Statistical Properties of Random Cross-Linked Rubbers

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ABSTRACT: Starting from equilibrated melts of linear polymers chains, we investigate the static properties of randomly cross-linked polymer networks. Distributions of strand length, dangling ends, and self-cross-links are investigated. We find that the distributions are well described by simple exponentials. We also study systems where the chain ends are cross-linked. Here also the distributions are very well described by a simple exponential, however, with a strongly enhanced probability for short and long strands between cross-links.

I. Introduction

Highly cross-linked polymer systems have been of great scientific and technological interest for more than a century.[1-3] Many modern materials made from polymers are cross-linked in order to enhance their stability and to improve their mechanical properties. While there are a significant number of experimental results for rubbers, our theoretical understanding of these important materials is based largely on a number of crucial assumptions, many of which are beyond direct experimental verification. Rubbers are generally made by cross-linking melts of linear polymers, though there are many other techniques.[4,5] Two common ways this is done are to add active groups or irradiate the sample. However, in both of these cases as well as for all other cross-linking techniques we are aware of, the process cannot be controlled microscopically. There are always many defects such as dangling ends or loops that do not contribute to the elasticity. Since experiments mostly measure macroscopic properties such as the elastic modulus or swelling ratios, they provide only limited insight into the microscopic properties of these cross-linked systems. Neutron scattering provides a more direct method to probe the microscopic properties in cases where it is possible to label the cross-linking agent or cross-link a mixture of deuterated and hydrogenated chains.[6] By this the motion of the cross-links or the change of chain dimensions under swelling or elongation can be investigated.[7,8] But even here the interpretation of the data is difficult due to the lack of a detailed knowledge of the microscopic structure of the system.

The situation for analytic theory is similar. In order to provide a complete description of the system, detailed information of the microscopic structure is needed. For a realistic system, e.g., one prepared by radiation cross-linking, the number of connections on any given chain fluctuates strongly. Since the chains cannot cut through each other, entanglements are permanently entrapped. The entanglement density also fluctuates and is a function of both the chain length and cross-link density. In order to make the problem tractable, most theories of rubber elasticity make a number of very strong approximations that may have little to do with the real experimental situation. It is usually assumed that the strand length between cross-links is the same for all strands and that the system has no dangling ends or self-connections. Entanglements that are trapped by the cross-links are usually also neglected even though they are expected to be very important.[9] In addition, the network is usually assumed to be a phantom network, in which the chains are subject only to those constraints that arise directly from the connectivity of the network.[10-12] Infringements of chains and junctions on one another have no effect on the elasticity, which is purely entropic. Normally one assumes that the functionalities of all the cross-links are the same; however, it is straightforward to take into account that there is polydispersity in the functionality of the cross-links.[13] Recently Higgs and Ball[14] used the random resistor network analogy to account for the polydispersity of the strand length between cross-links, though still within the context of the phantom network model where entanglement effects are explicitly disregarded. The contribution to the stress from trapped entanglements for cross-linked polymer networks has been included using a slip-link model.[15] From this discussion, we think that it is clear that a more detailed understanding of the microscopic properties of polymer networks is urgently needed. One way to obtain such detailed information is to carry out computer simulations, which have the potential to lead to considerable new insight into the properties of polymer networks. However, well-equilibrated computer samples of many chain polymer melts have not been available until very recently.[16,17] Prior to the present study, computer simulations for the static properties of cross-linked melts were limited either to random-walk chains placed randomly in space without regard to overlap[18,19] or to short chains fixed between two points. The latter were used to study the force chains exert on the cross-links during stretching.[20] Thus these studies involve a significant number of crucial assumptions, which themselves need to be tested.

In order to overcome these difficulties, one has to start with a more "realistic" model. Here "realistic" does not mean that it is necessary to perform the simulations on a model that includes the full details of the chemistry. What it does mean is that we have to use a model that includes excluded-volume effects and preserves entanglements. One can indeed show that simulations using a more complicated approach easily lead to unreasonable

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demands on computer resources.[21] It is the motivation of the present study as well as a series of upcoming studies on polymer networks[22] to investigate the properties of cross-linked polymer systems by using simulations for a simple polymer model that fulfills the above criteria without being unnecessarily complicated. In the course of an extended study of the dynamics of entangled polymer melts,[16] we now have available a number of well-equilibrated samples that we can use to study polymer networks. In this paper, we will use these equilibrated melts to generate polymer networks and analyze their static properties. In future work, we will also discuss their dynamic properties.

