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Modeling of branching and gelation in living copolymerization of monomer and divinyl cross-linker using dynamic lattice liquid model (DLL) and Flory–Stockmayer model

Piotr Polanowski [b], Jeremiasz K. Jeszka [c], Krzysztof Matyjaszewski [a,]*

[a] Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA
[b] Department of Molecular Physics, Technical University of Lodz, 90-924 Lodz, Poland
[c] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-365 Lodz, Poland

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ABSTRACT

The random living copolymerization of vinyl and divinyl monomers with fast initiation and slow propagation was simulated using two Monte Carlo methods: one, purely statistical, corresponding to the mean-field Flory–Stockmayer (FS) theory and the dynamic lattice liquid model (DLL). The results were compared with experiments in which atom transfer radical polymerization (ATRP) method was used. Molecular weights, polydispersities and the cross-linking/cyclization of macromolecules were modeled as a function of conversion for various cross-linker concentrations. The results obtained by the DLL and FS methods and experiments are presented and the sources of discrepancies are discussed. The DLL method yields gel points, molecular weight distributions and critical exponents closer to experimental values and gives an insight into cross-linking processes near the gel point (leading to gelation). More realistic gel structure is obtained due to an appropriate modeling of intra-chain cyclization and diffusion effects, especially close to and above the gel point.

1. Introduction

Technological progress requires new advanced polymeric materials with precisely defined complex architecture. Synthesis of such materials is challenging, and requires better understanding of the polymerization processes. One of the most powerful methods of synthesis of well defined polymer materials of complex architecture is Controlled Radical Polymerization (CRP) [1], in particular Atom Transfer Radical Polymerization (ATRP) [2–7] . As compared with the conventional radical copolymerization where initiation is slow and chain growth is very fast, the CRP processes provide better control of molecular architecture and yield gels with preserved chain-end functionality and more homogeneous structure.

In ATRP and other controlled/living copolymerizations, gelation processes are different from polycondensation, radical copolymerization, classical rubber vulcanization or radiation cross-linking [8] which was the subject of statistical analyses of cross-linking [9–11]. Classical statistical models are based on the assumptions that the cross-links are randomly distributed and the excluded volume effects or chain structure have no effect on reactivity. These assumptions can be used only as a first approximation in modeling of a living copolymerization process.

For the copolymerization involving branching and gelation, computer simulations can provide important information on the parameters which are not easily accessible experimentally, such as the structure of large cross-linked macromolecules, the role of inter- and intrachain cross-linking (cyclization), detailed molecular mass distributions and others. Proper modeling of polymerization reactions faces problems related to the system size and density. The growth of complex macromolecules and their structure are usually governed by several factors, such as reaction kinetics, thermal motion, topological constrains etc. Moreover, possible changes of these factors during polymerization are the source of difficulties in controlling this process. Two boundary cases may be distinguished (i) kinetically controlled polymerization, and (ii) diffusion controlled polymerization. In the first case, the thermal motions of all components in the reaction mixture are fast enough to assume that all reactive species (radicals, monomers, catalysts, etc.) are fully accessible to each other. Moreover, all topological constrains are negligible. These assumptions are consistent with mean-field (MF) theory developed by Flory and Stockmayer (FS) [9,11]. The kinetically controlled polymerization can be modeled using Monte

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* Corresponding author.
E-mail address: km3b@andrew.cmu.edu (K. Matyjaszewski).

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Carlo (MC) methods (off-lattice models) that neglect topology, conformations, diffusion and distances between reacting species. Such models of polymerization, including cross-linking have been previously presented [12–14]. In the diffusion controlled processes, the limited mobility of reactive species may govern the reaction rates. In the extreme case of very slow diffusion, the molecules may be considered as frozen in space and interactions are possible only between the nearest neighbors. This case was considered by Stauffer using critical phenomena and percolation theory approach [15]. MC simulations including diffusion effects and cyclization were presented by Macosko and coworkers [16,17]. In the diffusion-limited regime, the MF theory is not appropriate. Computation should be done in dense system and in discrete space (a regular lattice is usually used), which also introduces conformational aspects of the growth of macromolecules. These methods do not precisely describe polymerization processes leading to gelation or bulk polymerization resulting in long chains and high viscosities.

In our previous paper [13], we presented some results of the simulation of the copolymerization of a vinyl- and divinyl monomers via ATRP using two simulation models: Flory–Stockmayer (FS) (off-lattice) model and Dynamic Lattice Liquid (DLL) model. We compared the gel points obtained using both methods with experimental data obtained for the ATRP copolymerization of methyl acrylate/ethylene glycol diacrylate mixtures. The influence of initiator/monomer/cross-linker ratios and the effect of solvent were studied. DLL model gave much better agreement with the experimental gel points.

In this work we present evolution of various parameters describing the copolymerization process such as degrees of polymerization, molecular weight distribution, cyclization and critical exponents as a function of monomer and cross-linker conversions using FS and DLL simulation methods and discuss the origin of quantitative differences between the two cases. These results are compared with experimental data, taking into account limitations of the experiment and simulations.

2. Simulation methods

The details of chemical structure of monomers and polymer molecules were disregarded in both DLL and FS models. However, in the case of DLL method, where the fcc lattice was used as topological skeleton, all geometrical relations and constrains in the system were preserved. The unit (monomer/mer built of many atoms) was considered as an elementary structure. Its status changed as a result of polymerization. Each reaction step resulted in irreversible formation of a linkage that reduced the number of molecules in the system by one. The reactivity of functional groups (probability of being selected to react) was considered to be constant (no substitution effects was taken into account). Moreover, two assumptions reflecting an ideal living copolymerization were applied (i) no termination and chain transfer reaction were considered (this is not strictly true for controlled/living polymerization, such as ATRP, but is a reasonable approximation), (ii) the reactivity of functional group (probability of being selected to react) was set constant and independent of chain length. Polymerization reaction is simulated according to the general scheme presented earlier [13,18] (Scheme 1).

