points b on any chain as

$$\rho = 2\nu/(kn_p) \tag{1}$$

Assumptions 2 to 5 result in a binomial distribution of the number of branching points for idealized uniform systems

$$P(n_p,\rho, b = i) = \binom{n_p}{i}\rho^i(1-\rho)^{n_p-i} \tag{2}$$

whereby i denotes the number of branching points on a chain and $P(n_p,\rho, b = i)$ the probability that the number of branching points b equals i on a chain of primary length n_p at the branching point density ρ. The normalized distribution function of the initial lengths $P(n_p)$ is used to generalize eq 2 to nonuniform systems. Separate calculation of the distributions below for each initial length n_p and combination of the results using $P(n_p)$ leads to the distributions for the complete system. Thus, it is sufficient to present the theory for uniform chains. Equation 2 establishes the independent consideration of sol or gel, because the probability of being part of the gel is related to the number of branching points on a chain.[7,8] The fact that each branching point connects to a part of another chain is guaranteed by the above restriction on cross-links connecting chains. The treatment of elastically active or effective material is also based on eq 2. ρ and n_p are fixed in the following. To simplify the presentation, we left the continual repetition of both terms aside; thus $P(n_p,\rho, b = i)$ is written more clearly as $P(b = i)$.

2.2.2. Dangling Chain Ends. The distribution of the lengths of the dangling chain ends can be deduced directly using the density of branching points ρ. With the probability $P(b = 0) = (1 - \rho)^{n_p}$ a chain of length n_p is unreacted and forms no dangling end at all. Chains without any reacted monomer have to be excluded from the distribution to obtain a correct normalization. To obtain a dangling end of length $n_e = 0, ..., n_p - 1$, the first (or last) n_e monomers of the chain have to be unreacted. Normalizing with the sum of all possible lengths leads to the distribution

$$P(n_e|b \geq 1) = \frac{(1-\rho)^{n_e}}{\sum_{i=0}^{n_p-1}(1-\rho)^i} = \frac{\rho(1-\rho)^{n_e}}{1-(1-\rho)^{n_p}} \tag{3}$$

whereby $P(n_e|b \geq 1)$ denotes the probability of obtaining a dangling end of length n_e, if the unreacted chains are neglected. Summation over all possible lengths results in the average value

$$\overline{n_e}(|b \geq 1) = \sum_{n_e=0}^{n_p-1} P(n_e|\, b \geq 1)n_e = \frac{(n_p\rho - \rho + 1)(1-\rho)^{n_p} - 1 + \rho}{\rho((1-\rho)^{n_p} - 1)} \tag{4}$$

2.2.3. The Length of Subchains. The calculation of the average length of subchains results from the mean value of the dangling ends. To form one subchain, at least two branching points have to be part of a chain. Chains with only one branching point reduce the number of cross-links which are involved in the formation of subchains. The sum of both dangling ends of such chains is $n_p - 1$. Thus, the sum of eq 4 has to be divided into two parts. This leads to

$$P(b \geq 1) \cdot \overline{n_e}(|b \geq 1) = P(b = 1) \cdot \frac{(n_p - 1)}{2} + P(b \geq 2) \cdot \overline{n_e}(|b \geq 2) \tag{5}$$

The number of chains with at least two branching points is given by $k' = kP(b \geq 2)$ and the number of branching points on these chains is $b' = 2\nu' = 2\nu - P(b = 1)k$. The number of branching points and the number of monomers forming dangling ends, $2n_e(|b \geq 2)k'$, reduce the number of monomers which can form subchains to

$$(n_p - 2\overline{n_e}(|b \geq 2))k' - b' \tag{6}$$

The number of subchains is given by $b' - k'$ because $b > 1$ for each chain. Thus, we can calculate the average length of the subchains as

$$\overline{n_s} = \frac{(n_p - 2\,\overline{n_e}(|b \geq 2))k' - b'}{b' - k'} \tag{7}$$

Equations 5−7 connect the averages of subchains and chain ends. If we want to obtain the distribution function of the subchains in the homogeneous case, we have to proceed as follows.

Equation 2 allows the separated calculation of chains of differing number of branching points. Any chain with $b = i$, $i = 1, 2, ...$, branching points consists of two dangling ends and $i - 1$ subchains. In the case of $b = 1$, the chain is split into two dangling ends. In this case, equal reactivity for each monomer of the chain results in

$$P(n_e|b = 1) = \frac{1}{n_p} \tag{8}$$

for the possible lengths $n_e = 0, ..., n_p - 1$. The distribution for chains with two branching points can be deduced from eq 8 by subjoining one additional branching point. For the second reaction $b = 2$, the probability for any subchain or dangling end of length $n = 0, ..., n_p - 1$ to react is proportional to its length:

$$P_{react}(n) = \frac{n}{n_p - 1} \tag{9}$$

This second reaction splits the subchain of length n into two subchains of length m and $n - m - 1$, whereby each length $m = 0, ..., n - 1$ is of equal probability $(1/n)$. To calculate the probability of the length m, one has to compute the probability that a subchain of length m reacts and reduces the frequency of occurrence of this length by one. Furthermore, one has to calculate the probability that any subchain of length $n > m$ generates one subchain of length m by subdivision. For $b = 2$ and $m = n_e$, this leads to

$$P(n_e|b = 2) = (1 - P_{react}(n_e))P(n_e|b = 1) + \sum_{n=n_e+1}^{n_p-1} P_{react}(n)P(n|b = 1)\frac{1}{n} \tag{10}$$

for the dangling ends and in the case of subchains with $m = n_s$ to

$$P(n_s|b = 2) = 2 \sum_{n=n_s+1}^{n_p-1} P(n|b = 1)P_{react}(n)\frac{1}{n} \quad (11)$$

because of $b = 2$ and the lack of subchains for $b = 1$. The factor of 2 in eq 11 results from the normalization of the distribution, and it is caused by the fact that just half of the dangling ends for $b = 2$ are divided into one subchain and one dangling end.

Because of

$$\sum_{n=n_e+1}^{n_p-1} P(n|b = 1)P_{react}(n)\frac{1}{n} = \frac{n_p - n_e - 1}{n_p(n_p - 1)} \quad (12)$$

it follows that

$$P(n_e|b = 2) = P(n_s|b = 2) \quad (13)$$

for each $n_s = n_e$. It follows by induction that eq 13 holds for each $b = 2, ..., n_p$ because of the same probability for subdivision of chain ends and subchains of equal length. Thus, we obtain for $i \geq 2$

$$P_{react}(n, i) = \frac{n}{n_p - i + 1} \quad (14)$$

leading to the recursion formula

$$P(n_e|b = i) = (1 - P_{react}(n_e, i))P(n_e|b = i - 1) + \sum_{n=n_e+1}^{n_p-i+1} P_{react}(n, i)P(n|b = i - 1)\frac{1}{n} \quad (15)$$

This permits calculation of the distribution function for each possible $b = i$. The complete distribution results from eqs 2 and 15 and the number of subchains $i - 1$ if $b = i$:

$$P(n_e|b \geq 1) = \frac{\sum_{i=1}^{\infty} P(b = i)P(n_e|b = i)}{P(b \geq 1)} \quad (16)$$

$$P(n_s|b \geq 2) = \frac{\sum_{i=2}^{\infty} P(b = i)P(n_s|b = i)(i - 1)}{\sum_{i=2}^{\infty} P(b = i)(i - 1)} \quad (17)$$

From eqs 16 and 17, we obtain $n_s < n_e$. The reason for this is obvious, fewer reactions of a primary chain mean greater average distances between branching points and a lower number of subchains. If we calculate n_s, we take into account a low number of long subchains and a high number of short subchains. When calculating n_e we always must take into account two chain ends per chain. Note that computation of eq 3 and eq 16 leads to the same result.[32] Equations 16 and 17 allow us to make a general calculation of the distributions of chain ends and subchains. We then require the distribution of the number of branching points of the chains in order to determine $P(b = i)$. As mentioned above, the number of branches determines the probability to be part of the gel and thus connects the sol−gel transition with the formation of chain ends and subchains.

