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Science China Chemistry

Published: 01/03/2018

Peer reviewed version

Cyswllt i'r cyhoeddiad / Link to publication

11. May. 2021

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Can Flory-Stockmayer theory be applied to predict conventional free radical polymerization of multivinyl monomers: a study via Monte Carlo simulations

Jing Lyu[1], Yongsheng Gao[2*], Zidan Zhang[3], Udo Greiser[2], Hongyun Tai[4], Wenxin Wang[1,2*]

[1]*School of Materials Science and Engineering, Tianjin University, Tianjin 300350, China*
[2]*Charles Institute of Dermatology, School of Medicine, University College Dublin, Dublin 4, Ireland*
[3]*Division of Polymer Chemistry and Materials, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium*
[4]*School of Chemistry, Bangor University, Deiniol Road, Bangor, Gwynedd, LL57 2UW, UK*

The conventional free radical polymerization (FRP) of multivinyl monomers (MVMs) inevitably leads to gelation even at low monomer conversion resulting in difficulties to control and monitor the reaction process. Flory and Stockmayer (F-S theory) studied it based on two fundamental assumptions: (1) independent and equivalent vinyl groups, (2) no intramolecular cyclization. However, until now its applicability to FRP of MVMs (especially regarding the extent of intramolecular cyclization) is still controversial. In this paper, Monte Carlo simulations are used to study FRP of divinyl monomers by two kinetic models: with/without cyclization models. The results of the simulations are compared with the calculated gel points based on F-S theory and the experimental data. It is found that the intramolecular cyclization has a negligible impact on the polymerization process and the gel point before gelation, which are in agreement with the prediction by F-S theory, but the effect becomes significant above the gel points.

Monte Carlo, F-S theory, FRP, multivinyl monomers, intramolecular cyclization

1   Introduction

70 years ago, the classic Flory-Stockmayer mean-field theory (F-S theory) predicted that the conventional free radical (co)polymerization (FRP/FRcP) of multi-vinyl monomers (MVMs) would inevitably lead to gelation even at low monomer conversion based on two fundamental assumptions: (1) all vinyl groups are independent and equivalent, (2) the intramolecular cyclization is negligible [1,2]. This theory has been verified experimentally

numerous times. For instance, Walling [3] investigated the copolymerization of methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA) and obtained the gel point in reasonable agreement with F-S theory in the presence of 0.2 mol% (or less) of divinyl monomer. Macosko and co-workers [4,5] also copolymerized methyl methacrylate (MMA) with EGDMA and observed the gel point at the monomer conversion about 9.7% in the presence of 0.57 mol% of EGDMA, which is consistent with the theoretical value predicated by F-S theory. The validity of F-S theory was further verified in experiments reported by Matsumoto and co-workers [6,7], in which the copolymerization of

*Corresponding authors (email: wenxin.wang@tju.edu.cn (W. Wang); yongsheng.gao@ucdconnect.ie (Y. Gao))

MMA and EGDMA resulting in a ratio of experimental gel point to F-S theoretical gel point of 1.3 (close to unity). However, it is still controversial about the validity of F-S theory in the FRP/FRcP of MVMs, particularly regarding the extent of intramolecular cyclization and its effect on the gel point. For example, Ide and Fukuda [8,9] copolymerized styrene with a small amount (less than 3 mol%) of 4,4'-divinylbiphenyl (DVBP) via FRcP and found the critical number of crosslinks calculated on the basis of the experimental results is 1 or 2 orders of magnitude higher than that predicted by F-S theory, which is attributed to the intramolecular cyclization neglected by F-S theory. The microstructure of the network in FRP of EGDMA was studied by Zhu [10,11] et al. who stated that the network prepared by FRP is very heterogeneous due to the presence of various cycles and microgels formed by the rapid intramolecular reactions. Similarly, Matyjaszewski and co-workers [12,13] indicated that the measured experimental gel point in FRP is typically 1 or 2 orders of magnitude higher than the predicted value of F-S theory mainly because of the significant intramolecular reactions deviating from the assumption of F-S theory that the intramolecular cyclization is negligible. Indeed, the traditional experimental methods are difficult to provide more clarity regarding this controversy because it is difficult to accurately characterize and analyze the soluble products before gelation in FRP/FRcP of MVMs. Moreover, it is challenging to monitor the reaction kinetics of whole polymerization process. Therefore, a new method is urgently needed to effectively study the mechanism of FRP/FRcP of MVMs and to solve the controversy regarding the applicability of F-S theory for FRP/FRcP of MVMs.