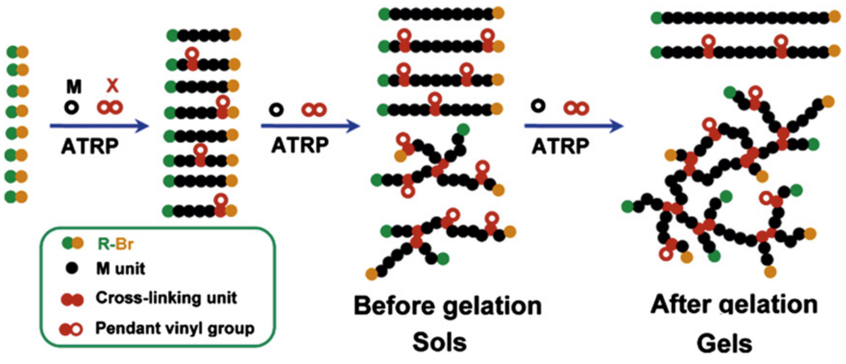
2.1. Flory–Stockmayer model

The monomer molecules were placed in a virtual reaction space without defining its size or dimensions. The molecules were dimensionless and had no coordinates or specific positions in space. The reaction took place between a pair of reactive groups selected at random from among all these groups available in the system. Physically, the model corresponds to the mean-field classical approach where many collisions between molecules occur before an active collision leading to bond formation can take place.

2.2. Dynamic lattice liquid (DLL) model

The DLL model is based on a lattice structure with beads representing atoms or small molecules. Positions of beads coincide with lattice sites. Assumption about dense packing of molecules leads to the consideration of a system with all lattice sites occupied by the beads (density factor $\rho = 1$). It is also assumed, that the system has small excess volume, so that each molecule has enough space to vibrate around its equilibrium position defined by its position in the lattice. However, the molecules cannot move freely over a larger distance, because all neighboring lattice sites are occupied by similar elements. Nevertheless, the DLL model ensures conditions for molecular translation over distances exceeding the vibrational range (long-range mobility). Each, large enough, displacement of the molecule from the mean position is considered as an attempt to move to a neighboring lattice site. For simplicity, directions of the attempts are assumed only along the coordination lines, but are independent and randomly distributed among q directions, where q is the lattice coordination number. Only those attempts can be successful, which coincide in such a way that along a path including more than two molecules, the sum of displacements is equal to zero (condition of continuity). This results in displacements of beads along self–avoiding closed paths (Fig. 1).

The DLL model described above has been implemented as a dynamic simulation algorithm for simple liquids and polymers in two and three dimensions [19–21]. A system of beads on the triangular and fcc lattice was considered. Generally it is possible to regard one molecule as two or more beads connected by non-breakable bonds. In this study a single bead represents substrate molecule. A field of randomly chosen unit vectors represents



Scheme 1. Illustration of the process of copolymerization of a monomer (M) and a cross-linker (X) using ATRP technique (fast initiation) leading to gelation (after ref. [18]).

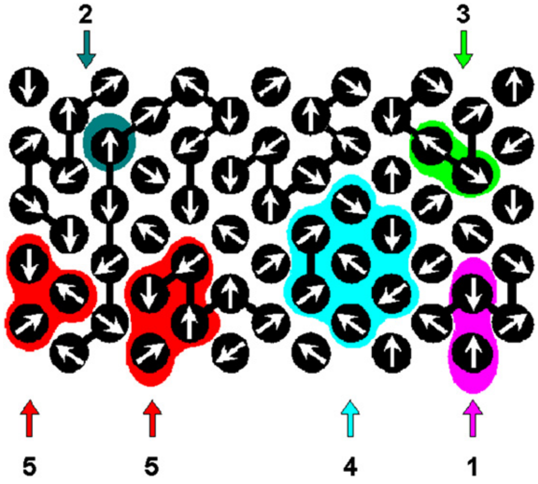


Fig. 1. An illustration of the vector field representing attempts of molecular displacements toward neighboring lattice sites in the DLL model. Labeled areas represent various local situations: (1) elements try to move in opposite direction (unsuccessful attempt), (2) an attempt of motion starts from an element that when moved would not be replaced by any of his neighbors (unsuccessful attempt), (3) attempted movement would lead to a break of bonds in the polymer chain (unsuccessful attempt), (4) the solvent particle would jump through a bond (unsuccessful attempt), and (5) each element replaces one of his neighbors (successful attempts) (after [20]).

motion attempts. These vectors are assigned to beads and point the directions of attempted motions. An example of such assignment of attempted directions of motion is shown at Fig. 1, for a system representing a polymer solution on the triangular lattice.

All beads, which do not contribute to correlated sequences (circuits) are immobilized. This occurs in cases 1–4.

After setting to zero all vectors giving non-successful attempts, only the vectors contributing to the closed loops remain. They constitute traces for the possible rearrangements (case 5). For the athermal system, all possible rearrangements are performed by shifting beads along the closed loop traces, each bead to a neighboring lattice site. Thus, the following steps can be distinguished: (i) random generation of the vector field, representing attempts of movement, (ii) elimination of non-successful attempts and (iii) replacing beads within closed loop paths.

Molecular systems, treated this way, can be regarded as provided with the dynamics consisting of local vibrations and occasional diffusion steps resulting from coincidence of attempts of the neighboring elements to displace beyond the occupied positions. Within a longer time interval, this kind of dynamics leads to displacements of individual beads along the random walk trajectories with steps distributed randomly in time.

In the DLL simulations, an $N_x \times N_y \times N_z$ fcc lattice with box dimension 100 × 100 × 100 was used. At the initial moment, the initiator, monomer and divinyl cross-linker were randomly distributed in the system with concentrations $[\mathrm{Ini}]_0$, $[\mathrm{M}]_0$ and $[\mathrm{X}]_0$. Because no termination reaction is assumed the $[\mathrm{M}]_0/[\mathrm{Ini}]_0$ ratio defines average linear chain length or degree of polymerization (target P_n) or $P_n(\alpha = 1)$ (see below) at conversion $\alpha = 1$.

The difference between the two approaches is that in the FS model there is no information on the space coordinates of the molecules while in the DLL model positions of all beads are known all the time during the simulation. In the FS model the probability of reaction with all molecules belonging to a given class is the same. In the DLL model the probability of reaction between two given molecules within a specific time period depends on the probability of coming into contact, thus, on the initial distance between them. An important implication of this fact is, for example, that the probability of the reaction with a reactive center on the same chain is generally much higher because the distance cannot exceed the length of the chain segment between the active center and the non-reacted double bond. Such effects are even more important in diluted systems and at high conversion.

