

POLYMER NETWORKS BY MOLECULAR DYNAMICS SIMULATION: FORMATION, THERMAL, STRUCTURAL AND MECHANICAL PROPERTIES

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Abstract A molecular dynamics simulation method is presented and used in the study of the formation of polymer networks. We study the formation of networks representing the methylene repeating units as united atoms. The network formation is accomplished by cross-linking polymer chains with dedicated functional end groups. The simulations reveal that during the cross-linking process, initially branched molecules are formed before the gel point; approaching the gel point, larger branched entities are formed through integration of smaller branched molecules, and at the gel point a network spanning the simulation box is obtained; beyond the gel point the network continues to grow through the addition of the remaining molecules of the sol phase onto the gel (the network); the final completion of the reaction occurs by intra-network connection of dangling ends onto unsaturated cross-linkers. The conformational properties of the strands in the undeformed network are found to be very similar with the conformational properties of the chains before cross-linking. The uniaxial deformation of the formed networks is investigated and the modulus determined from the stress-strain curves shows reciprocal scaling with the precursor chain length for networks formed from sufficiently large precursor chains ($N \geq 20$).

Keywords: Crosslinking; Polymer network; Network topology; Molecular dynamics; Mechanical properties.

INTRODUCTION

The elasticity of natural rubber and other elastomer has been of interest since early 19th century^[1], for they could sustain ten times or more reversible elongations with very small elastic modulus^[2]. Actually, the properties of natural rubber lead to the first theoretical treatments of the chain conformational statistics of an isolated polymer chain, and revealed the relevance of the chain conformation properties to the entropy elasticity and extensibility of polymer networks^[3–10]. However, rigorous treatment of the relationship between the microscopic structure of a polymer network and its mechanical property still remains a challenge. For instance, in the development of theory as well as the interpretation of experimental data, approximations and assumptions concerning the molecular causes of the investigated properties must be made. Most of the classical network theories, like the affine and the phantom model, replace the real molecular network by an idealized network of Gaussian chains^[11]. Although some models, like the Mooney-Rivlin model^[12], can be used to describe the experimental data of real polymer networks by fitting theoretical parameters, it is not always clear if the fitted parameter values are indeed relevant or representing sensible molecular data.

With the fast development of computer technology, computer simulations of polymer networks have already significantly contributed to the understanding of the properties of polymer networks, since they allow for

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control over the atomistic details of the polymer network and to study the effects of certain interactions on network properties in a systematic way. Various defect-free network topologies have been generated and used in molecular simulations^[2, 13–18], in which the modulus of three-dimensional diamond-like polymer network build from precursor chains of chain length were found to conform well with the reciprocal behavior on chain length as expected from classical theories^[2], while the affine assumption, postulating that the relative deformation of each network strand is the same as the macroscopic relative deformation imposed on the whole network^[11], was found to have only limited validity even for the defect-free diamond networks^[13]. Topological network defects with varying cross-linking density and chain stiffness were also investigated for such diamond-like networks^[19].

As early as the 1980s, Eichinger^[20] had already developed a realistic model of network building, in which the reactions were not conducted by a dynamic process but instead by resorting to probabilistic algorithms, namely by introducing a reaction probability and steric penalty, during which the molecules were essentially static and the capture radius for the cross-link reaction was gradually incremented^[21]. The reactive cross-linking of precursor chains into complicated networks has been frequently investigated using the bond fluctuation model in Monte Carlo (MC) simulations^[22–26]. Although the MC method gives proper sampling of configuration space and allows for the successful generation of polymer networks, it does not give realistic dynamics of the systems. Molecular dynamics (MD) simulations integrate the Newton's equation of motion and obtain trajectories in real space and time units, which can be analyzed to give information of structural, thermal as well as dynamic and time dependent properties. Using atomistic force field models, most MD simulation work realizes bond formation or cross-linking between non-bonded chain ends by using arbitrary distance cutoffs between 0.4–1.0 nm until a certain conversion is reached^[27–35]. Grest^[36] used distance cutoffs to prepare networks by cross-linking off-lattice bead-spring homopolymers with polyfunctional cross-linkers attached to chain ends; Doherty *et al.*^[27] used a polymerization molecular dynamics scheme with a reaction radius ranging from 0.4 nm to 0.6 nm to build cross-linked poly(methacrylates); Recently, such cutoff scheme was used to build epoxy-based polymer networks on the basis of equal activity of the primary and secondary amine in the cross-linker molecules^[28, 32]. Varshney *et al.* used four approaches with different assumptions concerning the amine reactivity and connection procedures. The dynamic cross-linking approach they proposed, in which pairs satisfying the cut-off conditions are reacted simultaneously instead of connecting only the nearest pair at a time, was found to be more efficient in building larger cross-linked networks^[30]. Albeit, the good correspondence of these network properties with experiments, the use of cutoff distance criteria for the formation of cross-link has some drawbacks. The selected cut-off distances are quite arbitrary and often too large compared with equilibrium bond lengths (*ca.* 0.15 nm for C—C). In addition, the length of the newly formed bonds systematically increases with the extent of the reaction^[30]. Even though there are also coarse-grained MD simulations in which cutoffs are smaller than the average coarse-grained bond lengths^[37–39], the introduction of new bonds by imposing criteria external to the core of the MD simulation algorithm will make it hard for exact continuation of the MD process.

In this work, we present and apply a method to generate polymer networks in MD simulations, in which the cross-links of well defined functionality are formed as an intrinsic part of the simulation algorithm. Simulation methods (MC or MD) have already been used in this spirit to study the behavior of *e.g.* self-associating small molecules and polymers^[40–43], which contain one or more strongly associating groups (“stickers”). In these studies, different attractive potentials have been used. Khalatur *et al.* and Ayyagari *et al.*^[42, 43] used the screened attractive Coulomb potential to investigate the aggregating process of telechelic polymer chains and the morphology of the resulting associated system; Heine *et al.*^[44] investigated the structure and relaxation of end-linked poly(dimethylsiloxane) networks by using an attractive potential being an harmonic bond at short distances and linear at larger distances; Cruz *et al.*^[45] used the Lennard-Jones 12-6 potential while leaving other interactions purely repulsive to model gel formation of charged chains. These potentials could well describe the micelle-like aggregation of chains^[43] with associative ends, while the aggregation number varied significantly due to the long range associative interactions^[43, 45], and several, up to tens of groups, cluster together. Using these strongly associating groups the functionality cannot be controlled.

In the simulation method discussed here, we can make sure that the cross-links in the polymer networks

have specified functionality, which is accomplished by a careful choice of the interaction potentials used for the cross-linker units and the complementary groups that can make bonds (cross-links) during the simulation run without using external criteria such as cutoff distances or discretely defined cross-links.

In the following section we shall present the details of our model and simulation procedures which have been already used in the study of end-linked networks of ideal chains^[46]. Next, the analysis of our simulation results and the structural and mechanical properties of the networks will be discussed. The conclusions are made in the last section.

METHODS

Model and Parameters

The systems investigated contain three sorts of particles: middle-units (M), end-groups (E) and cross-linkers (X). These particles compose two types of precursor chains, illustrated in Fig. 1, to be cross-linked into a network: one type with composition $E-M_N-E$ and the other type $X-E-M_N-E-X$ with the polyfunctional cross linkers attached, where N is the number of linearly connected middle-units M. By the attachment of the cross-linker units X to the end groups E of the precursor chains, the functionality of the cross linker unit is effectively reduced by one, but the maximum functionality remains that of the cross-linker unit.