Computer simulations can provide important information on the parameters which are not easily accessible experimentally. For example, Hamzehlou et al. [14] adopted a kinetic Monte Carlo approach to study the formation of polymer network in a classical crosslinking copolymerization of styrene and divinylbenzene (DVB). Mohammadi et al. [15,16] firstly investigated the composition and random distribution of simulated chains in free radical copolymerization (FRcP) via Monte Carlo simulation, and then reported the simulation of FRP of styrene including the comparative analysis of the conversion and molecular weight of the resulted polymers in a batch reactor and a spinning disc reactor. Gao et al. [17] used a novel simulation method based on the scaling of the reaction rate constants allowing for a reduction of the simulated number of molecules to study the explicit monomer sequence in acrylate copolymerization. The results obtained from the simulated copolymerization of EGDMA with MMA performed by Tripathi et al. [18] using a hybrid Monte Carlo method indicate that the level of primary cyclization fractions is extremely low. The computer simulation has become a powerful tool for

studying of intramolecular cyclization reaction extent in FRP/FRcP of MVMs and examining the validity of F-S theory in the prediction of FRP/FRcP of MVMs.

The influence of cyclization on crosslinked systems has been simulated for many years [19–22], yet there is no reported simulation work applying the exactly F-S model to FRP of divinyl monomers. Firstly, F-S theory is totally a mean-field theory, such as the Flory-Stockmayer model (FS model) used by Matyjaszewski et al. [23], in which all the reactants were placed in a virtual space neglecting their size and dimensions, and no coordinates or specific positions included. Secondly, given the first assumption of F-S theory, in this work, the reactivity of double bonds should be set equal. Thirdly, the second assumption - intramolecular cyclization is negligible proposed by F-S theory (in fact, the FS model used by Matyjaszewski et al. [23] mentioned above does not strictly correspond to F-S theory because the intramolecular cyclization is allowed in it) is based on the premise of undiluted system [1], in addition to that, considering the typical fast-growing nature of FRP [24,25] which ensures the fast enough movement of radicals, all reactive species in the simulations should be fully accessible to each other (kinetically controlled case [23]).

In order to elucidate the mechanism of FRP/FRcP of MVMs, to clarify whether F-S theory is suitable for FRP/FRcP and to find out to what extent intramolecular cyclization participates in FRP/FRcP of MVMs, herein, we simulated FRP/FRcP of divinyl monomers by the Monte Carlo method using two kinetic models, one model with cyclization (termed as **w.c.** model) and the second one without cyclization (termed as **wo.c.** model corresponding to the F-S theory) (Scheme 1). Using these two kinetic models, we studied the polymerization process (before and after gelation) and the simulation results were compared with the calculated gel points based on F-S theory as well as with the experimental data obtained from the polymerization experiments [26].
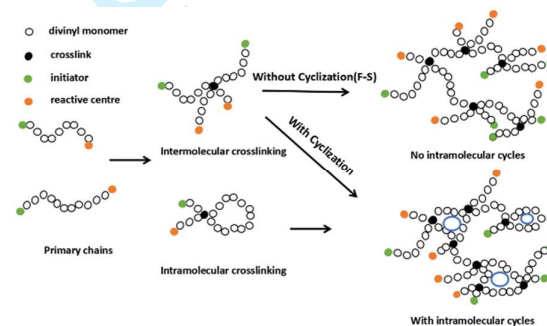
Scheme 1   Schematic presentation of the simulated FRP of divinyl monomers. If intramolecular crosslinking is allowed (With Cyclization, lower part) the macromolecules contain closed loops marked as blue open circles.

2   Simulation method

2.1 Algorithm description

Our simulation approach follows Gillespie's algorithm [27,28] based on the master equation for dynamic Monte Carlo simulation (i.e. in a defined volume, a random number distributed uniformly in the interval [0,1] is used to determine which reaction type will take place), and the probability of each elementary reaction is determined based on the reaction rate constant of each elementary reaction as well as the number of molecules in the reaction process. Corresponding to F-S theory, divinyl monomer concentration is set as 1.45 M which represents a high concentration. The number of total elements used by "FS model" in ref. [23] is 10^6, here, in order to produce a more accurate representation of the results, we checked the predictions of gel points which are indicated by the sharp maximum [13] in Figure 1 (the detailed definition of gel point is presented in section 2.2.3 and 3.2) under various system sizes (lager than 10^6). It was found that different system sizes had no appreciable effect on the predictions of gel point, thus the number of monomer elements (X_m) is set as 10^7 in this work.
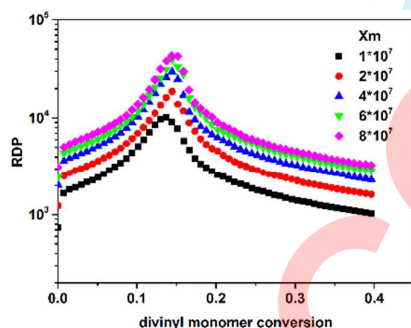