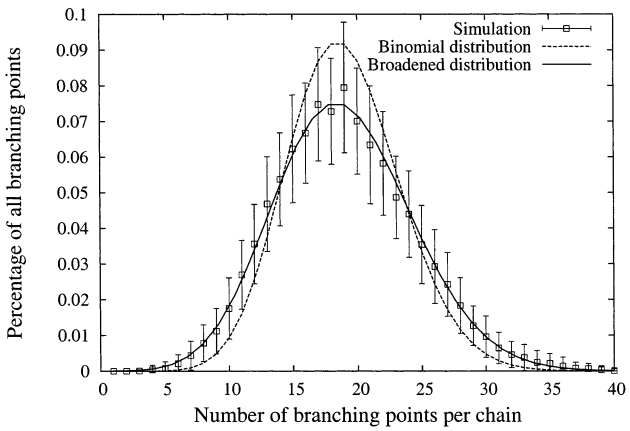

Figure 2. Distribution of the number of branching points on all chains after cross-linking in solution simulated with the BFM (cf. section 3.2.1) in comparison with the binomial distribution. The results displayed are averages of 100 independent cross-linked systems. For more details see ref 34.

The derivation above is accurate for idealized networks. Thus, no deviations should appear in the comparison with the simulated idealized model systems as presented in section 3.1.

2.3. Real Networks and Deviations from Idealized Behavior. This section deals with the influence of the spatial arrangement of chains on the length of the subchains formed by cross-linking. We deduce only general correlations for any kind of polymer; in reality these correlations are affected by the different chemical structure or stiffness of the polymers and the cross-linking agents used. For example, see the calculations of Tonelli and Helfand.[17,18] Our paper focuses on the general aspects of the length of subchains and chain ends in cross-linked polymer systems and on the basic mutual influence of cycle formation.

Thus, we give only a common basis for further investigations and neglect the particular structure of the polymer. As a simplification, we choose a Gaussian distribution function for the distances of monomers of any selected chain. Special cases of polymers can be treated analogously by replacing this distribution with a more appropriate function. As mentioned above, the ideal case for the formation of subchains is influenced by the formation of cycles. However, the formation of cycles already influences the number of branching points in the chains.

2.3.1. Number of Branching Points in a Chain. The independence of reactions which has been assumed cannot be maintained for cross-links which form cycles, but deviation from idealized behavior is remarkably small. Figure 2 shows the results of a simulated cross-linking reaction of type S11_low[33] in dilution with the exceptional fraction of more than 50% of cross-links that form cycles. The "correlation" of the second reaction generating the cycle leads to a broadening of the binomial distribution.

In real polymer systems, many other influences also disturb this binomial distribution: Density fluctuations of the cross-links generated by the mixing process

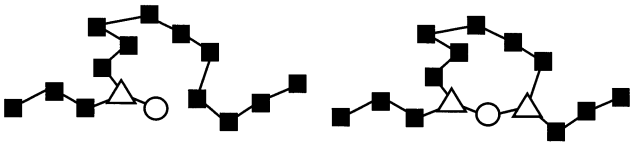

Figure 3. Sketch of the formation of a cycle: two reactions are needed to form a link between two different monomers of one chain.

broaden the binomial distribution and can hardly be measured. The length of the primary chains, the distance to the ends of the chain, or the dilution of the system alter the mobility of the monomers and, therefore, the cross-linking reaction. Most of these facts lead to an increasing number of very short and especially long subchains and chain ends, but also the contrary effect exists: The reduced mobility near already existing cross-links lowers this broadening. Since all these arguments can hardly be quantified, we maintain for our further discussions the binomial distribution as an approximation.[34] However, the theory presented is constructed in such a way that this distribution function can easily be exchanged. Next, we will deal with the direct influence of the cycle formation on the length of the subchains.

2.3.2. Primary Cycles. First, we consider the procedure of cross-linking of polymer chains (cf. Figure 3) and the formation of cycles, using a simplified example consisting of just one primary chain and one cross-link. Effects caused by the mobility of the reactants, by the dilution of the system or by another cross-link nearby are neglected in this first approximation. For a detailed discussion of some of these effects, see ref 12.

One cross-link has to react twice to form a link between two different monomers. Assumptions one and two imply equal probability for the monomers of a chain to react with any unreacted cross-link selected at random. This leads to the situation on the left of Figure 3. In attaching the cross-link to a chain, the further diffusion of the cross-link is confined to the diffusion of the chain. The link between the cross-link and the chain influences the probability for the second reaction of the cross-link. Monomers of the attached chain are more probable for the second reaction and obey different statistics.

Two monomers have to be in spatial contact to react (assumption 6), i.e., at the correct distance R to allow a reaction. In the Gaussian approximation subchains and chains have the same distribution of separation. If N denotes the number of monomers of any chain or subchain (i.e., the distance along the chain), this distribution is given[35] by

$$\Phi(\mathbf{R}, N) = \alpha\left(\frac{3}{2\pi N l^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2Nl^2}\right) \qquad (18)$$

whereby l denotes the average distance between two subsequent monomers of the chain.

We choose this more general form with an additional parameter α in the well-known equation above in order to obtain a better compatibility with our simulations, as explained in section 3.2.3. When applying this to our problem, we have to bear in mind that the cross-link has to be considered as the starting point of two subchains. The monomer of the chain linked to the cross-link branches onto two subchains following the link from the cross-link to the monomer. This monomer is excluded from further reactions (assumption 4). The number N as a distance from the cross-link is defined by the number of links along the chain and the link between cross-link and chain.[36]

The finiteness of the primary chains implies an additional restriction for the formation of cycles: any primary chain of length n_p can form at most cycles of length $N = n_p + 1$. This case leads to a subchain of length $n_s = n_p - 2$. There is just one possibility for arranging the monomers of the chain that has reacted with the cross-link to obtain this maximum length. It follows analogously that any cycle of N monomers can be arranged in $n_p - N + 2$ possible ways. With this in mind and remembering the branching onto two subchains, eq 18 has to be adapted for each possible length $2 \le N \le n_p + 1$. This leads to the length distribution of primary cycles $\Phi_c(\mathbf{R}, N)$:

$$\Phi_c(\mathbf{R}, N) = 2\Phi(\mathbf{R}, N)\frac{n_p - N + 2}{n_p} \qquad (19)$$

Note that cycles of N monomers generate subchains of $N - 3$ monomers, because of the definition of the subchains.