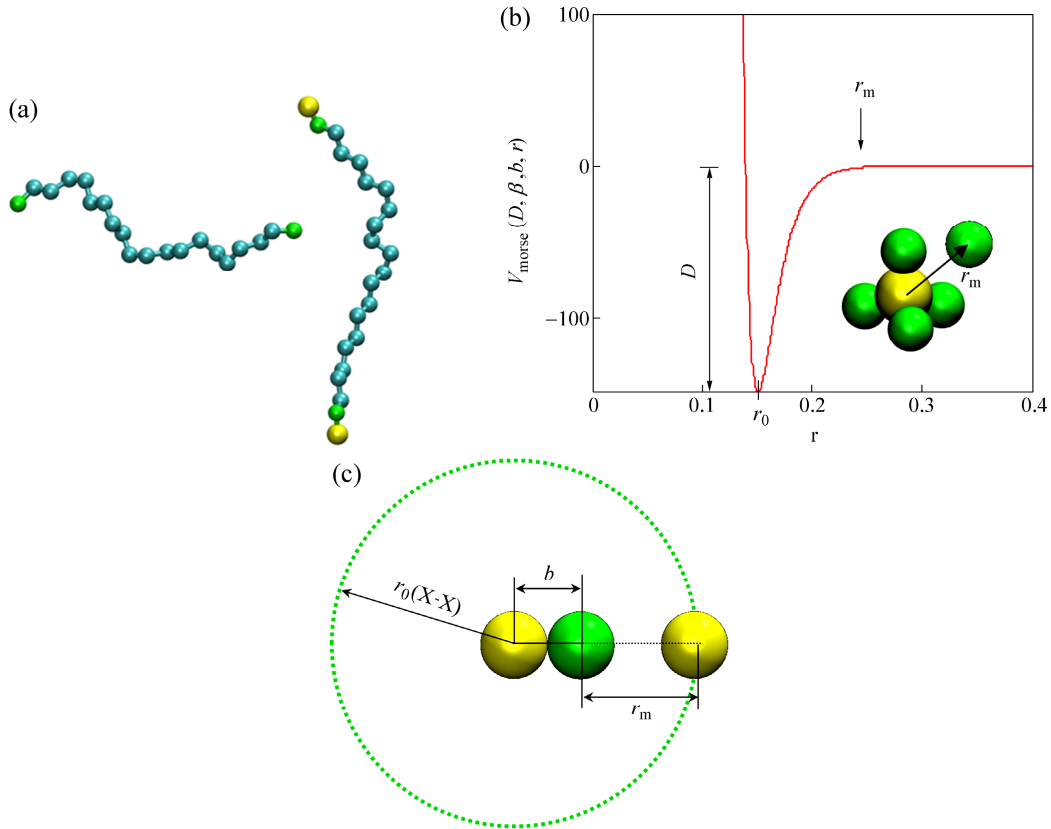


Fig. 1 (a) The two types of chains in the system, the left chain represents the $E-M_N-E$ chain and the right one represents the $X-E-M_N-E-X$ chain; (b) The shifted Morse potential and the criteria that appropriate sizes lead to the maximum close packing of four E around X (The interaction energy of X with additional E should be close to 0, *i.e.* $V_{\text{morse}}(r_m) \rightarrow 0$); (c) Each E is only allowed to connect with one X, which is controlled by the size of X, namely the minimal distance between a second X and the connected E should also have $V_{\text{morse}}(r_m) \rightarrow 0$, so $r_m \gg b$ or $r_0(X-X) \gg 2b$. Green spheres represent E and the yellow spheres represent X.

The functional forms of the interaction potentials and the force field parameter values used in the simulations are based upon the force field developed for united atom polyethylene (PE)^[47], which proved to give static and dynamics properties of a polyethylene melt in good agreement with experiments and explicit atom simulations^[48]. This force field was recently also used to investigate the thermal and elastic properties of semi crystalline polyethylene^[49]. The bonded interactions include bond stretching between two consecutive particles, angle bending between 3 consecutive particles and torsion dihedrals between 4 consecutive particles. The bond stretching is modeled by the harmonic potential,

$$V_b(r) = \frac{1}{2} k_b (l - l_0)^2 \quad (1)$$

where l_0 is the equilibrium bond length and k_b is the harmonic spring constant; the angle bending is modeled by the cosine based harmonic potential,

$$V_a(\theta) = \frac{1}{2} k_a (\cos \theta - \cos \theta_0)^2 \quad (2)$$

where θ_0 is the equilibrium angle and k_a is the force constant; the torsion dihedrals are modeled by a power law series,

$$V_{\text{tors}}(\varphi) = \sum_{n=0}^3 C_n (\cos(\varphi))^n \quad (3)$$

The interaction between X and E particles is modeled with the associative shifted Morse potential^[50],

$$V_{\text{morse}}(r) = D \left[1 - e^{\beta(r-b)} \right]^2 - D = D(e^{2\beta(r-b)} - 2e^{\beta(r-b)}) \quad (4)$$

The shifted Morse potential approaches zero at infinite r and equals $-D$ at its minimum b as shown in Fig. 1(b). Here, $b = 0.15$ nm is the equilibrium length of the bond formed between X and E, the association strength $D = 150$ kJ mol⁻¹ is chosen to be sufficiently strong so that when X and E are close together in space they form a bond on the time scale of the simulation, and the width of this interaction $\beta = 60$ nm⁻¹ is taken so that the associative interaction does not lead to secondary shell clustering of E around X which is already decorated with E as illustrated in Fig. 1(b). The same shifted Morse potential and similar parameters were also used in literature to model clusters with special geometries^[51].

All other non-bonded interactions, including those between particles in different chains and those within the same chain but separated by more than 3 bonds, interact by the Lennard-Jones 12-6 potential

$$V_{\text{L-J}}(r) = \varepsilon \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right] \quad (5)$$

where r_0 is the potential minimum or van der Waals diameter representing the characteristic size of particles, $\varepsilon = 0.391$ is the potential well depth. Different sizes of r_0 are used for different pairs of particles. Between M and all other groups r_0 is set to be 0.45 nm. To accomplish that one E-particle is allowed to form only one bond with one X-particle, a relatively large size $r_0(\text{X-X})$ is used, as a consequence a second X-particle approaching the E-particle connected to the first X-particle cannot form another bond to this E-particle as illustrated in Fig. 1(c). Varying the value of $r_0(\text{E-E})$, enables us to control the maximum number of E particles connected to X after bonding, *i.e.* the maximum functionality of the cross-linker unit X. All parameters for the non-bonded and bonded interactions used in the simulation during the formation of the network are listed in Table 1. For simplicity, the same atomic mass of a CH₂ unit (14.027 amu) has been assigned to all particles,

Simulation Procedure

NPT simulations were performed using the GROMACS 4.0 simulation package^[52], the non-bonded shifted Morse potential was realized with tabulated potentials. The equations of motion were integrated with the

Leapfrog algorithm with a time step of 1 fs for all simulations. A cut-off distance of 1.0 nm was used in all cases for non-bonded interactions. The temperature was controlled using the velocity rescaling method with a time constant of 0.1 ps, and the hydrostatic pressure was controlled using the Berendsen method with a time constant of 1.0 ps.

Table 1. Potential parameters used in the simulations

LJ	ϵ (kJ mol ⁻¹)	r_0 (nm)
X, X	0.391	0.50 ($f_m = 1$)
E, E	0.391	0.40 ($f_m = 2$) 0.35 ($f_m = 3$) 0.30 ($f_m = 4$)
C, (C, X, E)	0.391	0.450
Morse	D (kJ mol ⁻¹)	β (nm ⁻¹)
X, E	150	60
Bond	l_0 (nm)	k_b (kJ mol ⁻¹ nm ⁻²)
all	0.153	376141.6
Angle	θ_0	k_a (kJ mol ⁻¹)
all	110°	568.5927
Dihedral	C_0 (kJ mol ⁻¹)	C_1 (kJ mol ⁻¹)
all	6.497752	16.987040
		C_2 (kJ mol ⁻¹)
		3.627528
		C_3 (kJ mol ⁻¹)
		-27.112320

Model Preparation and Equilibration Run

In a typical molecular dynamics (MD) simulation, 150 E-M_N-E chains and 50 X-E-M_N-E-X chains are first randomly placed in a cubic box of length L with periodic boundary conditions, stoichiometric with X:E = 1:4¹.

Then an MD simulation run of 5 ns or 10 ns depending on the chain length is carried out to equilibrate the system. During the equilibration run, the associative interaction (Eq. (4)) between X and E is switched off, and X and E interact *via* the L-J 12-6 potential (Eq. (5)) with $r_0(\text{X-E}) = 0.45$ nm.

Network Formation Run

After the equilibration run, the associative interaction between X and E (Eq. (4)) is switched on to perform the cross-linking MD simulation for 20 ns for chains with $N < 50$ and 30 ns for chains with $N \geq 50$. The length of the simulation was chosen to reach a steady state in the extent of reaction. The cross-linking process is done under NPT-conditions to accommodate the volume changes upon cross-linking. After cross-linking the associative non-bonded potential for the newly formed bonds is replaced by the covalent bond, bending and dihedral potentials. The unreacted chains, if any, are removed and the LJ-parameter r_0 of all beads are set to $r_0 = 0.45$ nm.

Equilibrium Simulation (Annealing)

Further NPT equilibration runs of the thus obtained permanently cross-linked network are performed at various temperatures *via* an annealing approach, which starts from the equilibrated network at 500 K followed by successive decrease of temperature at the rate of 0.1 K/ps, at each selected temperature of interest the system is equilibrated for 2 ns before annealing to lower temperatures.

Network Deformation Run

In the final part of the simulation the equilibrated structures of the permanently cross-linked networks are subjected to a constant volume uniaxial deformation. The constant volume uniaxial deformation is realized by stepwise changing the simulation box along the z -axis at a deformation rate of 0.01 nm/ps for 10 ps, resulting in a deformation $\Delta L_z = 0.2$ nm per deformation step. At the same time, L_x and L_y are also changed appropriately at each time step so that the volume of the system at the end of this 20 ps run remains the same with that of the starting point. After each deformation, a 5 ns NVT run is performed to relax the polymer network with the new

¹ The effective functionality of the cross-linker is $f_m - 1$, since one of the f_m functionalities of X is used for the functionalization of the X-E-M_N-E-X type of chains.

box shape. Properties such as the average values of the components of the stress tensor are obtained from the second half of the 2 ns simulation, and then the deformation-equilibration procedure is repeated for subsequent values of deformation until the desired total deformation is reached. The network properties obtained after equilibration are found to be independent of the deformation rate and the equilibration time used during the deformation-equilibration cycle.