Figure 1 Effect of the system size (X_m) on the predictions of gel point. The growth of reduced degree of polymerization (*RDP*) [23] against divinyl monomer conversion in FRP of divinyl monomers (cyclization included).

The elementary reactions of FRP/FRcP of MVMs used in our simulation included: initiation, propagation (linear, intermolecular crosslinking, intramolecular cyclization), termination (only coupling termination was considered). In terms of FRP/FRcP, the propagation rate constant (linear) differs greatly from the initiation and the termination rate constants leading to great variations in the corresponding reaction probabilities. Therefore, a higher amount of random numbers is required to provide a correct simulation of the polymerization system to avoid an under-sampling for initiation and termination. In order to solve this problem, we adopted a biased sampling method [29] which can achieve the correct simulation of the polymerization system through generating less random numbers. In addition, the

simulation time can also be reduced whose effect has been checked by Yang et al. [29] (through comparing the results obtained by the improved method with those obtained by the method biased sampling not included, the efficiency and reliability of this treatment was demonstrated). Thus, the reaction probabilities can be calculated as follows:

$$R_d = k_d \times X_a \tag{1}$$

$$R_{pm} = k_{pm} \times X_m \times X_r \tag{2}$$

$$R_{pp} = k_{pp} \times X_p \times X_r \tag{3}$$

$$R_t = 0.5 \times k_t \times X_r \times X_r \tag{4}$$

$$S = R_{pm} + R_{pp} + C \times (R_d + R_t) \tag{5}$$

$$P_d = C \times R_d/S \tag{6}$$

$$P_{pm} = R_{pm}/S \tag{7}$$

$$P_{pp} = R_{pp}/S \tag{8}$$

$$P_t = C \times R_t/S \tag{9}$$

k_d, k_{pm}, k_{pp} and k_t are the microscopic reaction rate constants of initiation (*d*), propagation with divinyl monomers (*pm*), propagation with pendent double bonds (*pp*) and termination (*t*), respectively. R_v and P_v are the rate and reaction probability of reaction v ($v = d$, *pm*, *pp*, *t*). X_r and X_p are the number of active radicals and pendent double bonds in the system, respectively. S is the sum of all reaction rates and C is an arbitrary constant. This artificially biased sampling will be corrected and compensated in the subsequent calculations. The kinetic rate constants used in the models and all of the polymerization conditions of the simulation system are listed in Table 1.

Table 1 Summary of all parameters used in the simulation for FRP of divinyl monomers.

Parameters	Value	Ref.
$[X]_0/[M]_0/[Ini]_0$ [a]	100:0:1	[26]
$[X]$ (M) [a]	1.45	[26]
Number of monomer elements (X_m) [b]	10^7	this work
Number of initiator elements (X_a) [b]	10^5	this work
k_d (s^{-1}) [e]	9.8×10^{-6}	[18, 30]
k_{pm} (L/(mol·s)) [d]	150	[21, 31]
k_{pp} (L/(mol·s)) [e]	75	[13, 21]
k_t (L/(mol·s)) [d]	10^6	[21, 31]

a)The simulation system ($[X]_0/[M]_0/[Ini]_0$ and $[X]$) corresponds to ref. [26]. X represents divinyl monomers or crosslinkers, M represents monovinyl monomers, *Ini* represents initiators, b)The value of X_m (the system size) was estimated in this work, the value of X_a was calculated based on X_m - 100:1, c)The value of k_d was chosen according to the typical value for azo initiators (around 10^{-5}) which was calculated based on ref. [18, 30], d)k_{pm} and k_t were chosen based on the values used both in the universal simulation work (ref. [31]) and the work specifically for methacrylate monomers (ref. [21]), e)The value of k_{pp} was set twice smaller than that of k_{pm} as used in ref. [13]. According to the mean-field feature of F-S theory and the equal reactivity of all double bonds, the ratio of k_{pm} and k_{pp} used in

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Additionally, 500 parallel simulations were carried out for each polymerization system to establish reliability and reproducibility at National Supercomputer Center in Tianjin, and the calculations were performed on TianHe-1 (A).