In the present investigation, we are mainly concerned with highly cross-linked systems. This means that the number of cross-links is well above the vulcanization/percolation threshold. The vicinity of this transition is considered in a separate study.[22] There we show that the vulcanization/percolation threshold, p_c, measured in the number p of cross-links per chain, is independent of chain length, N, for large N. Thus the density of cross-links at the transition decreases as $1/N$ in agreement with Flory.[2] For random placement of cross-links, p_c is approximately 0.80, though this result depends somewhat on the details of the model. If we allow only intermolecular cross-links, we find $p_c \sim 0.60$, which is only 20% larger than Flory's mean-field result, $p_c = {}^1/_2$. The difference is that Flory's estimate only includes cross-links that increase the number of chains in the cluster. Obviously in a random process some cross-links connect chain segments that are already in the same cluster. For this reason, we prefer to specify the number of cross-links per chain p or per monomer, not the number of cross-linked chains. In the present study, we examine the region $0.5 \leq p \leq 6.0$.

In section II, we present a short description of the model and the criteria for generating equilibrated structures. There we also discuss how the cross-linking is performed. In section III, we present our results for the distribution of cross-links per chain, number of self-cross-links, and distributions of the length of the strands between cross-links and length of dangling ends. Special attention is given to the free ends of the chains. In section IV, we consider the properties of end-cross-linked systems, while in section V, we review our main conclusions.

II. Model and Method

Our starting points for the creation of randomly cross-linked polymer networks are equilibrated polymer melts. Such melts were generated in the course of an extensive study of the dynamics of entangled polymer melts.[16] The individual monomers are modeled by point particles interacting via a repulsive Lennard-Jones potential. Along the chain there is an additional anharmonic spring between subsequent monomers in order to keep the chain together. The interaction then is given by

$$U^0(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right] \quad \text{if } r \leq r_c$$
$$= 0 \quad \text{if } r > r_c \qquad (1)$$

where $r_c = 2^{1/6}\sigma$ is the interaction cutoff. Since the interaction is purely repulsive, for an isolated chain, this models the good-solvent limit. For monomers that are connected along the sequence of the chain, there is an additional attractive interaction potential (called the FENE potential) of the form[23]

$$U^{\text{bond}}(r) = -0.5kR_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right] \quad \text{if } r \leq R_0$$
$$= \infty \quad \text{if } r > R_0 \qquad (2)$$

The parameters $k = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$ are chosen to be the same as in ref 24. The actual simulations of the melt were done by using a molecular dynamics technique in which the monomers are very weakly coupled to a heat bath. Since we are interested in the static properties of the already equilibrated melts, we refer the reader to ref 16 for details of the technique and equilibration procedure. Here it is sufficient to note that the simulations were done at a number density $\rho = 0.85\sigma^{-3}$ and a temperature $T = 1.0\epsilon/k_B$ with periodic boundary conditions. The parameters in eq 2 were chosen so that bond crossing did not occur in the course of the simulations. In this paper we present results for a number of systems of size $25 \leq N \leq 200$, though we concentrate on two representative systems, of chain length $N = 200$ and 50. In the former case, our system contained $M = 100$ chains, while in the latter, $M = 80$. For comparison to experimental polymeric systems, the entanglement length $N_e \sim 35$, so that our two systems cover the range from short Rouse chains to entangled polymers.

In order to investigate the statistical properties of random cross-linking, we cross-linked our polymeric melts as follows. For each melt configuration, pM cross-links were placed at random in the system. For each cross-link we located the monomer that was the closest to it. This monomer can be thought of as "activated". A second monomer within a distance $r_x = 1.3\sigma$ of the first was then chosen at random. We chose this value of r_x since it equaled the persistence length of our chains, though the results are not sensitive to the precise choice of r_x. This second monomer then was considered to be connected to the first. In order to prevent an artificial strong coupling along the chain, monomers 1 or 2 chemical units away from the first monomer were excluded from forming a connection. This cross-linking procedure was repeated until the desired number of cross-links were added to the system. In contrast to the work of Shy and Eichinger,[19] every site along the chain was a potential cross-link site, and we did not allow chain scission. However, as was done in ref 19, the cross-linking was performed instantaneously for each configuration. This should be equivalent to irradiation cross-linking, which is done over a short time interval compared to the time it takes the monomers to move a few bond lengths. During our runs we saved the coordinates of every monomer every 60τ on magnetic tape. Here $\tau = \sigma(m/\epsilon)^{1/2}$. For the $N = 50$ system, we have 50 such configurations, while for $N = 200$, there are 400. To improve the statistics, for each value of p, we generated 50 sets of random cross-links for configuration for the $N = 50$ system and 10 for $N = 200$. Thus the data presented in the next two sections was averaged over a total of 2500 configurations for $N = 50$ and 4000 for $N = 200$ for each value of p. However, since the relaxation time for an entangled polymer melt is extremely long, these states were not statistically independent with respect to the overall configurations of the chain. During a time of 60τ, each monomer typically moved an average distance[16] of $\Delta r \sim 2.1\sigma$. Though this is certainly a small distance compared to the radius of gyration of the chains, it is just about ${}^1/_4$ of the tube diameter. However, what is more important for the present study is the change in the very local environment. For this the above time increment between different configurations and the total length of the run is