Summation of all possible values of N leads to the density of the chain d_c at the reaction distance R.

$$d_c(\mathbf{R}, n_p) = \sum_{N=2}^{n_p+1} \Phi_c(\mathbf{R}, N, n_p) \qquad (20)$$

The density d_c cannot be used directly to evaluate the total amount of primary cycles, but it can be used to normalize eq 19 and to calculate the average length of the primary cycles. To evaluate the total amount of primary cycles, the density of all polymers at a distance $\mathbf{R}$ has to be calculated depending on the type of polymer and cross-link chosen and depending on the total density and quality of the solvent. As an approximation one can proceed as Helfand and Tonelli.[17,18] Cycles consisting of more than one chain cannot be evaluated in this way. Up until now we have disregarded the effects and influences of other chains and cross-links in respect of the formation of cycles.

2.3.3. Remaining Cycles. Primary cycles remain cycles as long as no monomer of this cycle reacts with any other cross-link. We consider the formation of an additional link to any chain, which changes the length of the subchains of the cycle. Assumption 2 leads to the probability $(1 - \rho)^{N-3}$ for no additional reaction of any cycle of length N, because at least one of the $N - 3$ unreacted monomers has to form a new link. This results in the distribution of the remaining cycles

$$\Phi_R(\mathbf{R}, N, n_p) = \Phi_c(\mathbf{R}, N, n_p)(1 - \rho)^{N-3} \qquad (21)$$

These remaining cycles have an average length

$$\overline{n_R} = \frac{\sum_{N=2}^{n_p+1} N\Phi_R(\mathbf{R}, N, n_p)}{\sum_{N=2}^{n_p+1} \Phi_R(\mathbf{R}, N, n_p)} \qquad (22)$$

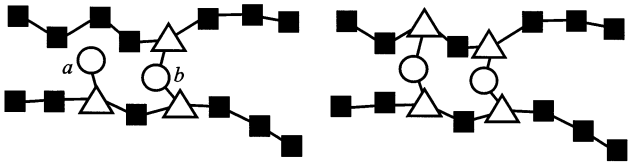

Figure 4. Monomers that are connected closely are more probable for the second reaction of the cross-link.

where the denominator is the density $d_R(\mathbf{R}, n_p)$ of the remaining cycles calculated according to eq 20.

For our further considerations, it is necessary to determine the fraction f_R of cross-links which form remaining cycles. Since we are merely interested in the general effect of cycle formation with respect to the resulting distributions of subchains and not in the total percentage and distribution of cycle formation, we determine this fraction approximately by the use of the simulated values of α. This is really not the best approach, but it is sufficient to show that our procedure and our concept of the mutual influence of both distributions (for idealized subchains and cycles) are correct.

Nevertheless, we can state that increasing cross-link density ρ leads to a decrease in the fraction of cross-links which form cycles and to a decrease in the average length of the remaining cycles. In other words, the effect of cycle formation is more significant at low extent of reaction or increasing $\bar{n}_s$.

2.3.4. Generalization and Consequences for the Multiple Cross-Linking of Several Chains. Above we restricted our considerations to cycles formed by one chain and one cross-link. As shown there, the length distribution of cycles is caused by the preference of closely linked monomers. With progressing extent of reaction, more and more chains are connected by cross-links and the number of closely linked monomers increases. Therefore, not only monomers of the same chain are preferred, but also monomers of other chains which are connected to the first chain. This means that the situation on the left-hand of Figure 4 leads to a possible reduction in the length of the subchain which will be formed by the missing reaction. For the whole system, this leads to a preference for very short (and in consequence additionally for very long) subchains. In the following, we call this effect the formation of short cycles of higher order, which is determined by the number of chains involved. To calculate their amount, eq 19 has to be modified concerning the mean number of linked monomers at a distance N. We start our considerations in a first approximation for cycles of second order.

As shown in Figure 4, only the second reaction of cross-link a (and in this way the possible length of the upper subchain) is influenced by the position of cross-link b. Let n_2 be the length obtained for the upper subchain depending on the length of the lower subchain n_1. We can then compute the distribution of cycles of second order:

$$\Phi_s(\mathbf{R}, n_2) = \frac{4\rho}{n_p - 1} \cdot \sum_{n_1=0}^{n_p-2} \left(\Phi(\mathbf{R}, n_2 + n_1 + 5) \times \frac{[n_p - n_1 - 1][n_p - n_2 - 1]}{n_p^2} (1-\rho)^{n_2} \right) \quad (23)$$

The factor ρ is caused by the condition that cross-link b must exist, and the factor of 4 results from the four possible arrangements of the distances n_1 and n_2 at the cross-link b. The unknown position of the first cross-link leads to the summation and averaging. The term $n_2 + n_1 + 5$ results from the distance along existing bonds between monomers,[37] and the rest is the well-known end-correction for both chains of $0 \le n_1, n_2 \le n_p - 2$ and the correction for the remaining of length n_2.

Since the factor 4ρ is rather small and the distance $n_2 + n_1 + 5$ along the chain is increased in comparison to eq 21, we expect only a small number of short cycles of second order even for densely cross-linked networks. In general, the formation of a cycle of any order O involves O chains and $O - 1$ cross-links between—analogous to Figure 4—and therefore needs a prefactor $\sim(2\rho)^{O-1}$ for the adapted version of eq 23. For this reason, we neglect effects of cycles of higher order for the determination of our distribution functions. Nevertheless, the existence of these cycles can be verified by simulations, and eq 23 was tested as presented below. Note that both chains displayed in Figure 4 must not be part of different primary chains.

2.3.5. The Complete Length Distribution of Subchains and Chain Ends of Cross-Linked Networks. The above considerations result in different distributions which influence each other and which cannot be combined by a simple weighted addition of the functions. There exists another possibility, however, to solve this problem.

Our problem is caused by the different mechanisms and statistics for reaction. Therefore, we have to distinguish between the branching points and subchains with respect to the particular mechanism for its generation. Only the remaining cycles form subchains that are produced by the mechanism of cycle formation, since cycles that not remain cycles are divided into subchains by the procedure of statistical cross-linking. Hence, we have to divide the subchains into two parts: remaining cycles and other subchains. The monomers of the remaining cycles are omitted by definition from further reactions and reduce the number of monomers which can form subchains to $kn_p - \overline{n_R}\nu f_R$. This leads to a new average chain length of $n_p' = n_p - (\overline{n_R}n\nu_R)/k$ and a new density $\rho' = \rho(1 - f_R/2)n_p/n_p'$ of branching points which obey the statistical mechanism. The term $f_R/2$ arises from the statistical first reaction and the cycle forming second reaction of the cross-link. By the using these new values for n_p' and ρ', eqs 3, 4, and 16 are corrected with respect to cycle formation.