2.2   Model description

In this work, the models are based on F-S theory (the classic mean-field theory), which kind of model has been developed by Matyjaszewski et al. named FS model (intramolecular cyclization included) for atom transfer radical copolymerization (ATRcP) simulations [23]. Similarly, here, to correspond to F-S theory, the statistical models were selected to use rather than others (such as lattice model [32]). A coarse-grain approach was used and the details of chemical structure of polymer molecules and monomers were disregarded. The reactants, such as divinyl monomer molecules and initiators were placed in a virtual reaction space with no definition of its size or dimensions. Furthermore, the specific coordinates or positions for all the molecules in the space were not taken into account (In this work, the consideration of no spatial dimension and no steric hindrance is reasonable because these assumptions correspond with F-S theory. But in diffusion controlled systems, such as reversible deactivation radical polymerization (RDRP), the influence of various reactivities of pendent double bonds and intramolecular cyclization will become significant, the gel points will be higher than the F-S theoretical value, then the spatial and steric effects should be considered [23]). The reactivity of functional groups i.e. probability of being selected to react was assumed to be constant (no substitution effect was considered here). The probability of reaction with all molecules belonging to a given class was considered to be the same. All elementary reactions take place between the two reactants selected randomly in the system.

In the following two models, the information regarding the individual chains or radicals is saved using a series of consecutive numbers during the simulation, by which different chains and radicals can be distinguished by their numbers.

2.2.1   **w.c.** model

In this model, if propagation with pendent double bond is the chosen reaction, an active radical is chosen at random followed by calculations of the fraction (denoted by *m*) of pendent double bonds on the chain where the chosen radical locates and the fraction '*1-m*' of pendent double bonds on other chains. In order to determine what kind of propagation (intermolecular crosslinking or intramolecular cyclization)

occurs, a random number *r* uniformly distributed in the interval [0,1] is generated. If *r<m*, the radical will react with a pendent double bond on its own chain, otherwise it will select a pendent double bond on other chains to react.

2.2.2   **wo.c.** model

Similarly, if propagation to pendent double bond is the selected reaction, an active radical is chosen at random, the chain that this particular radical belongs to can be determined and the corresponding number for this chain can be recorded as well (for example, chain *1* is chosen). Then, we select a chain number randomly in the simulation system (such as chain *x*). If *x=1*, we re-select a chain because the reaction between radical and same chain pendent double bonds is prohibited in this **wo.c.** model. Otherwise, the chosen active radical will react with the pendent double bond on chain *x*.

2.2.3   Parameters determined

The following parameters were monitored and calculated to obtain the structural properties of chains in the simulations:

- Number average degree of polymerization as a function of monomer conversion - $P_n(\alpha)$. For all macromolecules in the simulation system.

$$P_n(\alpha) = \frac{\sum_i i \cdot n_i}{\sum_i n_i} \qquad (10)$$

where α is the conversion of monomer, i denotes chain length of each polymer population in the system, n_i represents the number of molecules of chain length i.

- Weight average degree of polymerization as a function of monomer conversion - $P_w(\alpha)$.

$$P_w(\alpha) = \frac{\sum_i i^2 \cdot n_i}{\sum_i i \cdot n_i} \qquad (11)$$

- Dispersity as a function of monomer conversion - $Đ(\alpha)$.

$$Đ(\alpha) = \frac{P_w(\alpha)}{P_n(\alpha)} \qquad (12)$$

- Reduced degree of polymerization as a function of monomer conversion - $RDP(\alpha)$. RDP is the weight average degree of polymerization excluding the biggest molecular chain length which definition is in an analogous way as $P_w(\alpha)$, but without the biggest molecule in the system.

$$RDP(\alpha) = \frac{\sum_i i^2 \cdot n_i - i_{max}^2}{\sum_i i \cdot n_i - i_{max}} \qquad (13)$$

where i_{max} represents the biggest macromolecular chain length in the system. This parameter was proposed by Hoshen and Koppelman [33] and effectively used in the analysis of gelation processes [33,34].

3   Results and discussion

In this section, the evolution of macromolecular chemical structure and the effect of intramolecular cyclization are systematically analyzed. The results which are the averages of 500 parallel simulation experiments are compared to the corresponding experimental value [26] and the value calculated from F-S theory. The applicability of F-S theory to FRP/FRcP of MVMs and the extent of intramolecular cyclization in FRP/FRcP of MVMs are discussed. The simulations of FRcP of monovinyl and divinyl monomers are also included to provide further evidence to support the conclusions.