RESULTS AND DISCUSSION

Functionality of the Cross-linker Units X

We first studied by NVT simulation a mixture of 100 cross-linker units X and 400 end-groups E at the number densities of cross-linker units and end-groups which are also used in the corresponding study of the cross-linked polymers. We found that the cross-linker functionality is indeed efficiently controlled by our choice of interaction potentials, that end-groups can form at most one bond to a cross-linker unit and that the two chain ends of a precursor chain cannot form bonds to the same X-unit, preventing the formation of simple loops. The maximum functionality f_m of the cross-linker unit obtained from these simulations as a function of the potential parameter $r_0(\text{E-E})$ is summarized in Table 1.

Cross-linking Process

The initial system consists of 50 X-E-M_N-E-X and 150 E-M_N-E chains, 6 different chain lengths N varying from 10 to 100 have been chosen to generate polymer networks (see Table 2) and the system sizes range from 4.3 nm to 8.9 nm. The short chains were cross-linked at 300 K and the longer chains at 500 K. After cross-linking the linear size of the resulting network shrinks less than 0.5 nm with volume shrinkage of 4%–12%, which corresponds well with volume changes found in other approaches^[32, 53]. Figure 2 gives a snapshot of the network after the cross-linking process and Fig. 3 gives the evolution of the cross-linking process of the system with $N = 50$. Figure 3(a) shows the fractions of X connected with 1–4 E, f_{X_i} ($i = 1$ –4), and Fig. 3(b) shows the fractions of E connected with 0–1 X, f_{E_i} ($i = 0$ or 1). Since at the beginning of the reaction 100 X-units are already at both ends of the 50 X-E-C_N-E-X chains, f_{X1} starts from 1 and f_{E1} starts from 0.25. f_{X1} quickly disappears within 200 ps; f_{X2} reaches a maximum value and also disappears within 1 ns; f_{X3} also reaches a maximum but decays to a finite plateau value within simulation time; f_{X4} shows a sigmoidal shape and reaches in this case a plateau value of 90% as listed in Table 2. In the work of Varshney *et al.*^[30], different reactivity sequences were artificially defined during the cross-linking reaction of epoxy-based network and they found the dynamic cross-linking approach leads to a better equilibrated structure. Their dynamic approach is similar to our model in that all potentially reactive pairs are reacted simultaneously within their cutoff. Our model does not have any special definitions on the reaction sequence and all reactive pairs within the range of the associative potential will be cross-linked. The cross-linkers in our system predominantly react sequentially with the end groups: namely the X first reacts with one E, followed by a second E and then a third E until the upper limit of 4 E.

Table 2. Chain length N , cross-linking temperature T , cross-linking simulation time t , system size before and after cross-linking L_{ini} and L_{final} , glass transition temperature T_g , fractions of X (connected with 3 E and 4 E) $f_{X_i=3,4}$, the fractions of E that are reacted f_E and fractions of chains reacted f_{chain} .

N	T (K)	t (ns)	L_{ini} (nm)	L_{final} (nm)	T_g (K)	$f_{X_i=3,4}$	f_E	f_{chain}
10	300	20	4.28	3.78	281.3	3(0.24), 4(0.76)	0.94	1.00
14	300	20	4.63	4.24	281.0	3(0.25), 4(0.73)	0.93	0.99
20	300	20	5.09	4.79	282.1	3(0.25), 4(0.68)	0.90	0.985
30	300	20	5.72	5.46	285.2	3(0.27), 4(0.73)	0.93	0.985
50	500	30	7.24	6.78	280.7	3(0.10), 4(0.90)	0.975	1.00
100	500	30	8.89	8.53	288.2	3(0.16), 4(0.84)	0.96	1.00

Figure 3(b) shows the fraction of free and reacted end groups as a function of time, the fraction of free end groups, f_{E0} , decreases monotonically, meanwhile the fraction of reacted endgroups, f_{E1} , increases correspondingly. f_E reaches plateau values at about the same time as $f_{Xi=3,4}$ do. The plateau values of f_{Xi} , f_E and fractions of chains reacted f_{chain} are listed for all systems in Table 2. From the Table we find that only systems with $N = 10, 50$ and 100 have all chains connected to the network. From these data we can at least conclude qualitatively that the extent of reaction is larger at higher temperatures. Also the fraction of reacted end groups and the effective functionalities of the cross-linker units are higher at higher temperatures. This effect may very well be related to the vicinity of T_g at the low reaction temperature ($T = 300$ K) whereas the high reaction temperature, $T = 500$ K, is well above T_g .

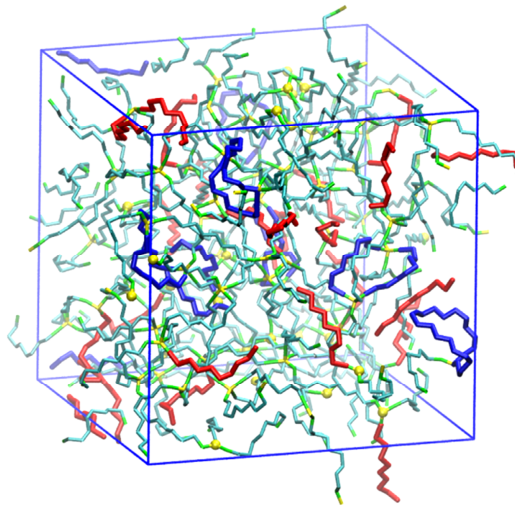


Fig. 2 Snapshot of the network with $N = 10$ after the cross-linking reaction

Loops are highlighted with blue bonds and the dangling ends are represented with red bonds, the big yellow balls are cross-linkers connected with 3 end-groups (the unsaturated cross-linkers). In this and all subsequent figures the cross-linkers units are colored yellow, the end-groups are colored green and the cyan bonds are the middle chain segments.

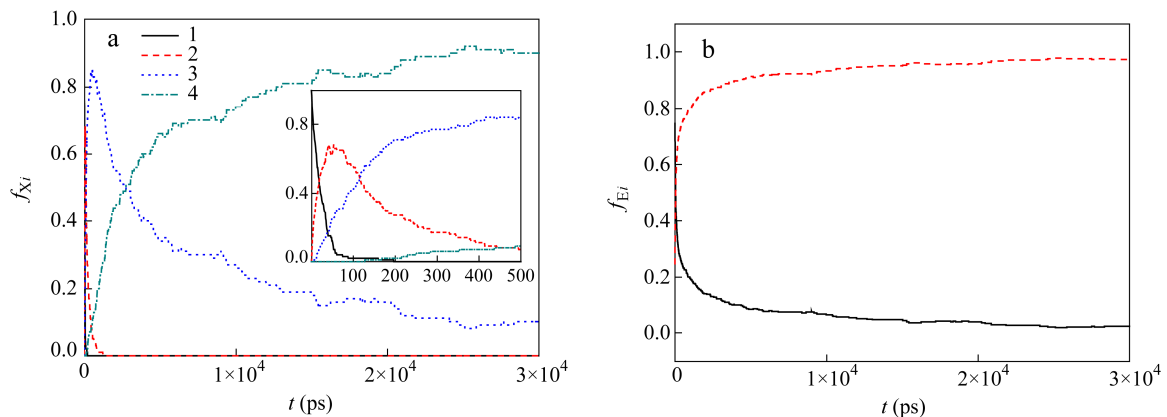


Fig. 3 Time evolution of the cross-linking reaction for the system with $N = 50$, (a) fractions of X, f_{Xi} , connected with i (1–4) E represented by solid, dashed, dotted and dash-dotted lines sequentially (the inset figure shows the initial 500 ps), (b) fractions of E, f_{Ei} connected with X, $i = 0$ (solid line) and 1 (dashed line)

At the beginning 100 X are already connected with E, so f_{X1} starts from 1 and f_{E1} starts from 0.25.

Gelation during Cross-linking

We may also show the reaction progress with respect to the reaction extent p , which is the ratio of the number of formed bonds to the maximum possible number of bonds^[11]. According to branching theory^[54], the critical condition of gelation, *i.e.* the gel point, occurs at the critical extent of reaction, p_c ,

$$p_c = \frac{1}{f-1} \quad (6)$$

where f is the functionality of the cross-linker. Due to the functionalization of the precursor chains with X, the effective functionality of X is 3 instead of 4 and p_c according to Eq. (6) is $p_c = \frac{1}{2}$.

Moreover, realizing that the reaction extent p is identical to f_E , depicted in Fig. 3(b), the simulation data can also be presented as a function of the extent of reaction p as depicted in Fig. 4, in which p_c is indicated by the vertical dotted line. Figure 4(a) shows f_{X_i} versus p , we find that after the gel point there are still X connected with only one E, *i.e.* the unreacted X-E-M_N-E-X chain ends. f_{X_2} reaches a maximum around $p = 0.4$ and f_{X_3} reaches maximum around $p = 0.7$. At the gel point f_{X_2} is already decreasing while f_{X_3} is still increasing. At the gel point f_{X_4} becomes nonzero. At $p = 0.8$ f_{X_3} is still larger than f_{X_4} and there are thus a lot of end groups not connected to the network.