Table I
Average Number of Potential Cross-Linking Sites within Distance r_x of a Monomer for the Systems Studied[a]

	M/N				
	800/25	80/50	20/100	100/200	100/200 $\rho = 0.40\sigma^{-3}$
inter	4.50 ± 1.60	4.24 ± 1.71	4.17 ± 1.94	3.94 ± 1.73	5.7 ± 2.8
intra					
(a)	0.70 ± 1.01	0.90 ± 1.16	1.11 ± 1.25	1.13 ± 1.33	2.5 ± 2.2
(b)	1.30 ± 1.24	1.49 ± 1.36	1.71 ± 1.48	1.77 ± 1.50	

[a] N is the length of the chain, and M is the number of chains in the system. The upper line gives the number of monomers on different chains, while the second line gives the number on the same chain provided they are (a) more than 2 chemical units away or (b) more than 1 chemical unit away. The density $\rho = 0.85\sigma^{-3}$ for all N, except for $N = 200$, where there is an additional run for $\rho = 0.40\sigma^{-3}$. For $\rho = 0.85\sigma^{-3}$, $r_x = 1.3\sigma$ while for $\rho = 0.40\sigma^{-3}$, $r_x = 2.0\sigma$. The fluctuations indicate the width of the distributions and not the error in determination of the mean. The statistical error is of order 1–2%.

sufficient to obtain good statistics for properties discussed here. The reason is that the very local environment governs the cross-linking statistics. In order to obtain some insight into the question of how many inactive strands due to self-cross-linking are formed as the polymer density is varied, we made some new runs at $\rho = 0.40\sigma^{-3}$. In this case, we increased the maximum distance two monomers could be separated and still be cross-linked to 2.0σ. This was necessary in order to ensure that there would always be a neighboring monomer available for cross-linking.

In addition to placing random cross-links in the system, we also consider the case of end cross-linking. This case is treated in a very similar manner, except that the first "activated" monomer is always a chain end. They are then connected to a nearby monomer, either on the same chain or on another chain, depending on the local environment. As in the previous case, we also exclude two monomers that are less than 2 chemical units away from each other from cross-linking. This process was continued until all the ends were cross-linked. Note that this end-cross-linking procedure is different from what is often quoted in the literature by the same name, where networks are formed by linear or star molecules in which the ends of the chains carry a (multi)functional unit that only can connect ends to each other.[5]

III. Distribution Function for Random Cross-Linked Systems

For a completely random cross-linking process, as occurs in irradiation cross-linking, two monomers are linked together without regard to whether they belong to the same chain or not. However, for rubber elasticity, it is very important to know more about such self-connections. They are usually accounted as inactive for elasticity, even though they can form loops that may contribute to the elastic modulus. We checked the number of such intraconnections relative to the interconnections. Table I gives our results for chain lengths $25 \le N \le 200$. In addition to these data for $\rho = 0.85\sigma^{-3}$, we also include data for the $N = 200$ system at $\rho = 0.40\sigma^{-3}$ for comparison. What is striking about these data is the large number of intrachain monomers that are within an activation distance of one persistence length and are therefore candidates for cross-linking. This number increases with N and reaches an asymptotic value for large N. For very short chains, where approximately 13.5% of the potential cross-linking sites are on the same chain, this number increases to 22% for large N, where it seems to saturate. One can estimate the