3.1   Polymerization process

Figure 2 shows the polymerization process of FRP homopolymerization of divinyl monomers from the **w.c.** and **wo.c.** simulations at a constant molar ratio of divinyl monomer to initiator (100:1). The polymerization degrees and dispersity are displayed as a function of divinyl monomer conversion in these two simulations.

In both cases, the degree of polymerization rises rapidly to a high value at the beginning - divinyl monomer conversion: 0%-8%, reflecting the typical, fast-growing nature of FRP [24,25]. After that, a fast increase of P_w and $Đ$ is observed - divinyl monomer conversion: 8%-16%, characteristic of the crosslinking process (the gel point can be roughly regarded as the inflection point of P_w and $Đ$ [32], here, it is around 14%). After this rapid increase - divinyl monomer conversion: >16%, P_n and P_w tend to reach finite values due to the limitation of the simulation volume size [23]. It can be seen that the curves under the two types of simulation models are almost the same before the gel point demonstrating minimal effects of intramolecular reaction on the multivinyl FRP before gel point - even allowing for cyclization. However, in the later stage (above the gel point), differences appeared in P_n and $Đ$ between the two models (**w.c./wo.c.**). In the case of "cyclization is not allowed", an abrupt increase of P_n and decrease of $Đ$ can be observed. This discrepancy is due to the fact that - after gelation, a large and increasing fraction of polymer mass forms big macromolecules with numerous active radical species and pendent double bonds. Here, the probability of intramolecular cyclization is hence much greater than that of intermolecular crosslinking. From this point of view, if propagation with pendent double bond is selected to occur, the active center will be more inclined to cyclize with the pendent double bond on its own chain. However, intramolecular cyclization is not allowed in the **wo.c.** model, the active radical can only select a pendent double bond on other chains to react with the result that different chains in

the system are quickly bound to the existing long chain. Therefore, the amount of chains in the system decreases much faster compared with that in the **w.c.** model and this is why a dramatic change can be observed in P_n and $Đ$ in **wo.c.** model. Notably, initiation exists during the entire polymerization process which ensures the constantly generation of primary chains. Thus, the evolution of P_n and $Đ$ becomes steady again at end. On the other hand, in the **w.c.** model, the frequency of intermolecular crosslinking is greatly reduced because intramolecular cyclization is allowed, in addition, due to the existence of initiation, the decrease of the number of chains is mostly "neutralized", thus a steady evolution of P_n and $Đ$ can be observed. There is no significant difference in P_w between **w.c.** and **wo.c.** models, this phenomenon can be attributed to the different definitions of P_n and P_w. According to Equation 10 and 11, the calculation of P_n is number averaged, thus it is sensitive to the change of the number of chains in the system. However, P_w is weight averaged which is more sensitive to the change of chain length. As mentioned above, there will be a big macromolecule or chain length in the system above the gel point, compared with which the increment of chain length will be relatively small. In summary, above the gel point, the effect of intramolecular cyclization on the FRP process is not negligible.
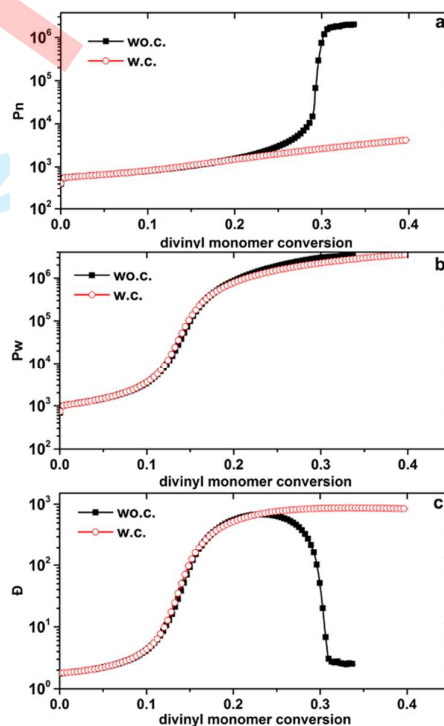

Figure 2   FRP of divinyl monomers. The growth of (a) number average chain length (P_n), (b) weight average degree of polymerization (P_w), (c) dispersity ($Đ$) with divinyl monomer conversion. The initial ratio $[X]_0/[Ini]_0$

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= 100:1. (**w.c.**-With Cyclization model, **wo.c.**-Without Cyclization model).