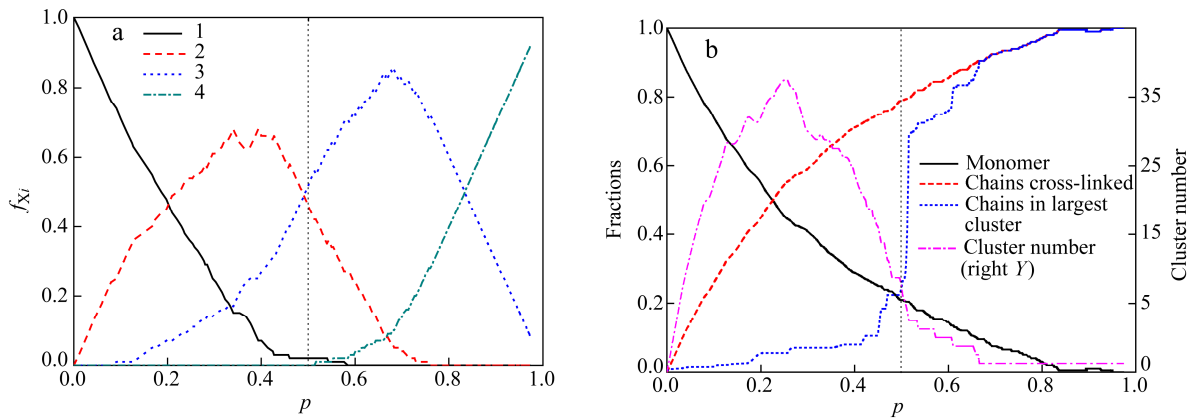


Fig. 4 (a) Fractions of X, f_{X_i} , connected with i (1–4) E versus extent of reaction p (represented by solid, dashed, dotted and dash-dotted lines sequentially); (b) Fractions of monomer (solid line), chains cross-linked (dashed line) and chains in largest cluster (dotted line) as well as the number of clusters (dash-dotted line) Results are for the system with $N = 50$. The vertical dotted lines are the theoretical gel point from the mean-field model.

Figure 4(b) shows the evolution of the number of clusters and the fractions of monomers, cross-linked chains and chains in the largest cluster. We see that the fraction of monomers monotonically decreases and becomes zero near the end of the reaction; in contrast the fractions of reacted chains increase monotonically until all are reacted. The number of clusters reaches its maximum at $p \approx 0.3$, *i.e.* far below the theoretical p_c and at that point many branched molecules exist in the system. Below the gel point p_c there are only finite-size branched polymers, while above the gel point p_c there is one cluster present spanning the whole volume^[11]. The size of the largest cluster in the system (represented by the fraction of chains in the largest cluster) has a sharp increase around p_c , showing that at this time the smaller clusters merge to make larger clusters and the volume spanning network forms at this time. This result is similar with Varshney's work where a sharp increase in the weight-average molar mass of the largest cluster was observed near the gel point, which was believed to have been caused by the reaction between the largest and the second largest cluster^[30]. The largest cluster continues to grow by attachment of the smaller branched molecules, clusters and the remaining monomers to the largest cluster.

The fraction of reacted chains and the fraction of chains in the largest cluster coincide for $p \geq 0.7$ when the number of clusters has decreased to 1, *i.e.* the cluster that spans the complete volume of the simulation box. At this point, there is still a significant amount of precursor chains in the system and the further growth of the gel comes from incorporating the remaining precursors, instead of merging between branched molecules.

At the time when the system contains only one network, f_{X4} is just 0.1 seeing from Fig. 4(a). For $p \geq 0.83$, nearly all monomers are attached to the largest network, while f_{X4} continues growing from 0.4 to 0.9 at $p = 0.98$, thus further reactions or further increase of f_{X4} is accomplished by intra-network reactions, namely the connecting of dangling chains to unsaturated cross-links in the network. This was also observed in other work that toward higher conversion ($p \geq 0.8$) most of the reactions happening are intramolecular reactions^[30].

Summarizing the details in the above section, the formation of the network is divided into subsequent steps:

- (1) Before p_c limited size branched molecules are formed and prevalent in the system;
- (2) Around p_c large branched entities are formed through integration of smaller branched molecules, and finally one volume spanning network comes into existence;
- (3) For $p > p_c$ the remaining monomers and smaller branched entities attach to the volume spanning network;
- (4) Further completion of the reaction is accomplished by intra-network connection of dangling ends to unsaturated cross-linkers.

Particle Interactions before and after Cross-linking

Before the associative interaction between X and E is turned on the system was equilibrated with the L-J 12-6 interaction for all particles. The radial distribution functions (RDF) between X and E for the system $N = 50$ before and at the end of the reaction are shown in Fig. 5(a). Before the reaction, X and E interact with the L-J 6-12 potential and the RDF is typical of a L-J fluid. After cross-linking a sharp peak around 0.15 nm is present showing the bonds formed between X and E during the cross-linking reaction as a result of the associative Morse potential between E and X. No secondary shell of E particles around the X particle is seen from the RDF, which demonstrates that the associative interactions between X and E units are short-ranged and do not lead to clustering of more than four E units connected with X. The RDF between E and E, shown in Fig. 5(b), shows similar effects. The E-particles connected to the same X lead to the sharp peak around 0.245–0.260 nm (geometric considerations give for the perfect trimer $\sqrt{3}b \cong 0.25$ and for perfect tetramer $\frac{2\sqrt{6}}{3}b \cong 0.245$). Other

E units, not connected through X, interact *via* non-bonded interactions, are homogeneously distributed in the system.

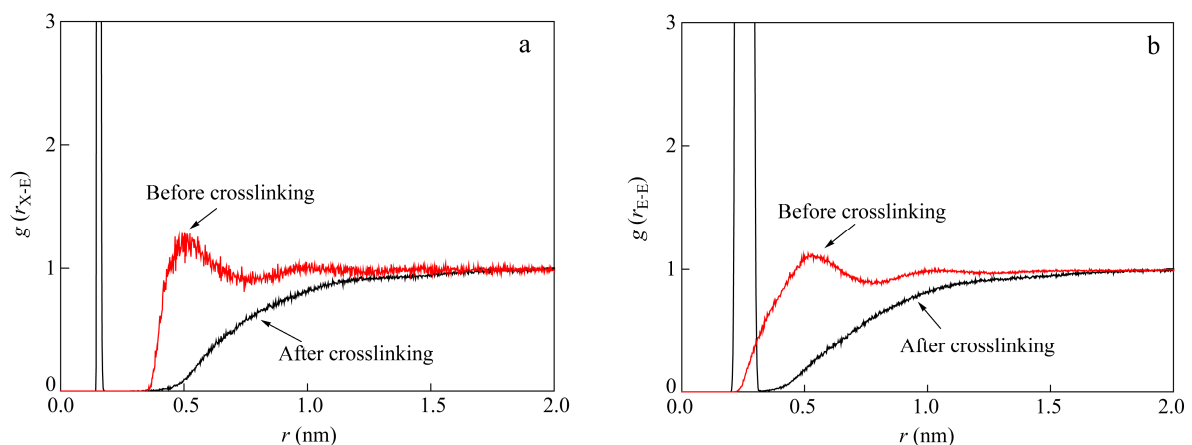


Fig. 5 Radial distribution functions (a) between X and E and (b) between E and E before and after the cross-linking reaction for the system with $N = 50$

The RDF's between X and X before and after cross-linking are given in Fig. 6. For the shorter chains ($10 \leq N \leq 30$ shown in Figs. 6(a) and 6(b) before and after cross-linking, the intramolecular correlation between X particles connected to the same chain X-E-M_N-E-X must be visible in the X-X radial distribution function. This is clearly seen for $N = 10$ around 1.0 nm, for $N = 14$ around 1.5 nm, for $N = 20$ as very small and broad peak at longer distance. The other peaks in Fig. 6(a) corresponds to the L-J 12-6 interactions between X units.

After the reaction, realistic network topologies are formed, and the correlations between X units become more complicated as can be seen in Fig. 6(b). From Fig. 6(b) we may still discern the single strand correlation for $N = 10$ around 1.0 nm, for $N = 14$ around 1.5 nm and for $N = 20$ around 2.0 nm. The typical peaks due to L-J interactions at 0.5 nm disappear after cross-linking, showing that the distribution of X units is not dominated by the L-J interactions between “free” X units, but rather by the network connectivity. Moreover, the primary peaks split into two parts with the first being shoulder-like for longer strand lengths and being a prominent peak for the shorter strands. The splitting of the primary peak after cross-linking is believed to be caused by two parts of the interactions in the system. The peaks or shoulders at shorter distance stem from the X units directly connected by a strand, which are more seriously correlated for smaller N . This is very similar as for the system before cross linking has taken place (depicted in Fig. 6a). The peaks at larger distance (situated at *ca.* 1 nm) arise from X units not connected by strands and correspond to the second peak in $g(r_{X-X})$ before cross-linking.