2.3. Parameters determined

Structural properties of the chains obtained in the simulations were monitored by calculating the following parameters:

- Number average degree of polymerization of all macromolecules $P_n(\alpha)$ as a function of conversion

$$P_n(\alpha) = \frac{\sum_{i=1} n_i p(\alpha, n_i)}{\sum_{i=1} n_i} \tag{1}$$

where α is conversion (of the monomer or the cross-linker), n_i represents chain length of each polymer population (i.e. monomer is not taken into account) and $p(\alpha,n_i)$ represents the fraction of molecules of chain length n_i ($\sum p(\alpha, n_i) = 1$ for each α). - Weight average degree of polymerization $P_w(\alpha)$ as function of conversion

$$P_w(\alpha) = \frac{\sum_{i=1} n_i^2 p(\alpha, n_i)}{\sum_{i=1} n_i p(\alpha, n_i)} \tag{2}$$

- Reduced degree of polymerization (*RDP*) equal to the weight average degree of polymerization without the biggest chain defined in an analogous way as $P_w(\alpha)$, but excluding the biggest molecule in the system:

$$RDP(\alpha) = \frac{\sum_i n_i^2 p(\alpha, n_i) - n_{\max}^2}{\sum_i n_i p(\alpha, n_i)} \tag{3}$$

where $n_{\max}$ denotes the chain length of biggest macromolecule in the system (formed of the biggest number of beads). This parameter (also referred to as “reduced average cluster size”), found to be very useful in the analysis of gelation processes, was proposed by Hoshen and Koppelman [22] and was used also by Shy and Eichinger [17,23] Gupta [17] and others.

- Gel points: the gel points were defined as the monomer and cross-linker conversions respectively, at which the $RDP(\alpha)$ reached the maximum value.

3. Result and discussion

In this section we present, a series of Monte Carlo simulations based on two types of models (FS and DLL) for various sets of parameters. During the simulations we considered chemical structure of polymers using quantities (1–3). The results obtained using DLL and FS method for systematically changing initial molar ratios of initiator, monovinyl monomer, and divinyl cross-linker are compared. The relation of simulation results to available experimental data is discussed.

3.1. Effect of cross-linker amounts on polymerization degrees and gel points

Figs. 2 and 3 show the results of the simulations of bulk copolymerization of a vinyl monomer and a divinyl cross-linker for

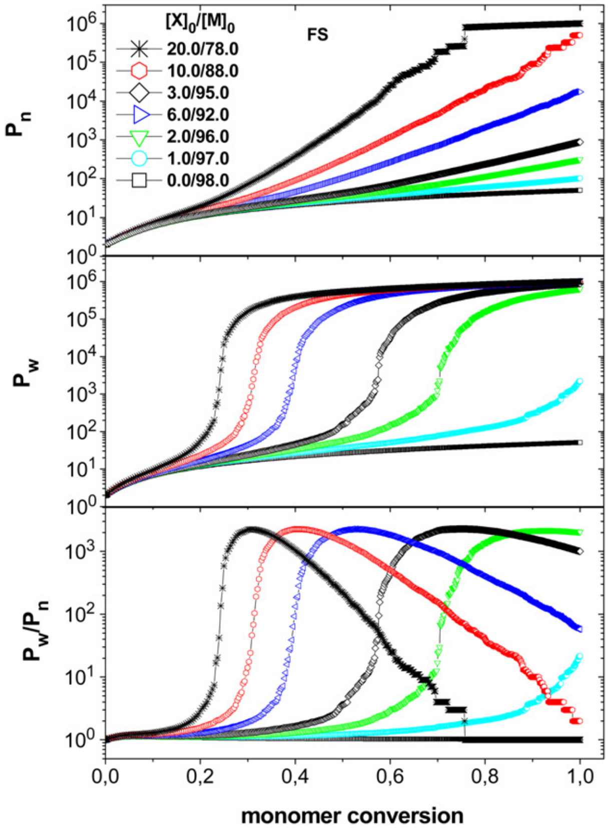


Fig. 2. FS simulation. The growth of number average chain length (P_n) (upper figure), weight average P_w and polydispersity (P_w/P_n) (lowest figure) with monomer conversion, for varying target degrees of polymerization as indicated in upper figure. Initiator concentration 2%.

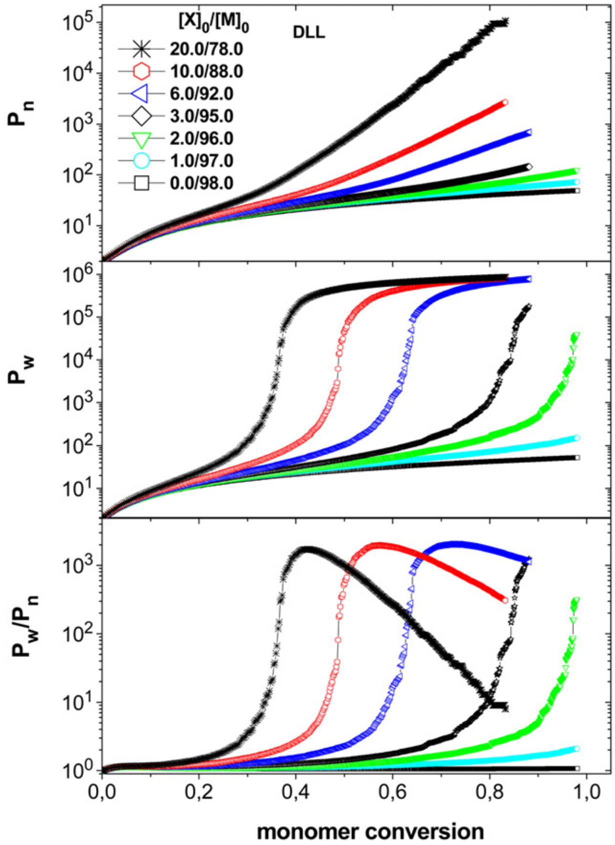


Fig. 3. DLL simulation. The growth of number average chain length (P_n) (upper figure), weight average P_w and polydispersity (P_w/P_n) (lowest figure) with monomer conversion, for varying target degrees of polymerization as indicated in upper figure. Initiator concentration 2%.

various ratios $[\mathrm{Ini}]_0/[\mathrm{X}]_0/[\mathrm{M}]_0$. The case of linear chains ($[\mathrm{X}]_o = 0$) is also shown for comparison. One can observe a typical evolution of polymerization degrees as a function of monomer conversions in FS and DLL simulations respectively.