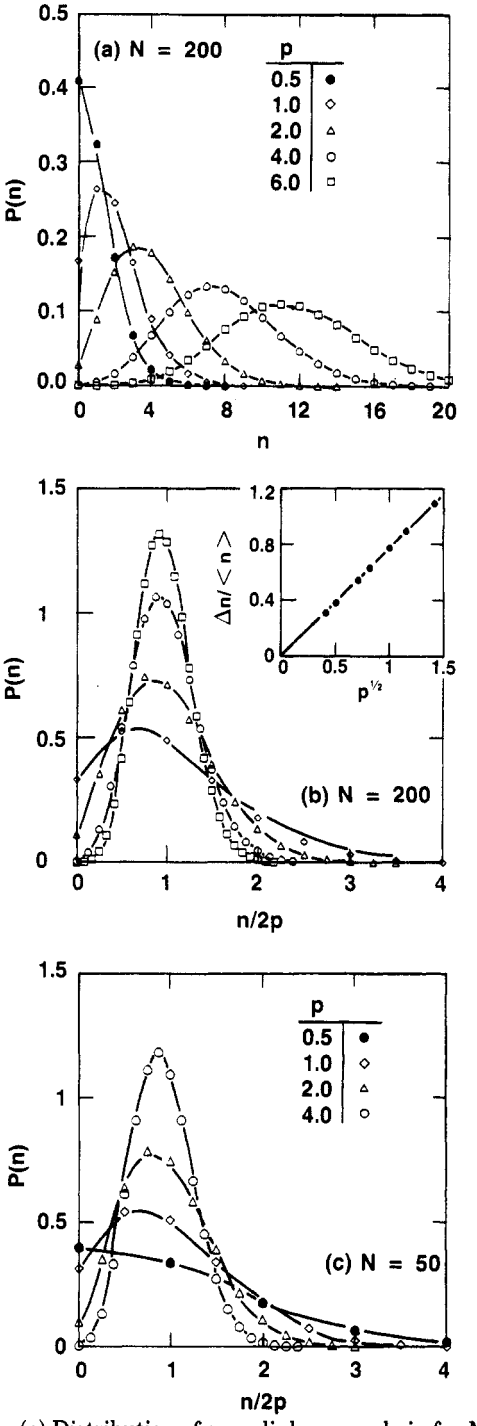

Figure 1. (a) Distribution of cross-links n per chain for $N = 200$ and $0.5 \le p \le 6.0$ cross-links per chain. (b) Same data as in (a) normalized by the average number of cross-links per chain, $2p$. (c) Same as (b) for $N = 50$ and $0.5 \le p \le 4.0$. Inset in (b) is the standard deviation divided by the mean, $\Delta n/\langle n \rangle$ vs $p^{-1/2}$, which shows that the distribution is statistically random.

potential number of self-cross-links by random-walk statistics. By assuming the probability that a given monomer of the same chain is near an activated monomer is constant and equal to its value at $\Delta R = 0$, we can obtain an upper limit to the number of potential self-cross-links. This can be estimated by integrating the random-walk distribution $\Phi(\Delta R,n) = (3/2\pi n l^2 l_p^2)^{3/2} \exp(-\Delta R^2/nl^2l_p^2)$ from n equal to 2 to ∞ and taking $R = 0$, where $ll_p = 1.3\sigma$ is the persistence length. Since most monomers are inner monomers of the chain, this result then has to be multiplied by 2. This gives an upper limit of 1.38 monomers on the same chain for each "activated" monomer that is far from the end of the chain. Although this is a

rather rough estimate for the number of nearby monomers, it is consistent with the numerical results given in Table I. If we allow next nearest neighbors along the chain to participate in the cross-linking, the probability for an intrachain connection increases to approximately 30%. One may of course say that, during a typical radiation cross-linking procedure, bonds between monomers only a few chemical units apart on the same chain are very unusual. While this is true for real polymers, in our coarse-grained model, a single monomer corresponds to several chemical monomers.[16] From our studies of the dynamics of the melts, we find that $N_e \sim 35$. For polystyrene (PS) this corresponds to an entanglement molecular weight $M_e = 18\,000$ or approximately 5 PS monomers for each 1 of our monomers. Thus, allowing third neighbors along the chain to form small loops seems to be quite reasonable. Also included in Table I are the root-mean-square fluctuations of the number of potential contacts. For the intrachain contribution, this fluctuation is about the same size as the average itself.