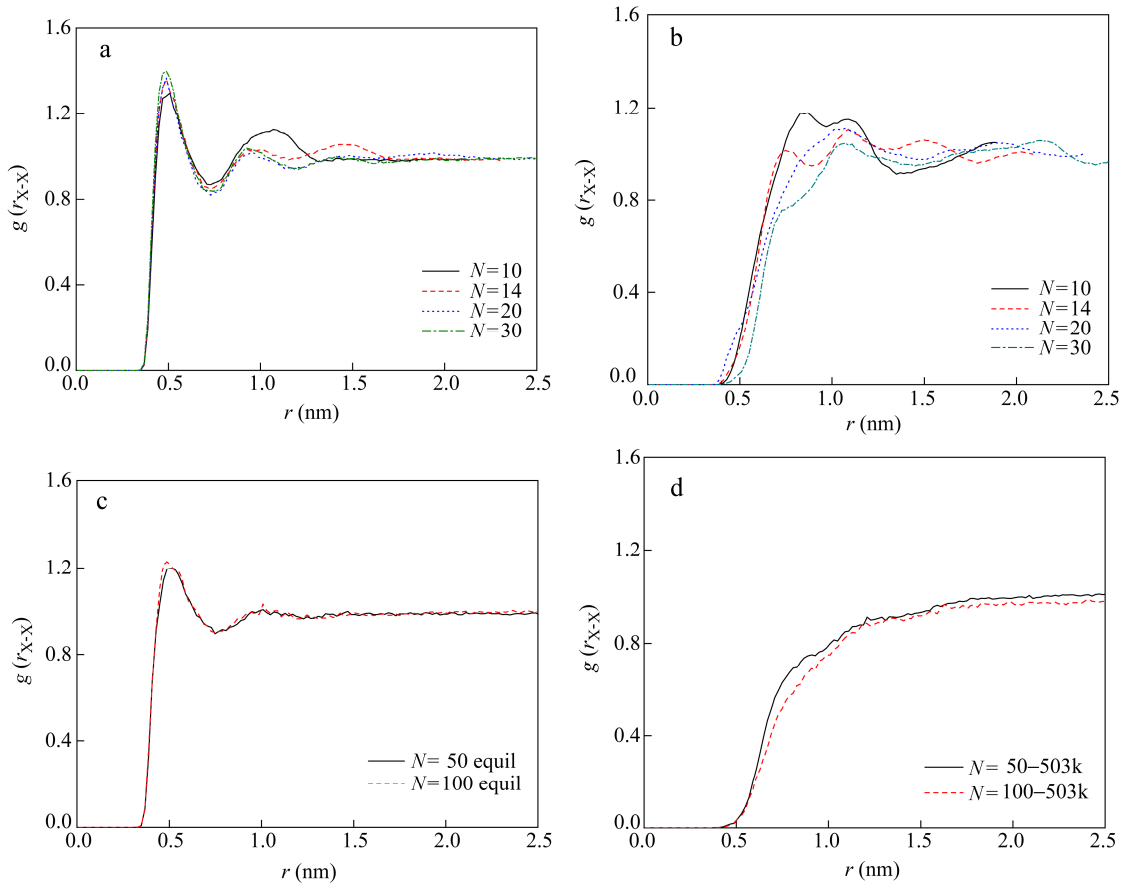


Fig. 6 Radial distribution functions $g(r)$ between X and X (a) before reaction and (b) after reaction for systems with $N = 10$ (solid line), 14 (dashed line), 20 (dotted line) and 30 (dash-dotted line); $g(r)$ between X and X (c) before reaction and (d) after reaction for systems with $N = 50$ (solid line) and 100 (dashed line)

For the longer chains ($N = 50$ and $N = 100$, depicted in Figs. 6(c) and 6(d) before and after cross-linking respectively, the correlations between X units at the ends of the same chain are not observed in $g(r_{X-X})$. After

cross-linking the normal L-J peak between X units also disappears due to chain connections which make it unlikely for two X units to interact directly through non-bonded interactions. For $N = 50$, a small shoulder is still seen caused by the correlation between X units connected to the same strand, for $N = 100$ this correlation is further reduced and nearly no shoulder can be seen.

Chain Conformations before Cross-linking and Strand Conformations in the Network

The end-to-end distributions of chains before and after cross-linking are plotted in Fig. 7 versus reduced distances. Both distributions of the chains before cross-linking and the strands in the network are similar at smaller distances but deviate at longer distances due to the chain length difference. After cross-linking only small changes are found in the distributions, showing that the chains maintain in very good approximation the original chain conformational distribution before and after cross-linking, especially for systems with longer strands. For systems with shorter strands, the distribution becomes slightly wider, which shows that after cross-linking the short chains have to stretch slightly to connect between cross-links.

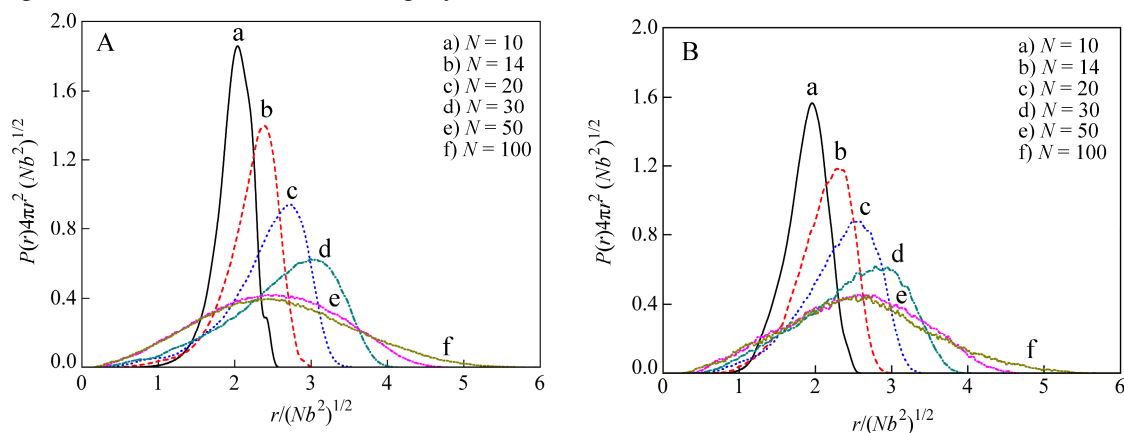


Fig. 7 End-to-end distribution functions of (A) chains before cross-linking and (B) strands in the networks with chain length $N = 10$ (solid line), 14 (dashed line), 20 (dotted line), 30 (dash-dotted line), 50 (dash-dot-dotted line) and 100 (short-dashed line) (The simple loops are not considered.)

Further detailed information can be obtained from the dihedral distributions before cross-linking and strands in the network plotted in Fig. 8 for the $N = 50$ system. The distributions of dihedrals before and after cross-linking are nearly the same but a small increase in the population of the *trans* state can be observed, indicating a slightly more extended conformation in the network. This effect becomes more pronounced with decreasing N .

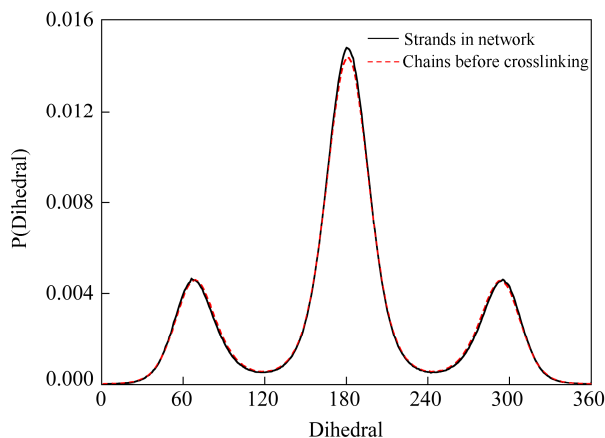


Fig. 8 Dihedral distribution functions of chains $P(\text{Dihedral})$ before cross-linking (dashed line) and strands in the network (solid line), for $N = 50$

Specific Volumes of the Undeformed Networks

Annealing runs are performed to obtain the equilibrium properties of the networks in the temperature interval of 500–250 K in steps of 50 K. The specific volume $V(T)$ at the investigated temperatures is determined from the second half of the 2 ns equilibration runs and are plotted with respect to $1/N$ in Fig. 9(a), linear fits of these values show clear $1/N$ dependence at all temperatures. With the decrease of strand length, the cross-linking density increases as well as the density of the networks increases.