For both cases, a fast increase of P_n, P_w and P_w/P_n can be observed, characteristic of the cross-linking process (e.g. [9,12,17,22,24]). For higher conversions the P_n values lie on straight lines indicating that the increase of P_n is approximately exponential. Without cross-linker, a linear increase of P_n and P_w with conversion is observed, as expected for a living system with fast initiation. In both cases (DLL and FS) one can observe that the increase in P_n with conversion deviates from linearity earlier and more markedly for increasing concentrations of the cross-linker. The maximum P_n values for the FS simulations are close to 10^6 (the total number of elements in the simulation box) while for the DLL they are lower – ca. 10^5 the difference is most probably caused by the steric hindrance, which is not taken into account in the FS model.

It can be seen that in the case of FS simulation the rapid increase of P_n takes place for lower monomer conversions than in the DLL case. This effect is due to underestimating of intrachain cross-linking in the former case (discussed in detail in the Section 3.3). At the beginning the acceleration of the P_n and P_w growth is due to interchain cross-linking only as the decrease of the number of linear chains is negligible. It should be noted that "saturation" of P_n and P_w below 10^6 is related to the finite size of the simulation box. In the experiment, the increase of molecular weight is also limited (by termination reactions and steric hindrance) but at much higher level.

Since the formula for P_w involves n_i^2, it is more sensitive to the presence of large molecules than P_n and formation of branched molecules leads to a much faster increase of P_w as a function of monomer conversion. Similar results were obtained using other methods of MC simulation based on FS model [12,17]. In both DLL and FS cases this rapid increase takes place at lower conversion as the proportion of cross-linker to monomer increases. However one can observe that the rapid growth takes place earlier (at lower monomer conversion) in FS case for the same ratio $[\mathrm{X}]_0/[\mathrm{Ini}]_0$. Moreover, these differences between DLL and FS lead to different positions of gel point in particular cases as discussed below.

In polymerizations leading to gelation, the polydispersity P_w/P_n increases until the gel point is reached and then decreases (e.g. as in ref. [12]). Also in our simulations, for higher $[\mathrm{X}]_0/[\mathrm{Ini}]_0$, such trend is observed. At first sight P_w/P_n shows a similar conversion dependence as in the case of linear chains in ATRP but it should be noted that Fig. 2 has a logarithmic scale and the P_w/P_n values reach ca. 2000. The P_w/P_n values for conversions for which neither P_n nor P_w approach 10^6 are exact. Otherwise, the results must be treated with care. The simulated polydispersities exceed 10^2 and are much higher than those found experimentally (of the order of 5) [12]. This discrepancy could be explained by limitations of chromatographic techniques. First, large microgel molecules cannot be observed in chromatography but they are taken into account in simulations; they strongly increase the P_w value. Second, the size of branched molecules in chromatography is underestimated (see also discussion in the next section). It is worth to note that the maximum P_w/P_n has practically the same value regardless of the $[\mathrm{X}]_0/[\mathrm{Ini}]_0$ value and the simulation method. The details of polymerization degree (chain length) distributions will be discussed in next section.

Fig. 4 shows the mass of the biggest molecule in the system as a function of monomer conversion. Also in this case an abrupt

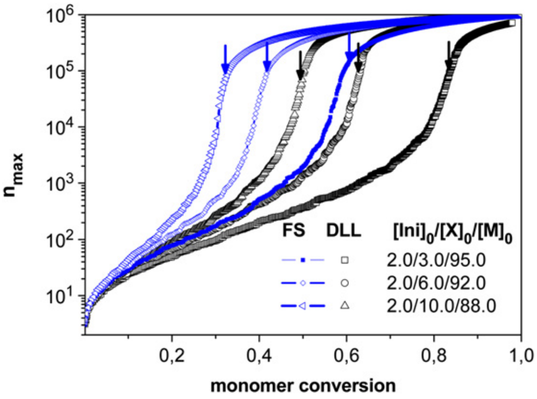


Fig. 4. Evolution of maximum chain length with monomer conversion, obtained from FS and DLL simulations for various $[I]_0/[X]_0/[M]_0$ ratios.

increase of n_{max} is observed using DLL and FS methods. The leveling off is related to the finite size effect. According to the exact FS theory n_{max} should increase to infinity at gel point. In DLL and experiment, a gel point is depressed because diffusion and macromolecular topology constraints delay the cross-linking process and gel formation. Cross-links between some of the nanogels cannot be formed, at least in a reasonable time, due to their extremely slow diffusion and possible interpenetration.

Fig. 5 illustrates reduced degree of polymerization (weight average molecular weight of polymers without the biggest chain) for FS and DLL simulations at various molar ratios of cross-linker to initiator $[X]_0/[I]_0$. A sharp maximum observed in such plots is a good indication of the gel point [22] and it does not significantly depend on the size of simulation box. For both simulation methods, when cross-linker concentration was higher, gelation occurred earlier (at lower monomer conversion). For the FS simulations, the *RDP* values at gel point are by ca. an order of magnitude lower, as compared with the DLL simulations. The gelation takes place also at much lower monomer conversion, as compared with DLL simulation and the experiment [13]. Another important feature is that in the FS case the decrease of *RDP* is slower, the maximum is more symmetric (in agreement with theory and other simulations [17]) while in the DLL simulations *RDP* falls down rapidly after the gel point is reached. In other words, the formation of infinite clusters is much faster. In the DLL simulations, cross-linking reactions between big molecules is favored as compared with statistical probability as a result of their proximity in space and possibly even interpenetration. However, comparison of Figs. 4 and 5 shows that the P_{max} at gel point is similar (ca. 10^5) in all cases. Comparing the gel points with position of polydispersity maxima one can see that the maximum is observed for conversions somewhat smaller than those corresponding to the gel points.