Concerning the subchains, we have to proceed as follows. Subchains, which are generated by the statistical mechanism of cross-linking, can be calculated by using the new value of branching points $b'' = b(1 - f_R/2)$, the new n_p' and ρ', the modified eqs 3 and 4 for the chain ends as mentioned above, and the new equivalent distribution for the number of branches for a chain (eq 2) analogous to subsection 2.2.3. The resulting adapted distribution of the statistically generated subchains and the distribution of the remaining cycles can now be weighted with their average value of subchains formed, and can simply be added, since they are now independent. This procedure is not exact, because the new value for n_p' has to be rounded up or down and does not accord with the length distribution of the chains. The results are additionally influenced by the accuracy of the

Table 1. Size of the Simulated Networks[a]

networks	S11	S27	S38	S81	S100	S200
lattice sites	96^3	128^3	144^3	176^3	192^3	232^3
chains, k	280	288	289	257	271	243
length of the chains, n_p	239	559	779	1639	2019	4019
no. of cross-links, ν	2672	2736	2752	2440	2574	2308
tot. no. of monomers	69 592	163 728	227 883	423 663	549 723	978 925
density (%)	62.9	62.5	61.1	62.2	62.1	62.7

[a] The idealized simulations use only the values of k, n_p, and ν. The number of lattice sites defines the size of the system for the BFM and determines the density of the monomers in the simulation. The name of the network is defined by the estimated average number of monomers between cross-links. Additional simulations at lower density were performed for the types S11, S27, and S81. We chose 144^3, 192^3, and 256^3 lattice sites respectively to simulate cross-linking in solution at occupation densities of 18.6%, 18.5, and 20.2% and indicated these systems with S11_low, S27_low, and S81_low.

determination of f_R. Thus, it is more convenient for the calculation of the average value of the subchains for highly cross-linked systems of uniform chain length to calculate this value directly using

$$\overline{n_s} = \frac{(n_p - 2\overline{n_e'})k - 2\nu}{2\nu - k} \tag{24}$$

but this is only possible if $P(|b \geq 2) \approx 1$ for the new ρ'. The applicability of the above procedures was verified by the simulations.

2.4. Generalization of the Theory. The six simplifying assumptions of section 2.1 are not essential for this theory and can therefore be generalized. We summarize the fundamental ideas briefly.

If the polymer chains and cross-links are not arranged homogeneously and statistically in space, we can divide the system into parts, which are almost homogeneous, and calculate the whole distribution approximately as the weighted sum of the distributions of these parts.

If each monomer of any chain does not react with the same probability, we have to distinguish between two different cases. If the monomers of higher reactivity are placed at random along the chains, nothing changes. Otherwise we have to divide the chains into parts of higher and lower density of branching points. Then we can add the resulting distributions as explained above.

If our system consists of cross-links of higher functionality, we must keep in mind that only the first reaction of each cross-link is statistical. Every further reaction is influenced by all chains attached to the cross-link and can contribute to the fraction of cycles.

If the monomers of the chains can react more than once, then the number of reactive monomers of the chains is not reduced by the cross-linking reaction (to a good approximation).

It is hard to find a general method of handling dependent cross-linking reactions. One must consider how the dependency works and how the homogeneity of the system and the rate of the reaction influence each other.

Concerning the last assumption: no reaction is possible if the reactants are not close enough to react.

3. Comparison of Theory and Simulations

This section is divided into two parts by analogy with the theory section. First, we discuss idealized simulations of cross-linking reactions which are independent of the spatial arrangement of the polymer in order to prove eqs 3, 4, 7, 16, and 17. Additionally we use the analysis of these idealized systems to discuss the effects of the finite size of the simulations and to obtain a clear differentiation between statistical noise and the relevant results.

Second, we study more realistic networks using the BFM of Carmesin, Kremer, Deutsch, and Binder.[27,28,38] In these simulations, the spatial arrangement of the chains is responsible for the subchains formed. In the case of the high density simulations, the chains exhibit nearly Gaussian behavior. This simplifies the comparison of the simulations with eqs 19 and 21.

Both kinds of simulations, idealized simulation and simulation with spatial arrangement, allow us to separate effects caused by the randomness of the reaction or caused by the geometry of the system.

3.1. Idealized Monte Carlo Simulations. 3.1.1. Description of the Simulation. In section 2.2.1, we defined the system as a set consisting of k primary chains of identical length n_p and of ν reacted cross-links. The simplest configuration of monomers for a statistical reaction is a two-dimensional array of $k \times n_p$ lattice sites. The simulated values of k, n_p, and ν are listed in Table 1 and the idealized networks are identified with the suffix "_id" in the text. The prefix consists of a capital "S" followed by a number. The capital letter denotes a network that is cross-linked statistically, analogous to our previous work,[39] and the number specifies the average length of the subchains as we expected prior to this work.

To simulate a purely statistical cross-linking, two unreacted monomers of that array are selected at random and connected by one cross-link, independent of their place on the lattice. The extent of reaction is defined simply by the number of cross-links used (100% extent of reaction refers to the average of 19 branching points per chain). The length of the subchains and chain ends in units of monomers can be easily determined by counting the unreacted monomers on the lattice along the direction of n_p.

3.1.2. Comparison with Theory. To test the theory presented, we created 1000 idealized systems of type S11_id, S27_id, S38_id, and S81_id, to reduce the statistical noise, and compared the results with the theory of section 2.2. Figure 5 shows the simulated length distribution of the chain ends at three different extents of reaction r in comparison with the theoretical prediction of eq 3. The network of type S11_id was chosen because of the lowest statistical noise, but each simulated system is in good agreement with our theory. As indicated in the theoretical part, only chains with at least one reacted monomer are included in the statistics.

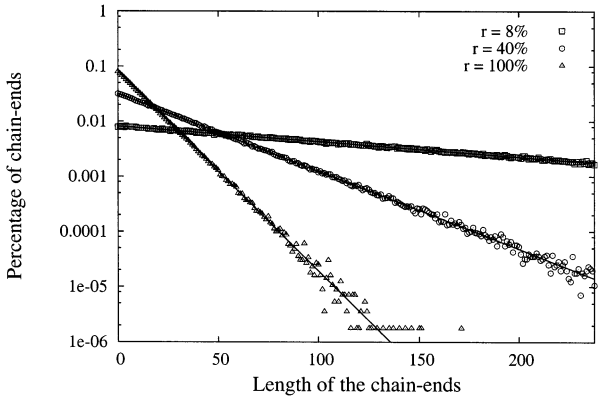

Figure 5. Comparison of the simulated length distribution (symbols) of chain ends and the theoretical prediction (lines) at different extents *r* of reaction.

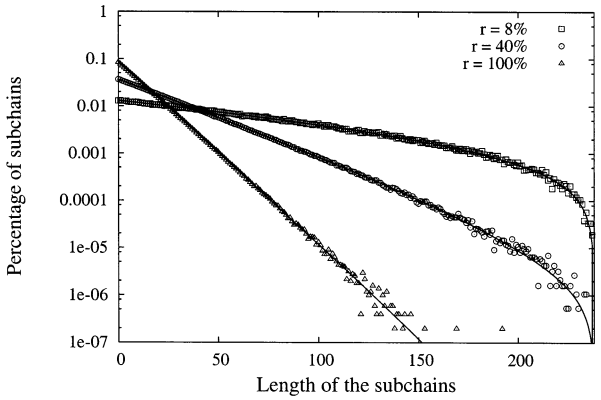

Figure 6. Comparison of the simulated length distribution (symbols) of subchains and the theoretical prediction (lines) at different extents *r* of reaction.

Independent of the extent of reaction, the length distribution of chain ends and subchains is different. For comparison, see Figure 6, which shows the subchains at the same extents of reaction as Figure 5 does. Short chains are more frequent, particularly at low extents of reaction. Over the whole spectrum of chain lengths there is good agreement between eq 17 and the simulated systems.