For an ideal random cross-linking, the individual connections can be treated as statistically independent events. Thus the distribution of the number of cross-links per chain, $P(n)$, should be a Gaussian distribution centered around the average number of cross-links per chain. Since each connection that is added to the system connects two different monomers, the average number of cross-links per chain is simply $2p$. Figure 1a shows the distribution of cross-links per chain, $P(n)$, for the $N = 200$ system for five values of p. In Figure 1b, we present the same distribution normalized by the mean $2p$. The results peak around $n/2p = 1$ as expected. It is apparent from the data that, as p increases, the distribution becomes more symmetric. We also found that these distributions do not depend on the specific model or the precise value of r_x. Results for random-walk chains placed randomly without regard to overlap at the same density as well as excluded-volume chains at a density $\rho = 0.40\sigma^{-3}$ give nearly identical results. For a completely uncorrelated process, the width of these distributions $\Delta n = \langle (n - \langle n \rangle)^2 \rangle^{1/2} \sim p^{1/2}$. The inset of Figure 1b shows $\Delta n/\langle n \rangle$ vs $p^{-1/2}$. The slope of the line is 0.77. Figure 1c shows the normalized distribution function for the $N = 50$ chains. Thus although the individual beads are strongly correlated via the chain connectivity, the overall structure of the liquid is isotropic as shown by these distribution functions. Thus we can conclude that, for $p \geq 2$, the number of cross-links per chain, the distribution closely approaches a random distribution independent of the details of the model.

Next consider the distributions $P_L(L)$ of strand length L between two cross-links. Figure 2 shows our results for $N = 200$ and 50. For a completely random process the distribution is expected to be a simple exponential with a decay length L^* given by the average length $\langle L \rangle$. Table II gives the results for the average strand length and the decay length for the chemical distance between cross-links. For short distances between cross-links the effect of intramolecular contacts is particularly significant especially for small p. Note that this length only can be defined when there are at least two cross-links on a chain. Thus for small p, this distribution, normalized to unit area, has to approach a limiting curve. In the limit of very small p, the expected decay length should be $N/3$, since all strands come from chains with the minimum number of cross-links per chain, namely 2. In Table II, we see that, for $p = 0.5$, this asymptotic value for L^* is found. As L approaches N there is a much stronger decay to zero than predicted by a simple exponential. For large p, the single