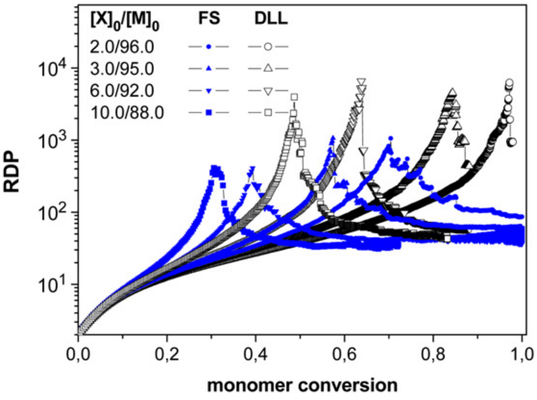


Fig. 5. Evolution of the reduced degree of polymerization *RDP* with monomer conversion, obtained from FS and DLL simulations for various $[I]_0/[X]_0/[M]_0$ ratios.

Fig. 6a shows the conversions of monomer and cross-linker at gel points obtained in a series of FS and DLL simulations, compared with available experimental results [13] for various $[X]_0/[Ini]_0$ ratios i.e. the average number of cross-links per primary chain. One can see that in the case of monomer conversion the DLL results are in quite good agreement with experimental gel points for $[X]_0/[Ini]_0$ ratios 1.0–5.0, while the values obtained in FS simulations are significantly lower than the experimental values. This discrepancy implies from fact that mean-field FS treatment does not take into consideration the intramolecular cyclization. In real systems, a significant fraction of cross-linker molecules is consumed by formation of intrachain loops, especially at the beginning, when the fraction of the beads forming of chains is still low, so the reaction with the double bond in the same chain is more likely.

In the case of cross-linker, conversion corresponding to gel points follow a different dependence on the cross-linker conversion and decreases quicker with increasing number of cross-links per chain. The experimental ATRP results approach the FS results for high $[X]_0/[I]_0$.

It is interesting to check how the positions of gel point obtained using *RDP* maxima are related to the Flory criterion:

$$\rho P_{w,0} = 1 \tag{4}$$

where ρ is the branching/cross-linking density defined as the ratio of the number of branching points to that of the total monomeric units in macromolecules, and $P_{w,0}$ is the weight average length of primary chains. The physical meaning of Eq. (4) is that a gel molecule emerges when, according to the weight average, each primary chain bears one branching/cross-linking point. Comparison of the position of gel point obtained by Flory criterion and that based on "discontinuity" of P_w at gel point is shown on Fig. 6b. The positions of gel points obtained for various ratios $[X]_0/[I]_0$ are in good agreement in all cases. Moreover, this analysis suggests that the network formation using FS mean-field simulation is almost perfectly fitted by classical Flory–Stockmayer model of gelation. It also means that the experimental and DLL results differ from this model.

3.2. Chain length distributions

Computer simulations can also provide detailed information on the chain size distribution. A problem arises for big branched molecules. Because of the finite size of the simulation box the number of such chains in the box is too small to give proper distribution in the linear scale. This problem can be overcome using a histogram with logarithmic bins, which can be directly compared with GPC results. Each bin is bigger than the previous one by a constant factor (1.18 in our case) so they are uniformly spaced on the logarithmic scale. It means that the higher is molecular mass, the bigger chain length range is spun by the bin. For instance, for primary chains a bin spans a few chain lengths only while for the chain length of the order of 10^5 a bin contains 1.18×10^5 chain lengths. Of course only a few of them can really be found in the simulation box, which contains 10^6 elements. Therefore the presented data, although averaged over 15 simulations still show some scatter.

Fig. 7 shows a typical molecular weight (M_w) distributions obtained using gel permeation chromatography (GPC) at successive stages of an ATRP copolymerization [13,18] compared with the corresponding distributions obtained from DLL and FS simulations. All figures show the results normalized to the height of the first

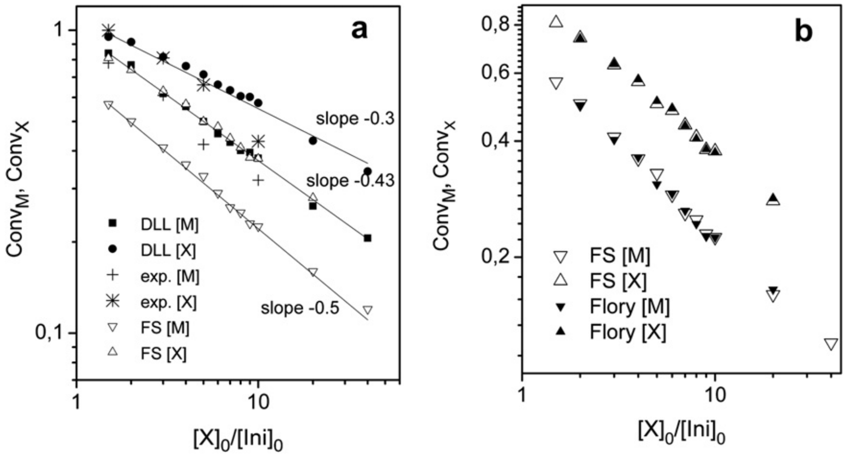


Fig. 6. (a) Comparison of gel points (corresponding monomer conversion – conv $_M$, and cross-linker conversion – conv $_X$) obtained experimentally (exp.) or using the FS and DLL simulation for various $[I]_0/[X]_0/[M]_0$ ratios. (b) Comparison of gel points obtained by FS simulation with gel points obtained using the Flory condition. Symbols DLL [M], DLL [X], FS [M], FS [X] correspond to the monomer [M] or cross-linker [X] conversion at gel point obtained form DLL simulations (DLL) or Flory–Stockmayer model (FS) respectively.

maximum, corresponding to linear chains. The simulated system ($[X]_0/[I]_0 = 3/2$) was chosen so that the gel point in DLL simulations is close to that in the experimental data. In the DLL and FS results the narrow microgel maxima above 10^7 g/mol are 5–20 times higher than the primary chain peak but their high is certainly much too low, anyway, due to the finite size effect.

The monomer unit (bead) in the simulations on *fcc* network corresponds to 1–5 monomer units of real polymers (depending on chain flexibility). In flexible vinyl polymers we can adopt the factor of ca. 1–2 monomer units per simulation bead. In the case of methyl acrylate it gives ca. $1–2\times10^2$. Similar relation is obtained comparing linear chain mass around the gel point. In DLL simulations the primary chain length is 44 and in GPC $M_w = 5000$.