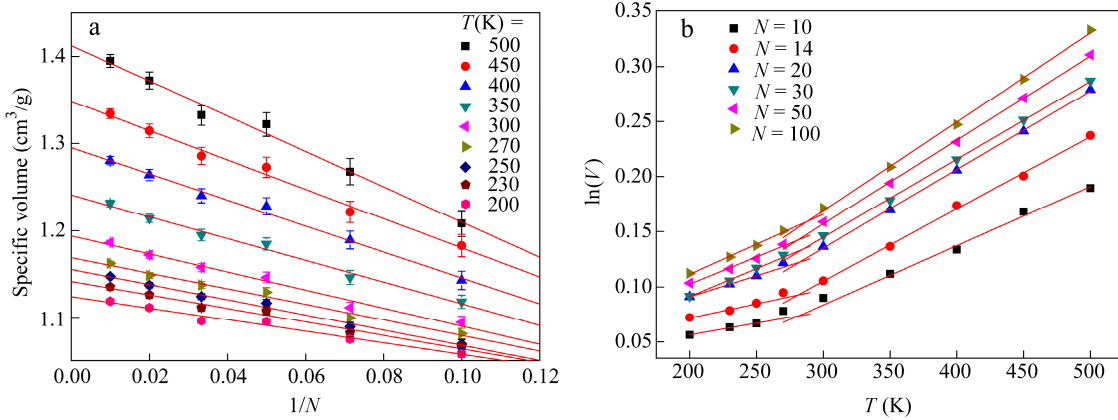


Fig. 9 (a) Specific volumes of the resulting networks versus inverse N at indicated T ; (b) Specific volumes of the resulting networks versus temperature at indicated N . Data points in the plots are from our simulation and the solid lines are the linear fitting of selected simulation data.

Figure 9(b) gives the temperature dependence of the specific volumes for the different chain lengths. As noted in the work of Buchholz *et al.*^[55] in a rather large temperature range the relation between $V(T)$ and T is non-linear but $\ln V(T)$ depends linearly on temperature both in the glassy region and in the melt region, *viz.*

$$\ln V(T) = a + bT \quad (7)$$

The temperature of intersection between the glassy and melt regions gives an estimate of the glass transition temperature T_g ^[30, 31, 55, 56] which is summarized for all investigated chain lengths in Table 2. Experimentally, cross-linked low density PE (LDPE) has T_g of 155 K and high density PE (HDPE) has T_g of 171 K^[57], both values are much smaller than those obtained in our simulations. The glass transition temperature obtained from MD annealing runs depend upon the much faster cooling rate (5 K/50 ps) implemented in the simulations, which leads to much larger values of T_g in simulation^[58]. The dependence of T_g on the cooling rate in MD simulation was systematically investigated in the work of Joachim *et al.*^[55]. Recently, Armand and Nouredine^[59] have shown that the MD simulations can also accurately predict the glass transition: they demonstrated the universality of the well-known Williams-Landel-Ferry equation for both experimental thermal dependence of polymer viscosity and atomistic simulations. The T_g values obtained for the networks do not seem to have a clear relationship with the cross-linking density, but accurate determination of T_g of the networks needs more systematic investigation, which will not be pursued here.

Defects in the Undeformed Networks

At the end of the cross-linking procedure we always get one network spanning the simulation box. The network structures we generated are not as perfect as those used in some previous works^[2, 13–18], but include defects such as dangling ends and loops (see Figs. 2 and 10). Dangling ends are strands having one end not reacted; their number can be directly calculated from f_E in Table 2. We determined two sorts of loops in our systems, simple and secondary loops. Simple loops have both ends of a single chain connected to the same cross-linker as shown in Figs. 10(a) and 10(f), and they are always elastically non-effective; secondary loops have two chains sharing

two cross-linkers as shown in Figs. 10(c) and 10(d), these loops can be either elastically active or non-active depending upon their connectivity to the network. For example, the secondary loop shown in Fig. 10(c) has one end connected to the network while the other ends of the two strands connected with each other, so does the left loop in Fig. 10(d), these loops are non-active; the loop shown at the right of Fig. 10(d) has both ends connected to the network and such loops are effective.

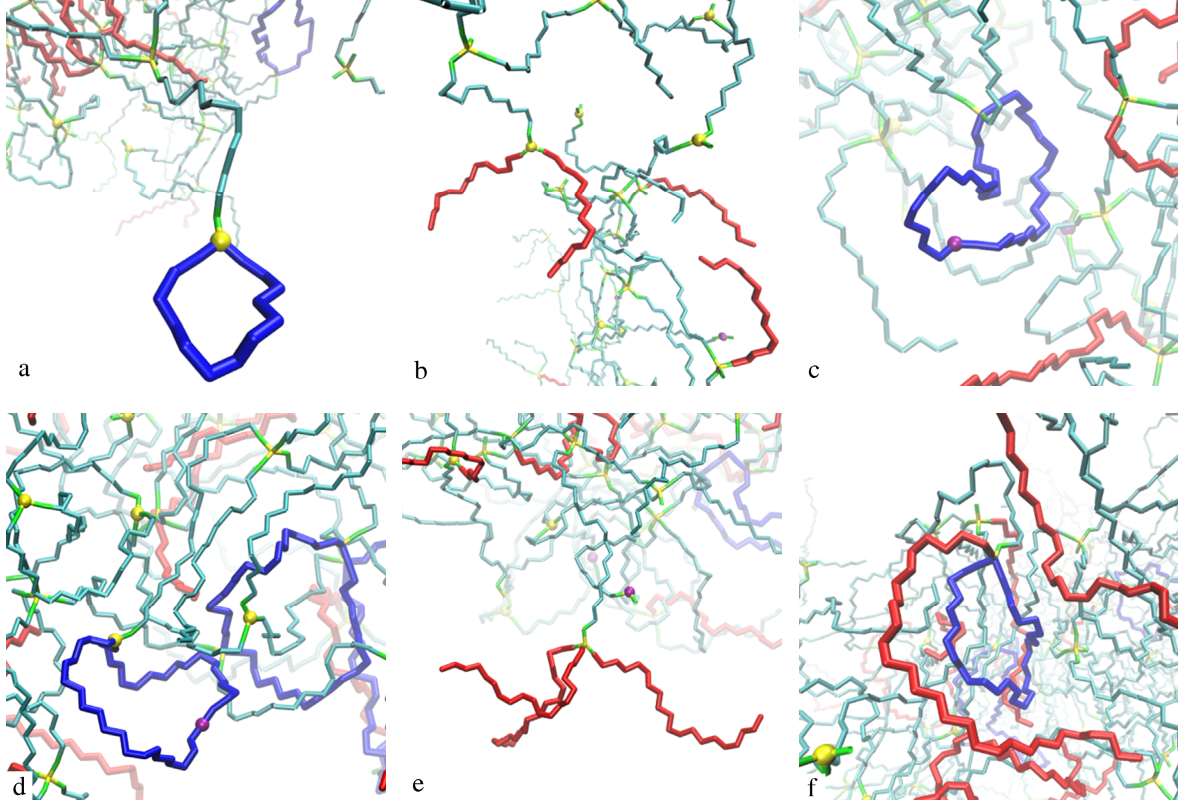


Fig. 10 Network defects: (a) dangling cross-linker with a simple loop, (b) dangling cross-linker connected with 2 dangling ends, (c) dangling secondary loop, (d) dangling cross-linker connected with a secondary loop, (e) dangling cross-linker connected with 3 dangling ends, (f) dangling cross-linker connected with a dangling end and a simple loop ((a)–(b) $N = 14$, (c)–(e) $N = 20$, (f) $N = 30$)

Simple and secondary loops are highlighted with blue bonds and the dangling ends are represented with red bonds, the big yellow spheres are cross-linkers connected with 3 end-groups and the purple ones are those connected with 2 end-groups, the cross-linkers units are colored yellow, the end-groups are colored green and the cyan bonds are the middle chain segments.

In addition to the dangling ends and the non-effective loops, we also found in our systems some dangling cross-linkers that are not elastically active, such as the dangling cross-linker having a simple loop at one end shown in Fig. 10(a), dangling cross-linkers connected with dangling ends shown in Figs. 10(b) and 10(e), and dangling cross-linkers with both simple loop and dangling end connected shown in Fig. 10(f). The number of dangling ends, N_{dangleE} , dangling cross linkers, N_{dangleX} , simple loops, N_{loop} , secondary loops, N_{loop2} , and non-effective secondary loops $N_{\text{loop2(non-effective)}}$ were determined for all investigated networks from a careful visual inspection of the 3D network structures and are summarized in Table 3. With these numbers we may derive the effective number of strands ν and the effective number of cross-linkers μ , according to

$$\nu = N_{\text{strand}} - N_{\text{dangleE}} - N_{\text{loop}} - 2 \times N_{\text{loop2(non-effective)}} - N_{\text{dangleX}} \quad (8)$$

$$\mu = N_c - N_{\text{dangleX}} - N_{\text{loop2(non-effective)}} \quad (9)$$

in which N_{dangleX} should be subtracted because the dangling cross-linkers are always connected with a strand that is elastically non-effective and the non-effective secondary loops always have one cross-linker not connected to the network as seen from Figs. 10(c) and 10(d), thus this number is also subtracted. The values of ν and μ are also collected in Table 3.