The difference between chain ends and subchains can be seen more clearly when analyzing the average values of the length of subchains and chain ends as a function of the extent of reaction (cf. Figure 7). The gel-point of the simulated system is at $r_c \approx 5.26\%$. For comparison, the mean value of a geometrical length distribution of infinite chains at the same cross-linking density ρ is shown. This mean value equals n_p at r_c. Near the gel-point, the geometrical approximation is not valid for the ends due to the finiteness of the chains. The average length of subchains is always lower in comparison to the chain ends, and both converge toward each other. To our knowledge this difference, which is most significant near the gel point, has not been discussed in any theory of the sol−gel transition to date. As a consequence, the fraction of elastically active or effective material is clearly overestimated in previous work. Miller and Macosko[7,8] assumed that the chain ends are only half as long as the subchains.

The above tests show that the theory of section 2.2 can be verified for the idealized case of statistical cross-

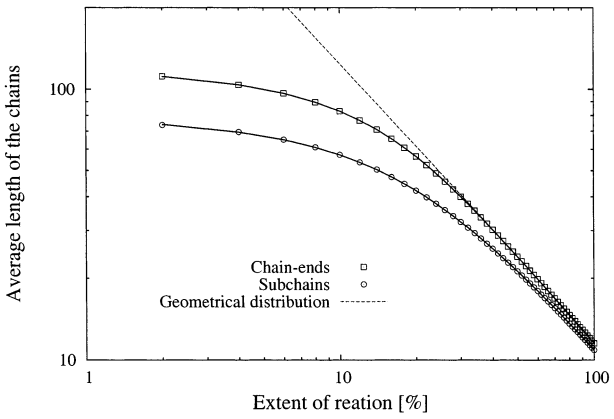

Figure 7. Average values of subchains and chain ends as a function of the extent of reaction for both, simulation (symbols) and theory (lines), in comparison with the equivalent geometrical distribution (dashed line) of the same ρ for the networks S11_id.

linking. One of the main results is that chain ends and subchains of polymer networks are of different average length after cross-linking. This difference is most significant near the gel point. Note that agreement between theory and simulation was obtained without any adjustable parameter.

3.2. Simulation of Cross-Linked Networks Using the Bond-Fluctuation Method. 3.2.1. Description of the Simulations. The results of paragraph 3.1 suggested that at least 100 statistically independent copies of each type of network should be generated in order to make a significant analysis possible. This causes problems concerning the available resources for computing. For this work, however, it is only necessary to obtain networks that are independent with respect to the cross-linking reactions. For this purpose we relaxed the whole un-cross-linked system for several million MCS and saved configurations in steps of more than 10 000 MCS. Since all monomers of the chains can react with the cross-links, only the position of the cross-link is the decisive factor for the reaction. Therefore, this step-size is sufficient to ensure approximately independent cross-linking reactions. This was verified by the correlation of the reactions of one cross-link for two subsequent systems. Indeed, this step-size is not sufficient to obtain independent chain-conformations for two subsequent systems, but this does not affect our results significantly. Additional simulations for the systems S11, S27, and S81 at low density were performed to study the effect of cross-linking in solution.

We summarize briefly the basics of the simulation method as far as it is required for understanding our discussions: The monomers of these simulations are represented by cubes occupying eight adjacent sites on a cubic lattice. The segments connecting the monomers are incorporated by a set of 108 bond vectors, which ensure that self-avoidance of the monomers implies a cut-avoidance of the bonds, while permitting maximum flexibility. The dynamics are obtained by random jumps of monomers by one lattice unit. We are only interested in general aspects concerning the structure of cross-linked networks. Thus, we chose the athermal case without van der Waals interaction in order to save

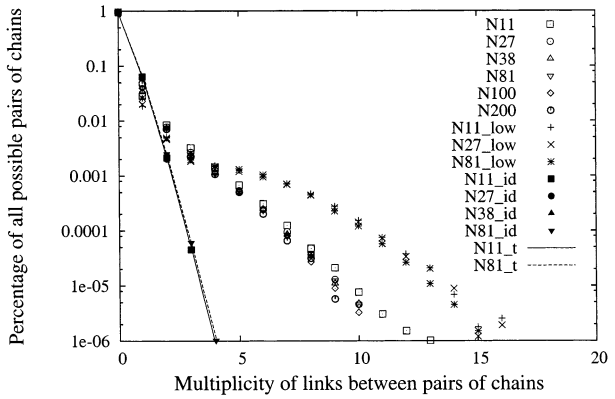

Figure 8. Multiplicity of links between pairs of chains. The hollow symbols show the results of the high-density BFM networks; the cross-like symbols stand for the low-density BFM networks, the filled symbols show the results of the idealized networks, and the lines denote the theoretical values for N11s and N81s to get a reference for the influence of the different numbers of chains used in the simulations. The suffix "_t" denotes the theoretical lines for the indicated networks. Each class of network exhibits its own type of correlation.

computing time. The system was confined in a box with impenetrable walls. The size of the box was chosen in order to define the occupation density of the lattice. No periodic boundary conditions were applied in order to facilitate simulations of swelling or deformation behavior (reported in ref 39).

The polymer chains were obtained by a chain polymerization process starting with a certain number of seed monomers and successively adding monomers until the length n_p was reached. After relaxation to equilibrium, the cross-links were inserted and curing was performed. The curing process was implemented in the same manner as in the simulations of Gilra et al.:[40] Whenever a chain monomer was in one of the six nearest-neighbor positions of a cross-link, the two monomers were connected by a bond.

The size of the simulations was originally adapted to previously simulated end-linked networks for a better comparison of the results. For the same reason the value of the cross-links was chosen in order to ensure a comparable volume of dangling chain ends (cf. ref 39).

The immediate succession of two branching points results in a subchain of length zero, which was not allowed in our recently simulated end-linked networks and is not implemented in our programs for the investigation of network structure described in refs 42 and 43. Therefore, we restrict the cross-linking reaction to monomers not linked directly to existing branching points. This affects our results particularly at high ρ and influences the formation of short subchains. The resulting deviations of the real behavior are discussed at the relevant points. Another influencing factor is given by the finite size of the simulations and is discussed in the next section. The details of the simulation[27,28] and the implementation of the cross-linking reaction[40] are described elsewhere.

3.2.2. Influence of Finite Size. To obtain an idea of the usability of the simulations, we study the effect of a small number of chains for cross-linking. A small number lead to higher connectivity of the chains than in infinite systems. To account for multiple cross-linking of the same chains, we analyze the correlation of cross-linking of given pairs of chains. In this connection, we recall the structural meaning of cross-links: cross-links connect chains which must not differ. In this way, cross-links define pairs of chains. If our system consists of k chains, we find $k(k-1)/2$ possible pairs of different chains and k pairs of identical chains. Cross-linking at random[41] means that we choose one of these pairs by chance $q = 2/((k+1)k)$. If we want to analyze the correlation of cross-linking, we have to compare the obtained frequencies of occurrence of the cross-linked pairs with this statistical expectation.

The number of branching points for statistical reactions is given by eq 2, which determines the distribution of the number of choices b for all chains and which is limited by n_p. The total number of chosen pairs of chains is given by the total number of cross-links ν. If there are b branching points on a chain, we can approximately calculate the probability of multiple links connecting one special pair of chains:

$$P(\nu, q, b) = \binom{\nu}{b} q^b (1-q)^{\nu-b} \tag{25}$$

which has to be weighted by eq 2.