Comparison of simulated molecular weight distribution with a GPC results shows good agreement in the low M_w range and significant differences for the high molecular weights. For low M_w both DLL and FS simulations reproduce well the shift of the M_w maximum, corresponding to primary chains, with increasing conversion and the presence of a local maximum corresponding to the twice higher M_w, which arises as a result of formation of one cross-link between primary chains (coupled chains). The ratio of fractions of linear and coupled chains is similar in simulations and slightly lower as compared with the GPC results. In both cases, it increases with the monomer conversion up to gel point and then slightly decreases, as in experiments.

The simulations do not reproduce quantitatively the broad GPC maximum at around 10^5 g/mol (the agreement with data presented in ref. [25] is somewhat better). One should however keep in mind that such comparisons must be made with care, because molecular weight scaling in GPC is based on the scaling of the hydrodynamic radius (R_{hyd}) of linear chains, while R_{hyd} of cross-linked molecules is generally much smaller than that of a linear chain of the same mass. Because this effect is more important for bigger (more branched and containing closed cycles) macromolecules, this results in a shifting and “compression” of the big molar mass tail in the chromatogram. GPC is also not suitable for studying microgels thus it is not surprising that the maxima due to microgels ($M_w > 3 \times 10^6$) are lacking.

The presented results reproduce however the same trends observed in the experiment: the chain length distribution broadens quickly as the copolymerization proceeds being rather uniform until shortly before the gel point it reaches its maximum length and intensity. Above the gel point a gap in the range of high molar mass appears and a distribution becomes bimodal with a group of relatively small and medium size molecules and very big microgels. Medium size macromolecules disappear from the system, as they are incorporated into the gel. This gap broadens with increasing conversion but a significant fraction of small chains remains up to high conversions, in agreement with the experiment.

The differences between the FS and DLL simulations result mostly from the lower gel point in the FS case: the primary chains are shorter at gel point and the microgels first appearing are also smaller. In the FS case, near the gel point the number of branched molecules in the range of $10^5–5 \times 10^6$ g/mol is also significantly smaller as compared with the DLL simulations. Thus, also in this respect the DLL simulations better reproduce the experimental data.

3.3. *Intermolecular cross-linking and cyclization*

The considered ATRP copolymerization process leads to formation of branched macromolecules which have many active centers and unreacted vinyl groups. Therefore, intramolecular cross-linking (cyclization) is more and more important, as the copolymerization proceeds. In the ATRP polymerization scheme, [13] intermolecular cross-linking is a bimolecular reaction, whereas the intramolecular cyclization is a monomolecular reaction. Of course, the cyclization processes do not contribute to the network formation and “consume” the cross-linker, slowing down the intermolecular cross-linking process. Figs. 8 and 9 show the ratios of cross-linkers, which create inter-chain connections to all fully reacted cross-linker as a function of monomer conversion for DLL and FS cases respectively.

One can observe that for both scenarios the cyclization processes are different. In the FS model, at low conversions cyclization is negligible and practically all intrachain connections are formed after gel point is achieved. In the DLL case, the cyclization takes place all the time during the copolymerization process. It is very important from the very beginning (only ca. 30% of cross-linker form intermolecular connections at 0.05–0.1 monomer conversion). The fraction of intermolecular cross-links increases for higher $[X]_0/[I]_0$ ratios until the gel point is achieved. However, it never exceeds 70%.

Above the gel point the fraction of interchain cross-links decreases in both cases but in the DLL case this decrease is significantly slower. This effect is certainly related to the fact that above

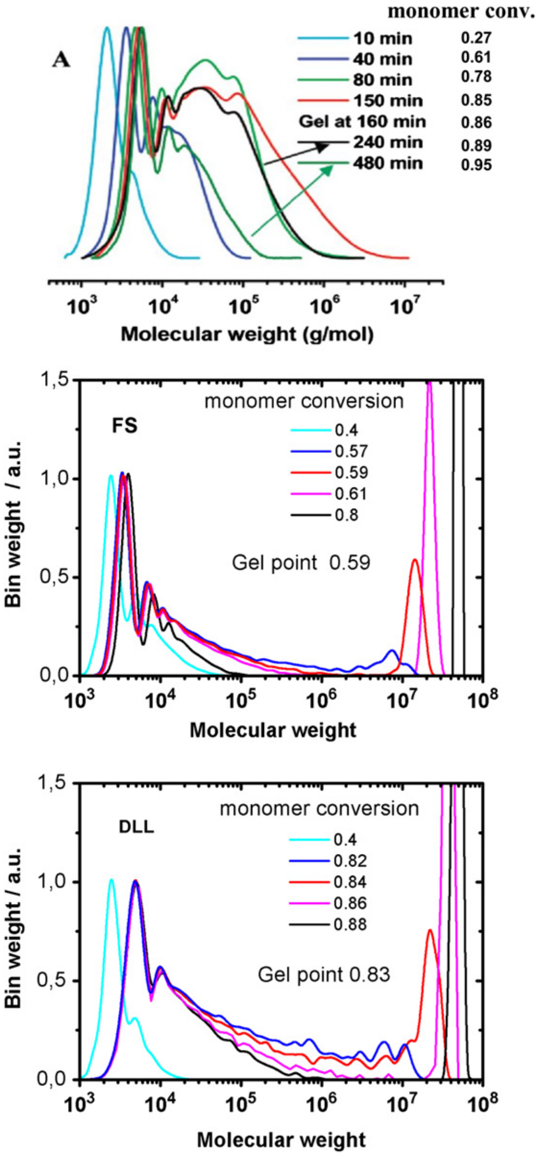


Fig. 7. Comparison of the molecular weight distributions obtained from FS and DLL simulations with GPC data. In the simulations molecular weight was calculated taking bead weight equal to 114 to match experimental results for primary chain length at gel point. Experimental results for the copolymerization of methyl acrylate/ethylene glycol diacrylate mixtures (from ref. [18]).

the gel point a large and increasing fraction of polymer mass forms very big macromolecules with numerous active centers and still reactive cross-linker groups. In all cases the intermolecular cross-linking is sensitive to the variation of $[X]_0/[I]_0$ but for the FS simulation similar rapid changes take place only above the gel point while in the DLL case it influences also the maximum fraction of intermolecular cross-links.