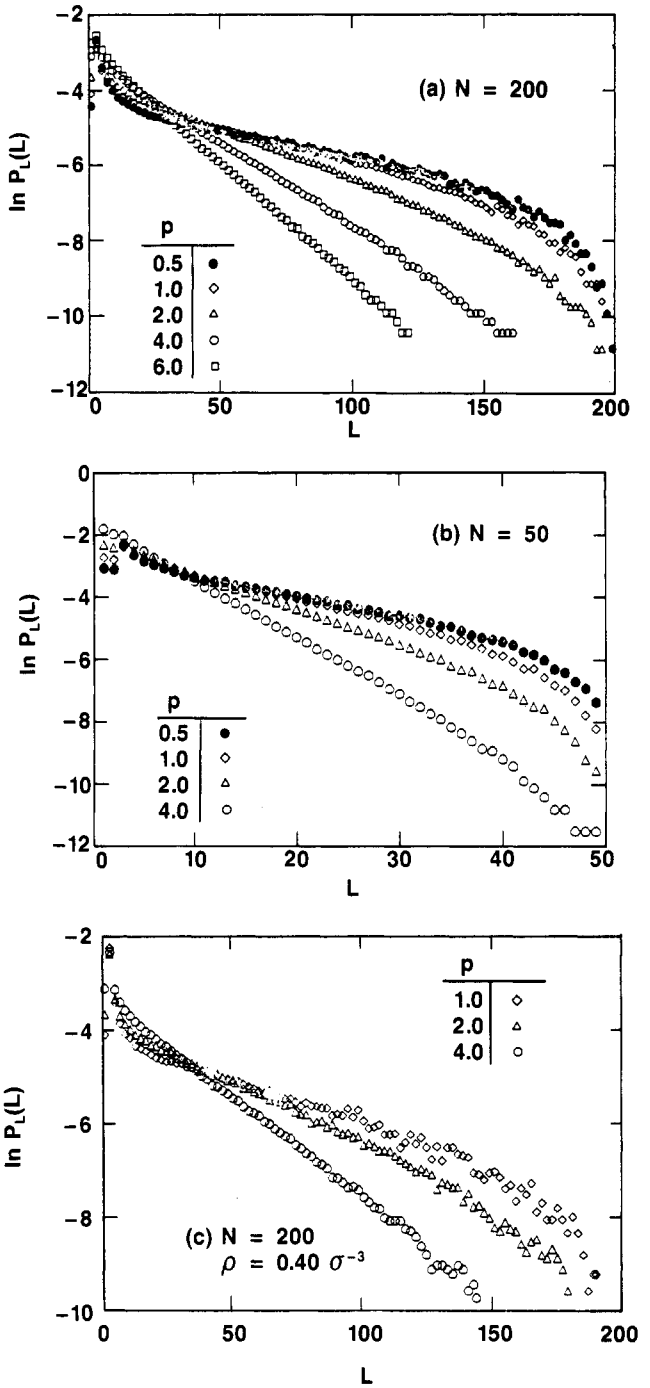

Figure 2. Semilog plot of the distribution of the length between cross-links L for (a) $N = 200$ and (b) $N = 50$ at density $\rho = 0.85\sigma^{-3}$ and (c) $N = 200$, $\rho = 0.40\sigma^{-3}$ for several values of p. For $N = 200$, only every second point is plotted. Note that there has been no smoothing of the data.

exponential is followed over almost the entire range of the data and L^* is only slightly larger than the expected value $N/(2p + 1)$. The decay length appears to approach this ideal value from above, while the average strand length $\langle L \rangle$ approaches it from below. For $p = 6$ and $N = 200$, $\langle L \rangle$ coincides with $200/(2p + 1)$ within our error bars. The approach from below can be explained by the enhanced probability for small L, which is a direct consequence of the intraconnections, which give rise to short loops, while this is not the case for intermolecular contacts. Figure 2c shows $P_L(L)$ for the $N = 200$ system for a somewhat lower density, $\rho = 0.40\sigma^{-3}$. As expected from the data in Table I, short intramolecular loops are even more important than in the higher density system.

Table II
Average Length $\langle L \rangle$ and Decay Length L^* for the Distance between Cross-Links and Average Length $\langle L_D \rangle$ and Decay Length L_D^* for the Length of the Dangling Ends for $N = 200$ and 50 at Density $\rho = 0.85\sigma^{-3}$ for Several Values of p, the Number of Cross-Links per Chain[a]

N	p	$\langle L \rangle$	L^*	$\langle L_D \rangle$	L_D^*
200	0.5	45.5	69.7	84.7	260
200	1.0	42.1	53.3	71.2	109
200	2.0	33.1	39.1	49.8	55.2
200	4.0	21.4	22.9	27.6	27.4
200	6.0	15.5	16.8	18.6	18.6
50	0.5	12.9	15.7	21.1	
50	1.0	11.5	12.8	11.5	
50	2.0	8.9	8.6	8.9	13.5
50	4.0	5.8	5.3	5.8	6.5

[a] The statistical errors for these data are approximately 1–2%.

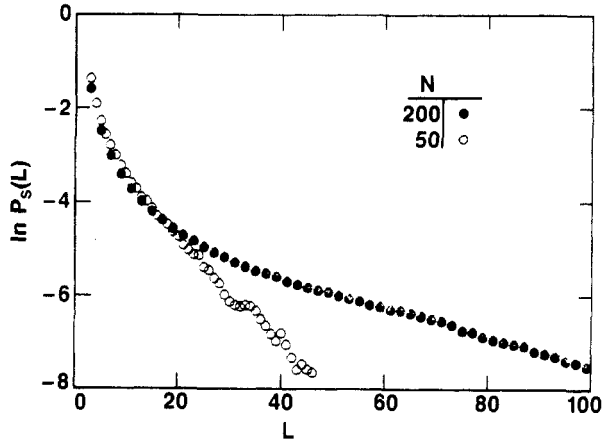

Figure 3. Probability $P_S(L)$ that a monomer that is a chemical distance L away is within a persistence length $r_x = 1.3\sigma$ for $N = 200$ and 50. The monomers at $L_S = 1$ and 2 have been excluded. Similar results have also been found for other values of r_x.[16]

To study the effect of intramolecular cross-links in more detail, we also measured the chemical distance between intramolecular cross-links. In Figure 3, we present the distribution $P_S(L)$ between two monomers on the same chain that are within a distance $r_x = 1.3\sigma$ for $N = 50$ and 200 on a semilog plot. Results for other values of r_x differ slightly for small L but are identical for large L. $P_S(L)$ was obtained by considering all potential intramolecular contacts and determining the chemical distance L between them. By this, we disregard any intermolecular/intramolecular contacts in between. Note that this quantity is different from the average distance between cross-links since only intramolecular contacts are considered. For long chains, one find as expected that $P_S(L)$ is universal, independent of N for $L \ll N$. As L approaches N, finite size effects set in and $P_S(L)$ must deviate from the universal curve. Figure 3 also shows the significance of short loops compared to long loops in agreement with the results presented in Table I. For the rubber elasticity of a network, this means that most of the self-loops do not contribute to elasticity since they are probably too short to trap entanglements.