Because of the small differences between the simulated values of k and ν and the comparable values of the particular form of eq 2, we can present the results of all simulated networks in Figure 8. The comparability of the systems with respect to their size is shown by the small deviation of the idealized networks and theoretical lines. The cross-linking reactions of the idealized networks are completely uncorrelated, because their values equal the theoretical expectation. The great difference between idealized and BFM networks shows that our results for the latter are not essentially influenced by the low number of chains chosen. This difference must be caused by the geometrical configuration of the chains.

The above results, in particular the nonzero values for the multiplicity greater equal two, triggered the analysis of the structure of cycles of second order. We also use this analysis as a benchmark for the BFM networks. If there are B_{ij} branches from chain i to chain j, with $i \neq j$, we find $(B_{ij}-1)!$ possible subchains as product of cycles of second order. For $B_{ij} = 2$, the length distribution is the same as the length distribution of the cycles for the idealized networks. For this reason, we chose the distribution of cycles for the idealized networks

$$\Phi_o(N, n_p) = \frac{2\,[n_p - N + 2]}{k n_p^{\,2}} \tag{26}$$

as a benchmark for our analysis. If the results of the BFM networks are of the order of magnitude of eq 26, no significant analysis is possible. We tested this for all kinds of simulated networks. Figure 9 shows the distribution of primary, remaining and all cycles of higher order in comparison to the values of eq 26 of the primary and the equivalent equation for the remaining cycles for the statistical network S11_id. It can be seen clearly that eq 26 defines a good possibility for comparison with the statistical noise. With this in mind we are equipped to analyze the networks.

Table 2. Fractions of Primary Remaining, and Secondary Cycles[a]

network	α	f_P	f_R	f_S^*	f_P(theor)	f_R(theor)	f_S(theor)
S11	8.03	28.06	17.27	0.87	30.95	19.37	1.02
S11_low	11.62	52.31	40.00	0.81	44.78	28.02	1.47
S11_id		0.356	0.033	0.036	0.359	0.036	
S27	7.38	27.18	19.42	0.74	30.31	21.91	0.78
S27_low	11.33	52.50	43.27	0.61	46.57	33.66	1.21
S27_id		0.344	0.034	0.033	0.348	0.035	
S38	7.25	26.93	20.26	0.58	30.35	22.93	0.70
S38_id		0.345	0.034	0.033	0.346	0.035	
S81	7.05	26.66	21.53	0.49	30.51	25.00	0.54
S81_low	10.77	49.77	43.71	0.46	46.55	38.15	0.89
S81_id		0.390	0.037	0.039	0.389	0.039	
S100	6.61	26.72	21.28	0.47	28.79	24.03	0.47
S200	6.18	25.21	21.82	0.35	27.41	24.01	0.34

[a] α = the fitting parameter of eq 18, as explained in the text. The fractions f_i are given in percent of all cross-links and the theoretical values are calculated by the use of α and eqs 19, 21, and 23. f_P stands for fraction of primary, f_R for fraction of remaining and f_S for the fraction of the relevant remaining cycles of second-order according to eq 23. For this table we analyzed the cycles of second order of different chains f_S^*. The number of second order cycles of identical chains is conspicuously lesser even for low-density networks and can be calculated in a good approximation by the us of f_R. The theoretical values of the idealized networks are calculated by use of eq 26 and denote the minimum value for these finite systems.

3.2.3. Comparison of Theory and Simulations. First of all we focus on the formation of cycles of any order, which can be counted easily in the simulation, in contrast to real experiments. The results of all simulated networks are summarized in Table 2. We will discuss them briefly, because they are not the actual point of interest, but they act as a basis for our further calculations.

The parameter α in eq 18 is determined as the ratio of the simulated to the calculated value for $N = 8$, because at this distance the effect of the self-avoiding cubes of the simulation is less significant and the statistics is still useable. The parameter α, which is the only adjustable parameter for our calculations, reflects the fact of the different size of the cubes in the simulation and the definition of the Gaussian distribution, which deals with unit volume. This is the reason the value of α is in the range of the size of the cubes for the high-density systems and is increased for the diluted systems. The decreasing α for increasing n_p is caused by the blockage of the nearest neighbors on the chain and the decreasing ρ.

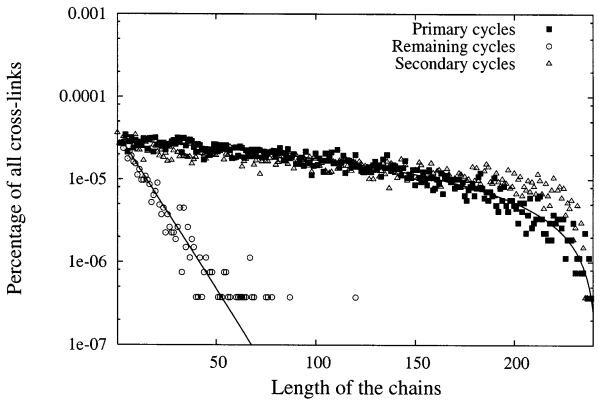

Figure 9. Distribution of primary, remaining and cycles of second order of the idealized networks N11_id in comparison with eq 26 and its equivalent form for the remaining cycles.

The differences for the high-density networks are rather small, because the Gaussian distribution function describes the conformations of the chains and subchains passably. In contrast, the low-density systems show greater differences, because the chains behave more like self-avoiding walks. In that case, a more convenient distribution function should be chosen. The blocking of the neighbors of the branching points in order to prevent subchains of length zero lowers the fraction of primary cycles significantly, because the shortest lengths of all cycles are most likely. The fraction of cycles of second order connecting different chains f_S^* does not reach 1% for any of these highly cross-linked networks and can thus be neglected to a good approximation. The fraction of second-order cycles connecting the same chain was lower than f_S^* for each network analyzed. Note that the difference for the theoretical value of f_S at S11 and S11_id originates only from the different values of α. All values for cycles of any order of the BFM networks are significantly higher than the values of the idealized networks. The data of Table 2 were used to calculate Table 3. We will now discuss these results in more detail.

First we compare the values of $\overline{n_R}$. The average value of the remaining cycles is higher than the theoretical value for all high density BFM networks. The most important reason for this is the blocking of length zero, which shifts the results of the simulation to higher average values. In contrast, this effect is more than

Table 3. Average Lengths of Remaining Cycles, Chain Ends, and Subchains[a]

network	$\overline{n_R}$	$\overline{n_e}$	$\overline{n_s}$	$\overline{n_R}$(theor)	$\overline{n_e}$(theor)	$\overline{n_s}$(theor)	$\overline{n_s^*}$(theor)
S11	4.26	11.68	10.87	3.14	12.42	10.43	10.52
S11_low	3.21	13.15	10.71	3.14	12.89	10.24	10.73
S11_id	11.57	11.53	10.88	10.89	11.52	10.88	10.89
S27	6.71	30.67	26.59	5.51	31.24	25.90	26.53
S27_low	4.82	35.50	26.06	5.51	33.06	25.43	26.32
S27_	27.71	28.35	26.85	26.85	28.42	26.84	26.84
S38	8.09	43.98	37.24	6.74	44.20	36.44	37.22
S38_id	39.90	39.98	37.69	37.69	39.90	37.69	37.69
S81	12.34	95.39	79.45	10.39	96.02	78.16	79.38
S81_low	8.86	109.1	77.93	10.39	103.0	76.89	78.60
S81_id	82.23	85.37	80.57	80.58	85.32	80.56	80.57
S100	13.57	117.5	98.08	11.67	118.1	96.69	98.01
S200	19.75	236.7	196.0	17.01	237.0	194.1	195.9

[a] Simulated and calculated average values of the length of remaining cycles $\overline{n_R}$, chain ends $\overline{n_e}$, and subchains $\overline{n_s}$. Differences for $\overline{n_R}$ and the blocking of the nearest neighbor are responsible for deviations of $\overline{n_e}$ and $\overline{n_s}$. The values of $\overline{n_s^*}$ are calculated by use of eq 24.