3.4. Critical exponents

An analysis that allows us to show how DLL and FS simulation methods are related to the mean-field and the percolation models of polymerization are scaling analysis. In this approach, changes of some quantities around a critical point are investigated. In our case it is gelation point. For example the weight average degree of polymerization P_w in the neighborhood of critical point can be expressed as:

$$P_w = A(p_c - p)^{-\gamma} \tag{5}$$

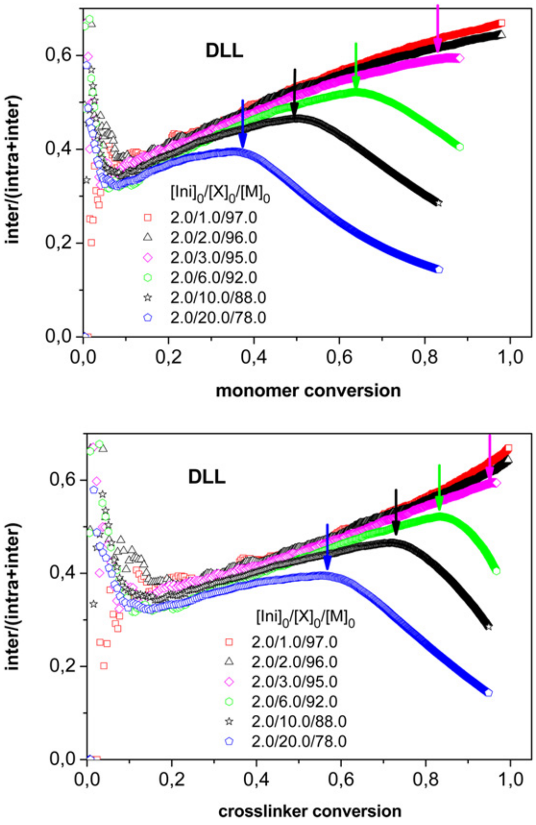


Fig. 8. Effect of an intramolecular cyclization in DLL simulation. Ratio of intermolecular cross-links per chain to all cross-links per chain versus (a) monomer, (b) cross-linker conversion. Arrows indicate gel points.

where p_c corresponds in our case to monomer (or cross-linker) conversion at the gelation point, γ is so called critical exponent and A is a constant.

Fig. 10 shows log–log plot of P_w around the gel point obtained from the DLL and FS simulations for various initial ratios $[I]_0/[X]_0/[M]_0$. One can observe that in the DLL case the exponent γ in all cases is close to 1.8 as predicted for percolation model [15]. In the FS case this exponent is about 1.1 what is close to 1.0, expected by the Flory–Stockmayer theory [11].

Another quantity, which can be monitored is the probability G that a randomly chosen element of the system (initiator, cross-linker or monomer) belongs to the infinite network. G is equal to the gel fraction and is non-zero only for p above p_c. The relation between G and the conversion level of monomer from DLL and FS simulation is shown in Fig. 11. The scaling behavior of this quantity around gel point can be described in a similar way as it was done for P_w

$$G = B(p - p_c)^{\beta} \tag{6}$$

In the FS model the exponents γ and β have similar values (1.1 and 1 respectively) as predicted by the Flory–Stockmayer theory, while in the case of the DLL method the exponent β is very close 0.45 and the exponents γ is 1.8 as predicted by the percolation model [15]. A scaling plot of gel fraction experimental data reported in [25] also yields the exponent β close 0.39. It means that close to a gel point, the cross-linking process is limited by the slow diffusion of big macromolecules.

4. Discussion

In the case of ATRP, values of the diffusion controlled rate constants are much higher than the kinetic constants for chain

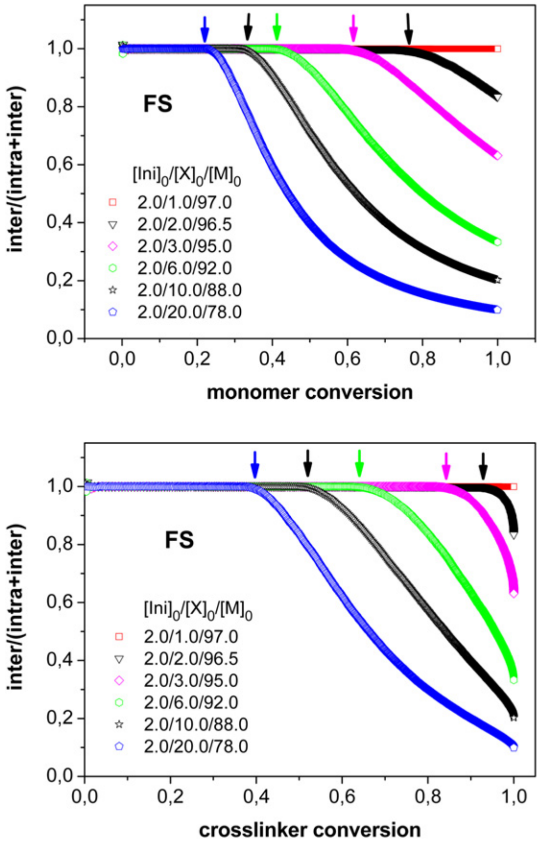


Fig. 9. Effect of an intramolecular cyclization in FS simulation. Ratio of intermolecular cross-links per chain to all cross-links versus (a) monomer, (b) cross-linker conversion. Arrows indicate gel points.

growth and diffusion can be neglected. This is certainly true for low molecular weight species such as monomers or oligomers, especially in solution. However, even in this case the diffusion range is finite and in practice only a fraction of the molecules present in the system is available for the reaction with a given active center. It may be taken into account in the simulation assuming some reaction radius (see e.g. [17]). For the monomer reactions, these effects are however in most cases negligible.

The situation changes if reactions between elements of big, branched molecules are important as it is the case in gelation and intrachain cross-linking. In the copolymerization process considered in this work, there are two mechanisms of the increase of molecular weight: (i) by adding monomer molecules and (ii) by forming cross-links between macromolecules. In the first case, diffusion effects are negligible at the beginning and small even at high conversions. The situation is however very different in the case (ii). Although, in principle, there are many partially reacted cross-linkers and active centers per macromolecule, their long-range diffusion is drastically limited by chemical bonds. Moreover, diffusion of big branched macromolecules (displacement of their centers of mass) is also by many orders of magnitude slower than that of the monomer (see for example analysis of star polymers dynamics [26,27]). In real systems, they can react only with the nearest neighbor macromolecules and only with the reactive groups on one side. The assumption of equal availability of all reactive species (FS model) becomes not appropriate. Because the fast increase of molecular weight observed in Figs. 2 and 3 is due to the mechanism (ii) it cannot be properly described by FS theory.