Table 3. Network structure properties: glass transition temperature T_g , average functionality of cross-linkers f_{av} , the numbers of strands N_{strand} , dangling ends N_{dangleE} , dangling cross-linker N_{dangleX} , simple loops N_{loop} , secondary loops N_{loop2} , non-effective secondary loops $N_{\text{loop2(non-effective)}}$, effective strands ν and effective cross-linkers μ

N	f_{av}	N_{strand}	N_{dangleE}	N_{dangleX}	N_{loop}	N_{loop2}	$N_{\text{loop2(non-effective)}}$	ν	μ	G^*
10	3.76	200	24	0	0	8	0	176	100	407.6
14	3.71	198	28	3	3	4	0	164	97	233.4
20	3.61	197	40	3	1	4	2	149	95	155.4
30	3.73	197	28	1	3	2	0	165	99	137.7
50	3.90	200	10	0	2	3	0	188	100	175.4
100	3.84	200	16	0	5	3	0	179	100	188.6

Uniaxial Deformation of the Networks

Constant volume uniaxial deformation of the network along the Z-direction of the simulation box was done in steps of $\Delta L = L_{z,i} - L_{z,i-1} = 0.2$ nm with $L_{z,i}$ and $L_{z,i-1}$ being the length of the simulation box in Z directions at iterations $i-1$ and i respectively. The systems undergo 5 ns relaxation after each deformation, and the procedure is repeated until the final total deformation is reached. The properties of the network during deformation are obtained from the second half of the relaxation run of each iteration. The average stress experienced at each deformation is shown in a double logarithmic plot in Fig. 11(a). The lines are fits to the initial linear region.

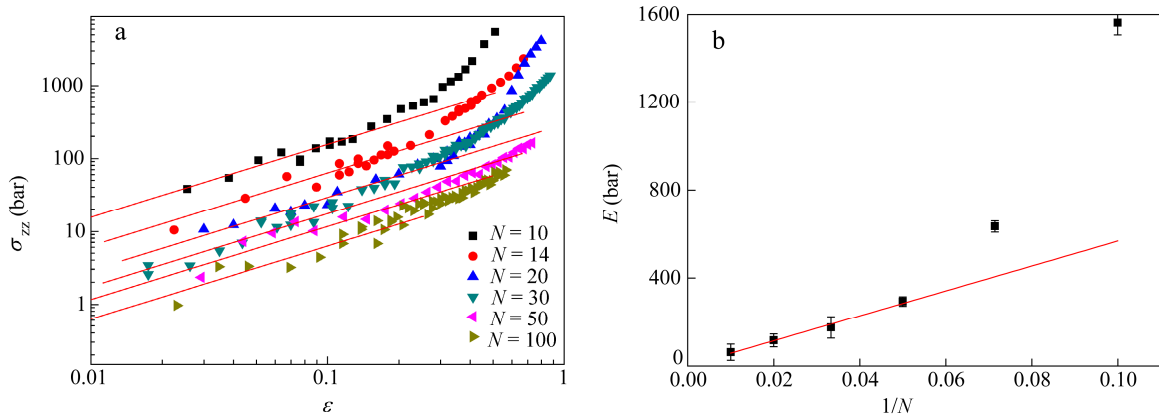


Fig. 11 (a) Double logarithmic plot of stress-strain relation during the uniaxial deformation for the systems with different chain lengths; (b) the modulus values obtained from the linear part of the stress strain curves (The solid lines are linear fits to the linear regimes.)

In general, the elastic stress-strain response obtained in the uniaxial deformation can be represented as

$$\sigma_{\text{true}}(\varepsilon) = E(\varepsilon)\varepsilon \quad (10a)$$

with the tensile strain $\varepsilon = \frac{L_z - L_{z,0}}{L_{z,0}}$, and $\sigma_{\text{true}}(\varepsilon)$ the true tensile stress, and $E(\varepsilon)$ the strain dependent elastic modulus. For small deformations, stress and strain are linearly related and Eq. 10(a) reduces to^[11]

$$\lim_{\varepsilon \rightarrow 0} \sigma_{\text{true}}(\varepsilon) = E\varepsilon \quad (10b)$$

with E the Young's modulus.

For larger deformation non-linear behavior is observed and at very large deformations the finite extensibility of the chains must be taken into account.

The classical affine^[8, 60] and phantom models^[9, 10] for uniaxial deformation of polymer network can be used to interpret our results and establish the applicability of these theories to our networks which may be assumed to have realistic network structures concerning connectivity, dangling ends, loops and varying functionality of the cross-links. For both the affine and phantom networks theories the true stress is related with the extension ratio λ according to^[11]

$$\sigma_{\text{true}}(\varepsilon) = G \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (11a)$$

and in reduced form

$$\frac{\sigma_{\text{true}}(\varepsilon)}{k_B T / V} = \sigma_{\text{true}}^*(\varepsilon) = G^* \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (11b)$$

in which G (G^*) is the (reduced) shear modulus, λ is the extension ratio $\lambda = \frac{L_z}{L_{z,0}} = \varepsilon + 1$, and V is the volume of

the network. In the linear elastic regime it can be shown that $E = 3G$. The initial modulus obtained from the linear fits of Fig. 11(a) is plotted in Fig. 11(b) with inverse N , where the networks with strand lengths $N \geq 20$ show a linear dependence with $1/N$ and the shorter strand networks show large deviations. These results are in agreement with the observations in the work of Ralf^[2]. The values of the initial reduced shear moduli determined from the simulation data are collected in Table 3. The relationship of the reduced modulus with the molecular parameters of the network depends on the theory used:

In the affine ideal network theory^[8, 61]:

$$G = \frac{\nu k_B T}{V} \text{ and } G^* = \nu \quad (12a)$$

And in the phantom network theory^[9, 10, 61]:

$$G = (\nu - \mu) \frac{k_B T}{V} \text{ and } G^* = (\nu - \mu) \quad (12b)$$

with ν the number of elastically effective network strands and μ the number of elastically effective cross-links. The reduced shear modulus values in Table 3 differ from the phantom network prediction that the reduced modulus should be close to $\nu - \mu$, while the modulus values are closer to the affine predictions with strand length $N \geq 20$. For the shorter strand networks the modulus from the simulation significantly deviates from the predicted modulus. The failure of the phantom network in predicting the modulus is presumably caused by the complicated topology of the network in which the chains are not allowed to pass through each other, the increase of modulus when not allowing the chains to pass through each other was also observed for the ideal networks with diamond-like connections^[2, 11, 46]

The strand end-to-end distance distributions at different values of the uniaxial deformation ratio λ are shown in Fig. 12 for the network with $N = 50$. With increasing deformation, the distributions gradually move on to the large r . At $\lambda = 1.2$ the distribution below $r = 2$ nm is nearly unchanged; at $\lambda = 1.4$ the distribution around 2.2 nm becomes larger than at $\lambda = 1.2$, which shows that some chains also shrink their size during deformation; at larger deformations of $\lambda = 1.6$, the distributions continue moving on to larger r .

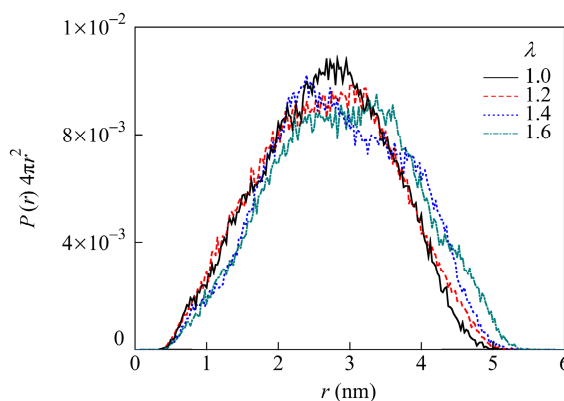


Fig. 12 End-to-end distributions of strands in networks with $N = 50$ at different indicated extension ratios λ

CONCLUSIONS

We have presented a molecular dynamics simulation method to create and investigate the properties of polymer networks. We started with the definition of cross-linker (X) units and chain molecules consisting of middle segments (M) and specific end-groups (E). The interactions between the different types of particles were defined by classical potential energy functions. By tuning the parameters in the interaction potential functions describing the X-X, E-E and X-E interactions the functionality of the X-linker can be varied and the strength of the cross-links formed can be tuned. During the simulation run for a mixture of chains with and without cross-linker units at both ends, the cross-linking reaction progresses and a network is formed. In many if not most simulation approaches the formation of networks is governed by specific rules external to the simulation method or by starting from specific network structures. In our method the networks are formed as a natural response to the interactions in the system and therefore the formation of the polymer networks in our simulation method resembles a real cross-linking reaction and makes it possible to create networks with topologies reminiscent of realistic networks.

The reaction process of cross-linking was monitored by the fractions of X connected with 1–4 E and the fractions of E connected with 0–1 X. The reaction extent was obtained from the fractions of E reacted and the reaction was investigated across the gelation point up to complete conversion. The gel point determined from the simulations, at which smaller branched molecules integrate and form a large volume spanning network, corresponds well with the branching theory. It was also found that the completion of the reaction was done by further addition of monomers onto the volume spanning network and in the latest stage of the reaction by intra-network connections of dangling ends to unsaturated cross-linkers.