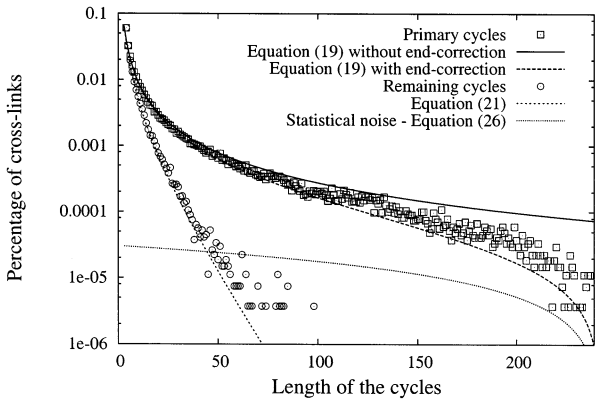

Figure 10. Percentage of cross-links that form cycles (primary and remaining) as a function of their length, in comparison to theory.

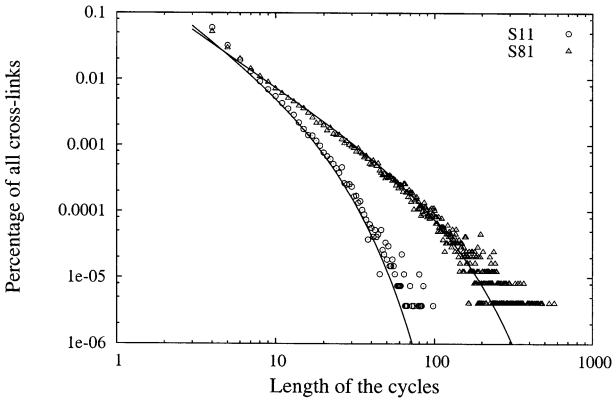

Figure 11. Effect of different density of the branching points: increasing ρ reduces the fraction of remaining cycles of the same length. The theoretical lines were calculated by use of eq 21 and the respective α.

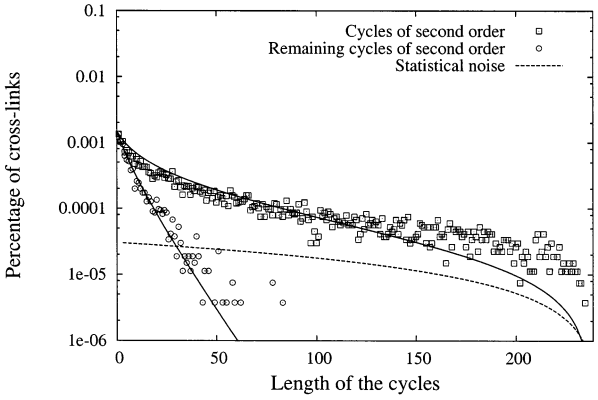

Figure 12. Cycles of second order of different chains and their remaining part analyzed for networks S11 in comparison with theory (lines, eq 23 with and without $(1 - \rho)^{n_2}$) and the statistical noise (dashed line) of eq 26.

compensated for the low density BFM networks, because of the increased probability for all short cycles. The values for the idealized networks are determined as averages of a comparatively low number of cases, but they are still in the expected range.

The values of the chain ends of the high-density BFM networks are in good agreement with our theoretical calculations. For short primary chains, we find a deviation which is caused by the higher mobility of the chain ends. This deviation is less important (because of the increasing average distance to the ends) for networks of long primary chains. The values of the low-density BFM networks are underestimated by our theory, owing to the underestimation of f_R. Again, the idealized networks show the best agreement.

The theoretical values of $\overline{n_s}$ are calculated following section 2.3.5 and using the modified equations, eqs 17 and 21, and the weighted addition of the resulting distributions. Therefore, the deviations of $\overline{n_R}$ and $\overline{n_e}$ are added and lead to a greater error than the calculation of $\overline{n_s}$* by eq 24. However, only the first procedure allows us to calculate the complete distribution.

The good agreement of calculation and simulation within the errors of $\overline{n_R}$ and $\overline{n_e}$ shows that it is sufficient to distinguish between remaining cycles and other subchains, as proposed in section 2.3.5 and to neglect cycles of higher order. All networks show the postulated property of $\overline{n_s} < \overline{n_e}$.

Having analyzed the mean values of the subchains and chain ends, we will now study the distributions which were obtained. Because of the lowest statistical noise, we show the results for the cycles of the networks S11 in Figure 10 again, as an example for the high-density BFM networks. We use this comparison in order to analyze possible influences of the finite size of our simulation and to obtain a well founded picture of the deviations mentioned above.

Since the simulation was performed on a lattice, it is affected by the lattice at short distances. The fitting of α at $N = 8$ shows good agreement for both very short and long cycles. Similiarly, the cross-linking reaction, which is performed at the lowest possible distance using the BFM, is influenced by the grid of the lattice. The enhancement of the simulated values for $M \geq 120$ originates from the finiteness of the system, which is additionally intensified by the back-folding of the chains at the boundaries. Nevertheless, we can conclude in conjunction with the results of Tonelli et al.[17,18] that only the conformation of the chains and cross-links is responsible for the formation of the primary cycles and the number of remaining cycles is controlled by the density of the branching points.

This can be seen more clearly when we compare two systems of different density ρ (cf. Figure 11). For a better comparison, we choose a logarithmic scale for the length of the cycles and we only show just the remaining cycles. Increasing ρ leads to a reduction in the fraction of remaining cycles of the same length. Note that the lengths of the cycles displayed differ from the lengths of the subchains formed. Another systematic difference between theory and simulation is caused by the blockage of the nearest neighbors and leads to the lack of data for the simulated length of three monomers. The blockage also affects the number of monomers of any cycle which can react. This results in a slight underestimation of the system S11. The property of self-avoidance can be seen even for these high-density systems in the increased values for cycles of about four to five monomers.

The fraction of cycles of higher order was neglected in our calculation of subchains and chain ends. Nevertheless, we can determine the amount and the corresponding distribution to test our theory. Again we show the results of the networks of type S11 in Figure 12,

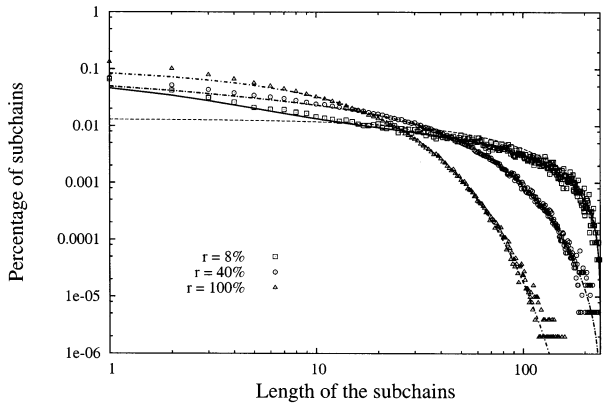

Figure 13. Comparison of the theoretical (lines) and simulated (points) distributions of the lengths of all subchains at different extents r of reaction. The dashed line shows the equivalent distribution for the idealized networks as an example at $r = 8\%$. We changed the scaling in order to focus on short lengths.