Underestimation of intra-chain cyclization in FS approach is also related to diffusion effects. The partially reacted cross-linker on the same chain cannot diffuse far from the active center on the same chain, thus it is more easily available for reaction than an average unreacted double bonds. Probability of intrachain cyclization is governed by chain statistics and depends strongly on the number of mers between the reactive centers [28]. Generally, the probability of the reaction with the double bond on the same short chain significantly exceeds an average value for other centers in the system. This argument applies also to some extend to intramolecular cyclization in big, branched macromolecules.

In summary, FS model suffers from two diffusion-related oversimplifications. First, it overestimates the concentration of cross-linker available for branching – due its consumption by underestimated intrachain cyclization. Second, it assumes that all active centers on distant branched macromolecules are available all the time for cross-linking reactions. The DLL model takes such effects into account, thus its predictions are closer to experimental results. Both simulation models suffer from finite size effects especially at high conversions and for cross-linker-to-initiator ratios exceeding 2.

In the present simulations, we assumed equal reactivities of all vinyl groups. The influence of changing the reactivity for groups

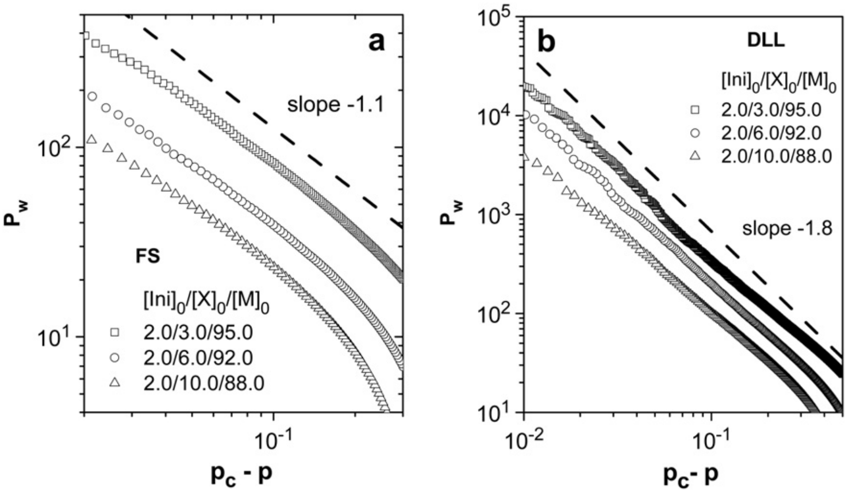


Fig. 10. Dependence of P_w on the monomer conversion as the gel point is approached ($p_c - p$) obtained from FS and DLL simulations.

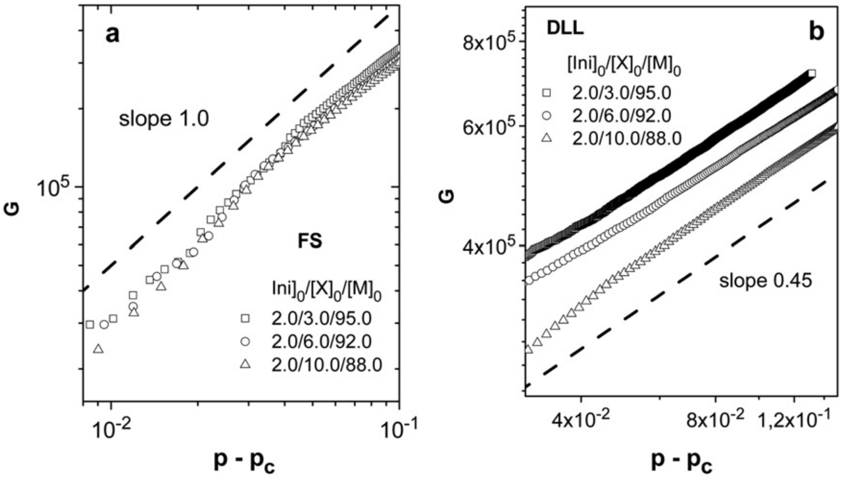


Fig. 11. Dependence of gel fraction G on the monomer conversion above the gel point ($p-p_c$) obtained from FS and DLL simulations.

build-in the chains is very interesting and it could improve the agreement of simulations with the experimental results. We plan to study the effect of varying reactivities on gelation processes in the near future.

5. Conclusions

The results of MC simulations of ATRP copolymerization of a monovinyl and divinyl monomers are presented. Two simulation methods are compared: one based on a purely statistical Flory–Stockmayer model and a more realistic DLL model taking into account positions in space, topology and conformations of the reagents. Gel points obtained using the two methods differ significantly and the DLL results are closer to experimental values. This discrepancy is attributed mostly to the fact that the FS treatment does not properly take into account higher probability of the intramolecular cyclization.

The simulations provide a deeper insight into reactions of large branched/cross-linked macromolecules, for which gel permeation chromatography cannot provide reliable information The analysis of the chain length distribution shows that the gelation process involves mostly formation of bonds between big molecules (more then 50 times bigger than primary chains), which practically disappear from the system in a narrow conversion range at and above the gel point. The number of linear chains after gelation is still high (of the order of half of the initial value) and decreases slowly.

Analysis of the inter- and intrachain cross-linking shows that in the DLL model the latter is important especially on the beginning of polymerization. In the FS model intramolecular cross-linking is negligible at this stage. It is certainly underestimated and consequently the number of intermolecular cross-links contributing to the network formation is overestimated which in turn gives too low values of the gel point.

The DLL model is closer to a percolation treatment, although it allows diffusion of all elements in the simulated system. The effect of diffusion is especially important near the gel point where cross-linking between big macromolecules (nanogels) (10^2–10^5 times bigger than the primary chains) is controlled by slow diffusion of such macromolecules. These effects will be studied in detail in a forthcoming work.

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