Figure 3 presents the simulation results of FRcP of monovinyl monomers and divinyl crosslinkers for various ratios $[X]_0/[M]_0/[Ini]_0$ from **w.c./wo.c.** model. The case of linear chains ($[X]_0 = 0$) is also shown for comparison and indicates that - without crosslinker, P_n and P_w both show a linear decrease with monovinyl monomer conversion. In this part, besides the results consistent with FRP homopolymerization system, the effect of crosslinker amounts on polymerization process and gel points can also be observed. In the presence of a crosslinking agent, as expected, P_w and $Đ$ have a fast increase due to intermolecular crosslinking which is the same as the aforementioned homopolymerization system. Furthermore, in both cases (**w.c./wo.c.**), it can be clearly seen that the increase is earlier and more significant with increasing concentrations of the crosslinkers. However, it should be noted that the rapid growth takes place at the same moment (at the same monovinyl monomer conversion) in both cases (**w.c./wo.c.**) for each ratio $[X]_0/[M]_0/[Ini]_0$, which again validates the results of the homopolymerization mentioned above (i.e. before the gel point, the intramolecular

cyclization has minimal effects on the polymerization process of FRP of MVMs system and only after the gel point the effect becomes significant). Compared with **w.c.** case, the rapid increase and decrease for P_n and $Đ$ can also be observed in **wo.c.** model which is similar to the homopolymerization system. However, because the change of the concentration of crosslinkers, some different behaviour between FRP and FRcP also appeared after the gel point in the model without cyclization. It can be noticed that the rapid change of P_n and $Đ$ becomes more and more invisible with the decreasing concentration of crosslinkers. It is rational to envisage that after the gel point, intermolecular crosslinking and initiation become a pair of competitive reactions which reduces and increases the number of chains respectively. However, the relative proportion of them will change with the content of the crosslinkers because the lower the content of divinyl crosslinkers the less favorable the intermolecular crosslinking. Thus with the decreasing of the concentration of crosslinkers, the decrease of the number of chains can be more easily neutralized by initiation, at the same time, the steady evolution of P_n and $Đ$ appears earlier.
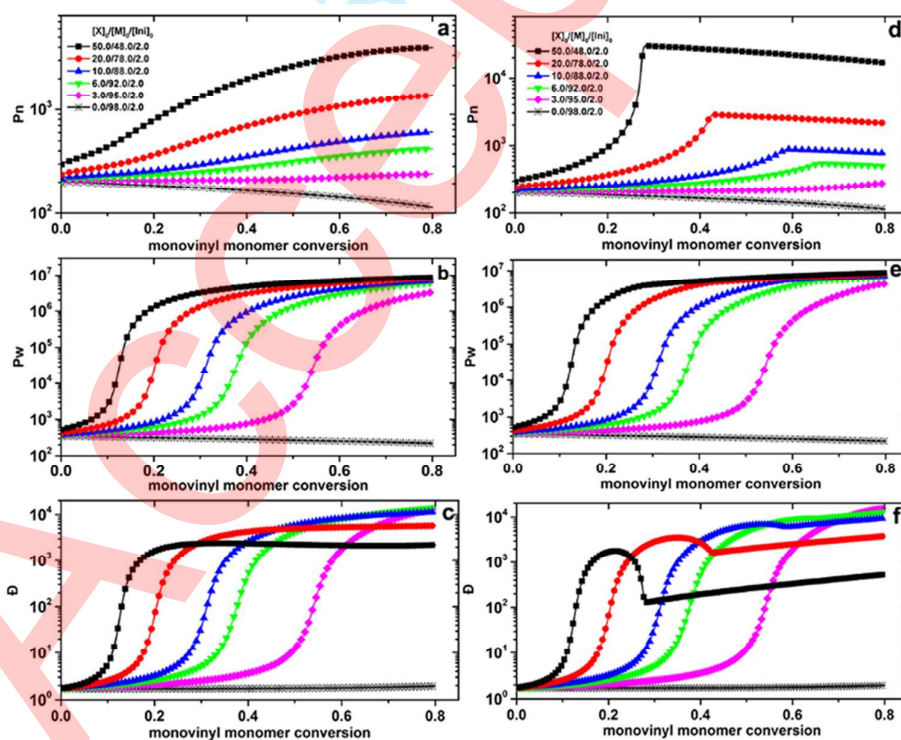

Figure 3   FRcP of monovinyl and divinyl monomers. The growth of number average chain length (P_n) with monovinyl monomer conversion for (a) **w.c.** model and (d) **wo.c.** model. The growth of weight average degree of polymerization (P_w) with monovinyl monomer conversion for (b) **w.c.** model and (e) **wo.c.** model. The growth of dispersity ($Đ$) with monovinyl monomer conversion for (c) **w.c.** model and (f) **wo.c.** model.