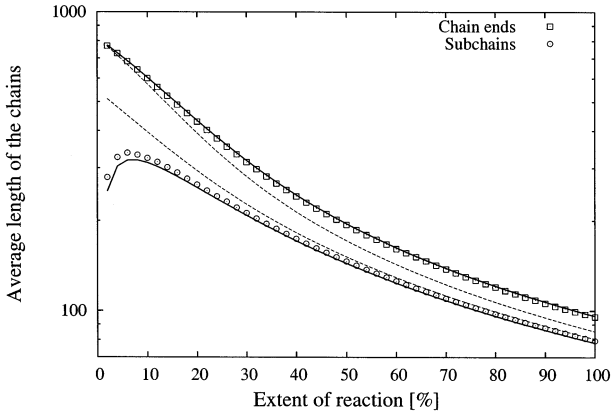

Figure 14. Average values for subchains and chain ends of the system S81 in comparison with theory (lines) and idealized theory (dashed lines). Theory and average values were calculated in steps of 2% only.

because at larger primary chain length the fraction of cycles of second order is smaller and shifted increasingly into the order of magnitude of the statistical noise.

The differences between theory and simulation are remarkably small and can be explained mostly by the restriction to different chains (which lowers the measured points for approximately 20% for this system; cf. f_R of Table 2). The effect of the back-folding of chains is increased due to the greater size of the combined chains. Since the frequencies of occurrence of the relevant remaining second-order cycles are more than one decade lower than the corresponding values of the remaining cycles, even for the systems of the highest ρ, they can be neglected to a good approximation.

To discuss the consequences of cycle formation for the resulting lengths of the subchains, we have to understand Figure 13, where the distributions of the lengths of all subchains are plotted for three different values of r. For a better comparison, the idealized distribution of subchains for $r = 8\%$ is shown additionally. The strong increase in the number of very short subchains is clearly to be seen as well as the decrease in greater lengths. The deviation for very short lengths is caused by the deviation for short cycles, as discussed above. At high extents of reaction very long lengths are also favored due to the consumption of cross-links as part of short cycles. The good agreement again proves the subdivision in remaining cycles and other subchains.

With respect to the distribution of the chain ends we must mention that the shape of the distribution is almost unchanged, but it is shifted to a lower slope. The lengths smaller than three monomers are significantly increased because of the higher mobility of the chain ends and the lower spatial density of the chain at its end. We can show the resulting general behavior, if we analyze the development of the average lengths of subchains and chain ends.

Displayed in Figure 14 are the values for the system S81, which was chosen due to the lower influence of the blockage of the nearest neighbors and the lower influence of the higher mobility of the chain ends. We find a clear shift for the values of chain ends caused by the formation of cycles, which is increased with increasing extent of reaction. At very low extents most of the subchains are cycles and decrease the average value of the subchains more significantly. The lack of cycles of length three in the simulation raises the average value of $\overline{n_R}$ and leads to a systematic shift of our simulated lengths for the subchains to higher values. We find a significant influence of the cycle formation on the average lengths of the subchains and chain ends, which can be expressed very well by our theory during the whole cross-linking reaction.

4. Conclusions

In this work, we developed the mathematical framework for an analysis of the lengths of subchains and chain ends in polymer networks. As a first step, we deduced equations for an idealized cross-linking reaction from statistical assumptions neglecting any spatial information on the position of the reactants. Our simulations verify, that these equations yield the correct values without any adjustable parameter. The addition of the spatial information leads to the well-known result that the conformations of the chains are responsible for the formation of short cycles. These cycles affect the distribution of subchains and chain ends. We showed that this cycle formation is not restricted to the chain directly attached to the cross-link, but to all chains attached to the cross-link dependent on their distance, but the amount of these cycles of higher order can be neglected even for high cross-linking densities. Distinguishing between remaining cycles and subchains allows us to calculate the total distribution of subchains. This is also the basis for the calculation of the effect of the cycle formation on the average length of the chain ends, which only requires the fraction of remaining cycles as parameter. We find that the average length of the subchains is clearly lower than expected in previous work. Thus, the fraction of elastically active or effective material was overestimated. The simplifying assumptions of section 2.1 can be generalized as described in section 2.4. Using our work we can conclude, that inhomogeneities of the system result in an increasing number of very short and very long subchains and an increasing amount of elastically inactive material. Systems consisting of cross-links of greater functionality form a higher ratio of cycles and a higher amount of dangling material. Cross-linking in solution favors the formation of cycles and increases the length of the chain ends. This should lead to a decrease in the elastic

Table 4. List of Symbols and Abbreviations:

r	extent of reaction
k	total no. of primary chains
k'	no. of primary chains forming subchains
n_p	no. of monomers of a primary chain
n_s	no. of monomers of a subchain
n_e	no. of monomers of a chain end
n_c	no. of monomers of a cycle
ν	no. of completely reacted cross-links
b	no. of branching points on a chain
$2\nu'$	no. of monomers reacted and part of any chain k'
ρ	average densitiy of branching points of a chain
α	parameter used to fit the distribution function $\Phi(\mathbf{R}, N)$
$P(b = i)$	probability for any chain to have i reacted monomers
$P(b \geq i)$	probability for any chain to have not less than i reacted monomers
$P(n_x)$	probability of chainlength n_x, x = p, s, e, c
$P(n_x\|b > i)$	probability of a sublength n_x if more than i monomers of the chain have reacted
$\Phi(\mathbf{R}, N)$	distribution function of end-to-end vectors
$\Phi_L(\mathbf{R}, N)$	distribution function of the length N of cycles
$\Phi_s(\mathbf{R}, n_2)$	distribution function of the cycles of second order
$\Phi_o(N, n_p)$	the minimal distribution function caused by the finite size of the system
$d_c(\mathbf{R}, n_x)$	density function of a chain at distance R
$d_R(\mathbf{R}, n_x)$	density function of the monomers of a chain without any branching point between
f_P	fraction of the primary cycles
f_R	fraction of the remaining cycles
f_S	fraction of the remaining secondary cycles
B_{ij}	no. of branches between the chains i and j
MCS	Monte Carlo step
BFM	bond-fluctuation method

properties. If cross-linking in solution leads to an increase in the elastic properties, the initial homogeneity of the system has to be questioned.

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(29) The handling of reactions connecting chains directly follows as a simplification.
(30) This extent of reaction is clearly different from the fraction of reactions which involve cross-linking agents.
(31) According to Dusek et al.,[12] we call structures as on the right side of Figure 1 cycles. The term intramolecular loops is also used in the literature.
(32) There exists no proof for this, but within the scope of accuracy of the algorithms used, the results were identical.
(33) The details of the simulations are discussed in section 3.2.1.
(34) The broadened distribution of Figure 2 is just a guide to the eye and was obtained by a simple trick which is not absolutely correct: We used the fraction of cycles f_C to transform the axes: $x' = n_p\rho + (1 + f_C)(x - n_p\rho)$ and $y' = y/(1 + f_C)$to show that the second reaction of the cycle forming cross-links obeys another rule disturbing the binomial distribution.
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