The radial distribution functions between particles show that the network formed are homogeneous throughout the network and no secondary shell clustering occurs due to the associative potential used for cross-linking between X and E units.

The specific volumes of the resulting network show good linear relationship with $1/N$ and the glass transition temperatures are determined although they are much higher than those obtained in experiments for both LDPE and HDPE due to the higher cooling rates used in the simulations. The defects of the network such as dangling ends, dangling cross-linkers connected with dangling ends and simple or secondary loops were determined, from which the effective number of strands and cross-linkers were obtained. Conformations of the strands in network are compared with those of the chains before cross-linking, and slightly broadened distributions are observed for short strand networks, indicating that the strands are a little stretched compared to chains in the melt before cross-linking. Conformations of the dihedrals in the strands show similar behavior that slightly more *trans* fractions are found in network strands than in chains.

The constant volume uniaxial deformation of the networks was studied. The stress-strain curves show linear relationship at small deformations, and the obtained moduli have good linear correspondence with $1/N$ for

$N \geq 20$. The strand end-to-end distributions are progressively broadened with the deformation, although some chains are found to shrink their size at certain deformation extent.

Our method will also make it possible to study the effects of cross-linking in combination with other effects such as changes in thermodynamic stability of the reacting mixture, or to include the formation of different morphologies due to the presence of other molecular components or nano-particles.

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REFERENCES

- 1 Erman, B. and Mark, J.E., *Annu. Rev. Phys. Chem.*, 1989, 40: 351
- 2 Everaers, R., *New J. Phys.*, 1999, 1: 12
- 3 Kuhn, W., *Kolloid Z.*, 1936, 76: 258
- 4 Kuhn, W., *Angew. Chem, Int. Ed. Engl.*, 1938, 51
- 5 Kuhn, W., *J. Polym. Sci.*, 1946, 1: 380
- 6 Treloar, L., *Trans. Faraday Soc.*, 1946, 42: 77
- 7 Treloar, L., "The physics of rubber elasticity", 3rd ed., Clarendon Press, Oxford, 1975
- 8 Treloar, L., *Trans. Faraday Soc.*, 1946, 42: 83
- 9 Guth, E. and Mark, H., *Monasch*, 1934, 65: 93
- 10 Mark, J.E. and Curro, J.G., *J. Chem. Phys.*, 1983, 79: 5705
- 11 Rubinstein, M. and Colby, R.H., "Polymer physics", Oxford University Press, New York, 2003
- 12 Mooney, M.J., *J. Appl. Phys.*, 1940, 11: 582
- 13 Schneider, S. and Linse, P., *J. Phys. Chem. B*, 2003, 107: 8030
- 14 Hamerton, I., Howlin, B. J., Klewpatinond, P., Shortley, H.J. and Takeda, S., *Polymer*, 2006, 47: 690
- 15 Mijovic, J. and Zhang, H., *J. Phys. Chem. B*, 2004, 108: 2557
- 16 Chiessi, E., Cavalieri, F. and Paradossi, G., *J. Phys. Chem. B*, 2007, 111: 2820
- 17 Wu, Y., Joseph, S. and Aluru, N.R., *J. Phys. Chem. B*, 2009, 113: 3512
- 18 Jiang, J.X., Trewin, A., Su, F., Wood, C.D., Niu, H., Jones, J.T.A., Khimyak, Y.Z. and Cooper, A.I., *Macromolecules*, 2009, 42: 2658
- 19 Edgecombe, S. and Linse, P., *Macromolecules*, 2007, 40: 3868
- 20 Leung, Y.K. and Eichinger, B.E., *J. Chem. Phys.*, 1984, 80: 3877
- 21 Escobedo, F.A. and Pablo, J.J.D., *Physics Reports*, 1999, 318: 85
- 22 Saalwächter, K., Kleinschmidt, F. and Sommer, J.U., *Macromolecules*, 2004, 37: 8556
- 23 Aguilera-Mercado, B.M., Genesky, G.D., Duncan, T.M., Cohen, C. and Escobedo, F.A., *Macromolecules*, 2010, 43: 7173
- 24 Balabanyan, A.G., Kramarenko, E.Y., Ronova, I.A. and Khokhlov, A.R., *Polymer*, 2005, 46: 4248
- 25 Chen, Y.C. and Chiu, W.Y., *Macromolecules*, 2000, 33: 6672
- 26 Wang, S., Chen, C.C. and Dormidontova, E.E., *Soft Matter*, 2008, 4: 2039
- 27 Doherty, D.C., Holmes, B.N., Leung, P. and Ross, R.B., *Comp. Theor. Polym. Sci.*, 1998, 8: 169
- 28 Wu, C. and Xu, W., *Polymer*, 2006, 47: 6004
- 29 Yu, S., Yang, S. and Cho, M., *Polymer*, 2009, 50: 945
- 30 Varshney, V., Patnaik, S.S., Roy, A.K. and Farmer, B.L., *Macromolecules*, 2008, 41: 6837
- 31 Lin, P.H. and Khare, R., *Macromolecules*, 2009, 42: 4319
- 32 Yarovsky, I. and Evans, E., *Polymer*, 2002, 43: 963
- 33 Bermejo, J.S. and Ugarte, C.M., *Macromol. Theory Simul.*, 2009, 18: 259

- 34 Yiapanis, G., Henry, D.J., Evans, E. and Yarovsky, I., *J. Phys. Chem. C*, 2010, 114: 478
- 35 Liu, J.W., Mackay, M.E. and Duxbury, P.M., *Macromolecules*, 2009, 42: 8534
- 36 Gresta, G.S., Kremer, K. and Duering, E.R., *Physica A: Statistical Mechanics and Its Applications*, 1993, 194: 330
- 37 Yang, W., Wei, D., Jin, X. and Liao, Q., *Macromol. Theory Simul.*, 2007, 16: 548
- 38 Rottach, D.R., Curro, J.G., Budzien, J., Grest, G.S., Svaneborg, C. and Everaers, R., *Macromolecules*, 2007, 40: 131
- 39 Rottach, D.R., Curro, J.G., Grest, G.S. and Thompson, A.P., *Macromolecules*, 2004, 37: 5468
- 40 Li, T. and Nies, E., *J. Phys. Chem. B*, 2007, 111: 2274
- 41 Li, T. and Nies, E., *J. Phys. Chem. B*, 2007, 111: 8131
- 42 Khalatur, P.G., Khokhlov, A.R., Kovalenko, J.N. and Mologin, D.A., *J. Chem. Phys.*, 1999, 110: 6039
- 43 Ayyagari, C., Bedrov, D. and Smith, G.D., *J. Chem. Phys.*, 2005, 123: 124912
- 44 Heine, D.R., Grest, G.S., Lorenz, C.D., Tsige, M. and Stevens, M.J., *Macromolecules*, 2004, 37: 3857
- 45 Cruz, M.O.d.I., Ermoshkin, A.V., Carignano, M.A. and Szleifer, I., *Soft Matter*, 2009, 5: 629
- 46 Wu, R., Li, T. and Nies, E., *Macromol. Theory Simul.*, 2012, 21: 250
- 47 Paul, W., Yoon, D.Y. and Smith, G.D., *J. Chem. Phys.*, 1995, 103: 1702
- 48 Paul, W., Smith, G.D. and Yoon, D.Y., *Macromolecules*, 1997, 30: 7772
- 49 Veld, P.J.i.t., Hütter, M. and Rutledge, G.C., *Macromolecules*, 2006, 39: 439
- 50 Morse, P.M., *Phys. Rev.*, 1929, 34: 57
- 51 Wales, D.J., *ChemPhysChem*, 2010, 11: 2491
- 52 Hess, B., Kutzner, C., Spoel, D. and Lindahl, E., *J. Chem. Theory Comput.*, 2008, 4: 435
- 53 Komarov, P.V., Yu-Tsung, C., Shih-Ming, C., Khalatur, P.G. and Reineker, P., *Macromolecules*, 2007, 40: 8104
- 54 Flory, P.J., “Principles of polymer chemistry”, Cornell University Press, Ithaca, 1953
- 55 Buchholz, J., Paul, W., Varnik, F. and Binder, K., *J. Chem. Phys.*, 2002, 117: 7364
- 56 Wu, C. and Xu, W., *Polymer*, 2007, 48: 5802
- 57 Khonakdar, H.A., Jafari, S.H. and Hässler, R., *J. Appl. Polym. Sci.*, 2007, 104: 1654
- 58 Han, J., Gee, R.H. and Boyd, R.H., *Macromolecules*, 1994, 27: 7781
- 59 Soldera, A. and Metatla, N., *Phys. Rev. E*, 2006, 74: 061803
- 60 Flory, P.J., *J. Chem. Phys.*, 1977, 66: 5720
- 61 Kloczkowski, A., *Polymer*, 2002, 43: 1503