Besides the number of loops, an additional important quantity for rubber elasticity is the amount and length of dangling ends. These sections of the network are also elastically inactive. Figure 4 presents our results for the distribution $P_D(L_D)$ for the length of the dangling ends L_D for $N = 200$ and 50 for several values of p. Following the same line of reasoning as for the strand length between cross-links, one might expect that, for $p > 1$, $\langle L_D \rangle = N/(2p + 1)$. However, as can be seen from Figure 4 and the results in Table II both the average length, $\langle L_D \rangle$, and the decay

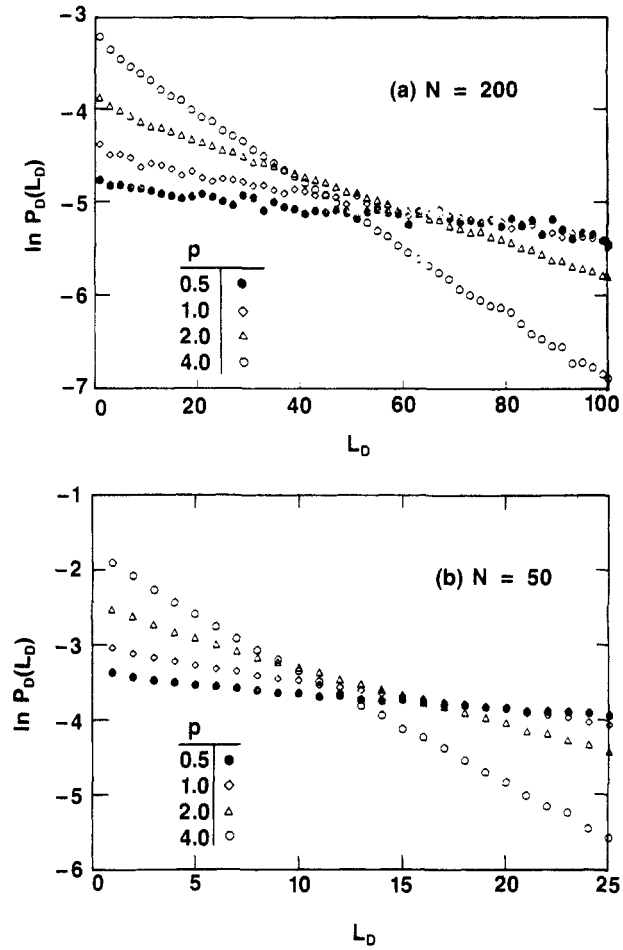

Figure 4. Semilog plot of the distribution $P_D(L_D)$ of the length of the dangling ends for (a) $N = 200$ and (b) $N = 50$ at density $\rho = 0.85\sigma^{-3}$ for several values of p.

length, L_D^*, are clearly larger than $N/(2p + 1)$. We do not have a complete explanation for this effect, but it is presumably related to the strong effect of intramolecular interactions. Not too surprisingly, however, as p increases, $\langle L_D \rangle$ and L_D^* approach the expected asymptotic value. In their paper on random cross-linked polymers, Shy and Eichinger[19] measured the number and weight average of the length of the dangling ends. Their results decay with p in approximately the form expected by the above analysis.

As we saw above, the self-cross-linkings are significantly enhanced for short chemical distances. For systems with only a very few cross-links, there will be many chains with only a single intramolecular connection. Since this intramolecular contact produces mainly short loops, one is left with two dangling ends that have a short middle strand and on average two long dangling ends. This is probably connected to the deviations from the expected behavior for $P_D(L_D)$.