3.2 Gel point

F-S theory defines the gel point as the moment when P_w tends to infinity [15]. In this simulation system, P_w tends to reach a finite value at the gel point due to the limitation of the simulation volume size [23], thus, in this work, the simulated gel point was defined as the moment when the weight-average degree of polymerization of all macromolecules, except the biggest molecule (*RDP*), reached a peak value [13]. Figure 4 illustrates reduced degree of polymerization (weight average molecular weight of polymers without the biggest molecule) as a function of divinyl monomer conversion, obtained using the two simulation methods (**w.c.**/**wo.c.**). In both cases, when *RDP* reaches its maximum, the corresponding divinyl monomer conversion is almost constant - approximately 14.05% (7.03%, calculated based on the double bond conversion).

$$p_c = \sqrt{\frac{[Ini]_0 \cdot IE_t}{2 \cdot [X]_0 \cdot M_w/M_n}} \qquad (14)$$

P_c corresponds to double bond conversion at the gel point based on F-S theory, $[Ini]_0$, $[X]_0$ are the initial concentrations of initiator and divinyl crosslinker, respectively. IE_t is the initiation efficiency of initiator, M_w/M_n is the dispersity of primary chains.

Equation 14 shows the theoretical gel point (P_c) derived from F-S theory based on the conversion of total vinyl groups [13]. When the ratio $[X]_0/[Ini]_0 =100:1$, P_c is 7.07% (here, IE_t and M_w/M_n are assumed to be 1, the actual theoretical gel point should be smaller than 7.07%), which is in agreement with the gel point value obtained from our simulation as well as the experimental gel point 6.5% previously reported by Wang et al. [26]. Furthermore, the

curves are almost the same in both simulation models before the gel point and this conclusion is in agreement with the results of the above curves of the degree of polymerization and the dispersity. Beyond the gel point (as discussed in section 3.1), the effect of intramolecular cyclization becomes significant. In the **wo.c.** model, the intermolecular crosslinking is much more severe than that in the **w.c.** model, and chains in the system show faster combination to form the biggest macromolecule with a great increase in chain length (n_{max}). In summary, we can observe that in the **wo.c.** simulation *RDP* drops rapidly after the gel point, while in the **w.c.** case the decrease of *RDP* is slower. Therefore, the above results reconfirmed the conclusion that there is nearly no intramolecular cyclization before the gel point which is in agreement with the assumption of the F-S theory that the intramolecular cyclization is negligible and as expected, its influence becomes more and more obvious after the gel point and cannot be neglected.
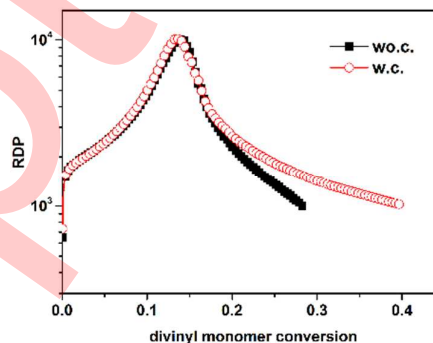

Figure 4 FRP of divinyl monomers. The growth of reduced degree of polymerization (*RDP*) with divinyl monomer conversion. The initial ratio $[X]_0/[Ini]_0=100:1$. (**w.c.**-With Cyclization model, **wo.c.**-Without Cyclization model).
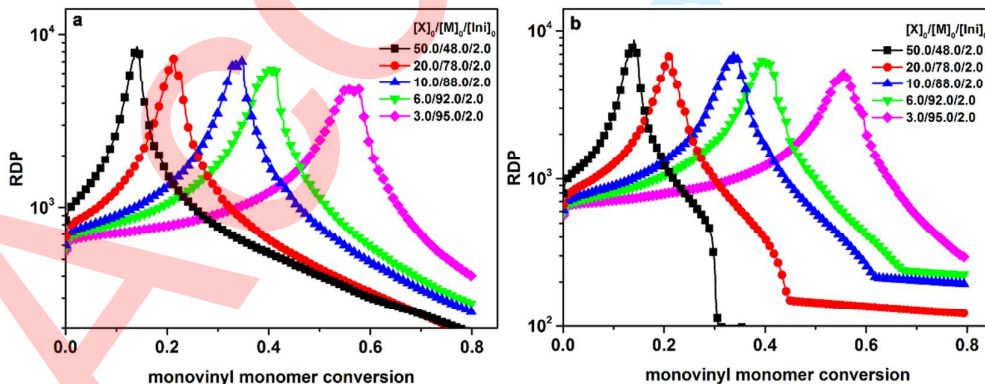