IV. Distribution Functions for End-Linked Systems

One way to avoid dangling ends is to cross-link the ends of the chains. Experimentally, end cross-linking is usually done by adding a multifunctional, active group at the end of the chain. Then these active groups link together to form a network.[4,5] However, in many cases not all of the ends react, leaving an undetermined number of dangling ends. This is particularly true for long chains in a melt where it is difficult for the chain ends to find each other. Here we follow a different scenario. In our case, all the

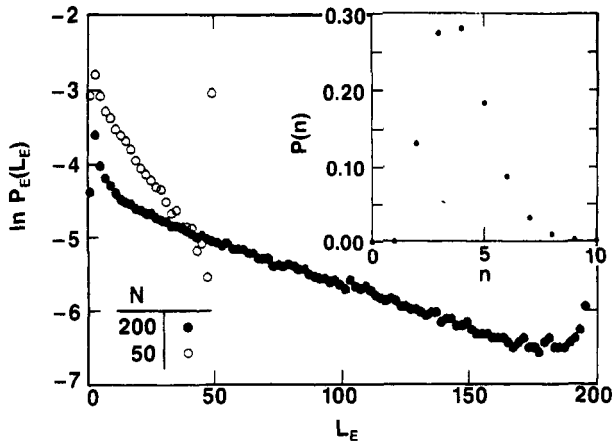

Figure 5. Semilog plot of the distribution $P_E(L_E)$ for the length between cross-links L_E for $N = 200$, $\rho = 0.85\sigma^{-3}$ for several values of p for the end-cross-linked case. The inset shows the number of cross-links n per chain.

chain ends are activated but the subsequent cross-linking is done in exactly the same way as in the random case in that each end monomer is linked to another monomer at random. This second monomer need not be at the end of the chain. The only requirement is that it be within a distance $r_x = 1.3\sigma$ and at least 2 chemical units away if both happen to be on the same chain. The fraction of intramolecular connections is 14% for $N = 200$ and 12% for $N = 50$, compared to 22% and 17.5% for the random cross-linked case. As the data show, the probability for producing a loop on the same chain is reduced significantly from the random case. This is because there is only one direction along the chain that can generate a self-connection, not two as in the previous case. Obviously, the local environment of a chain end contains more monomers on different chains or monomers on the same chain many chemical units away than does an inner monomer. From this simple counting, one might expect that the number of intramolecular cross-links would be roughly half. However, since the chain is typically more flexible near the end and the repulsive interaction between the monomers results in a slightly lower overall density near the ends, the reduction in self-connections is not as large.

This form of end crossing gives a universal distribution for $P_S(L)$, which is very similar to that shown in Figure 3 for the random case. In ref 16, we present results for the probability that a monomer is a chemical distance L from the chain end for two values of r_x, 1.5 and 2.0σ. This quantity describes the length distribution of self-loops in the limit of small p. As in the case of random cross-linking, the results depend only slightly on the value of r_x chosen. More interesting is the distribution of strand length between contacts $P_E(L_E)$ shown in Figure 5. On average each chain is cut into three segments, so that the $\langle L_E \rangle = N/3$. As found for the random case, there is a significant overshooting for small L_E. What is more interesting is the behavior as L_E approaches N where $P_E(L_E)$ is larger than expected. This increase in $P_E(L_E)$ for large L_E is directly connected to the increase for small L_E. A short loop at one end automatically produces a long "dangling end", which can only be shortened by additional connections. In many instances this "dangling end" is removed only when the other end of the chain becomes connected, leaving a chain with one very short and one very long segment. A similar behavior shows up in the decay length L_E^*, which is much larger than the average, similar to the decay length of dangling ends L_D^*, which is larger than $\langle L \rangle$ in the random case. As in that case, the longer chains, $N = 200$, deviate more strongly from the similar analysis than the shorter chains, $N = 50$. In the inset of Figure 5, we show the distribution $P(n)$ for the number of cross-links per chain for $N = 200$. Note that about 13% of the chains have only 2 cross-links and are thus connected to other chains only at ends.

V. Conclusions

In this paper, we have analyzed the statistical properties of an equilibrated polymer melt in which cross-links have been introduced instantaneously. As expected, the overall structure of the system was sufficiently homogenous that the average strand length between cross-links and the distribution of strand lengths follow the form predicted from simple probabilistic arguments. However, the distribution of the length of dangling ends deviates somewhat from the simple prediction. One very important finding of this study, which has implications on the elastic properties of the network, is the relatively large number of intramolecular cross-links. Though these loops can in principle contribute to the elasticity by trapping entanglements, many of them are significantly shorter than the entanglement length, N_e. If we assume that N_e is determined only by the probability of creating knots, this would mean that most of the intramolecular connections effectively produce additional dangling ends. This general result is expected to hold for experimental polymeric systems as well as for our computer model. This is because the structure of our polymer melt can be mapped onto chemical polymeric systems by mapping, e.g., the entanglement length, of one onto the other. Thus we believe that the present results should realistically describe the properties of irradiation cross-linked rubbers as long as no appreciable amount of chain scissions occurs.

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