Figure 5 FRcP of monovinyl and divinyl monomers. The growth of reduced degree of polymerization (*RDP*) with monovinyl monomer conversion for (a) **w.c.** model and (b) **wo.c.** model.

Figure 5 demonstrates the *RDP* plotted vs. monovinyl monomer conversion obtained from FRcP simulations for various ratios $[X]_0/[M]_0/[Ini]_0$ from **w.c.**/**wo.c.** model. The gel point appears at higher monovinyl monomer conversions as the decreasing proportion of the crosslinkers.

However, consistent with the results discussed in the homopolymerization system, the gel points simulated by **w.c.**/**wo.c.** model are constant when the proportion of crosslinker is constant.

3.3 Intermolecular crosslinking and intramolecular cyclization

It is well known that if intramolecular cyclization - a monomolecular reaction occurs, it will "consume" the crosslinkers and slow down the intermolecular crosslinking process but will not contribute to the network formation, leading to the delay of gel point. Figure 6 shows the ratios of inter-chain crosslinked units of all of the fully reacted divinyl monomers as a function of divinyl monomer conversion for the model with cyclization. The arrows correspond to the gel points (conversion of divinyl monomer = 14.05%, conversion of double bond = 7.03%). This analysis allows us to clearly show how the intramolecular cyclization occurred during the whole polymerization process of FRP of MVMs. It is found that before the gel point, nearly all pendent double bonds are consumed by intermolecular combination. Only beyond the gel point, the ratio of intermolecular crosslinking begins to decrease and the pendent double bonds begin to react with the active center on its own chain. In other words, for FRP of MVMs, cyclization is negligible before the gel point and practically all intra-chain connections are formed when the gel point is achieved.
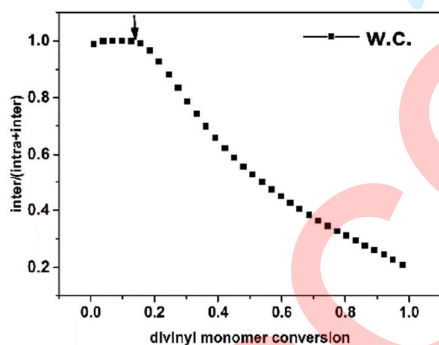

Figure 6 FRP of divinyl monomers. Effect of an intramolecular cyclization in **w.c.** simulation. Ratio of intermolecular crosslinks per chain to all crosslinks per chain versus divinyl monomer conversion. Arrows

indicate gel points.

Figure 7 illustrates the results of FRcP of monoviny monomers and divinyl crosslinkers for various ratios $[X]_0/[M]_0/[Ini]_0$. Similarly, we observed that before the gel point nearly no cyclization occurred - even the cyclization is allowed and the intermolecular ratio is maintained at around 1.
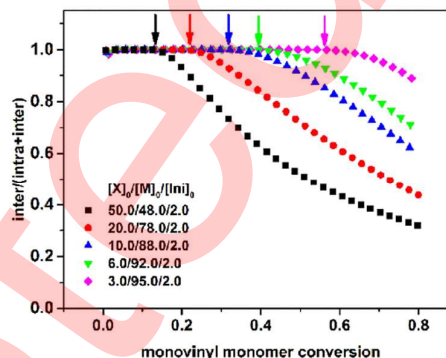

Figure 7 FRcP of monovinyl and divinyl monomers. Effect of an intramolecular cyclization in "with cyclization" simulation. Ratio of intermolecular crosslinks per chain to all crosslinks per chain versus monovinyl monomer conversion. Arrows indicate gel points.

4 Mechanism discussion

Based on the simulated results, it can be expected that the polymerization process can be divided into three stages. (1) The FRP reaction features slow initiation and fast propagation which results in the formation of a few long chains with pendent vinyl groups at the beginning of polymerization (linear propagation stage as shown in Figure 8a). Given the mean-field feature of the model (**w.c.** or **wo.c.**) - all of the topological constrains are negligible and all of vinyl groups are fully accessible to each other [23], the fraction of free monomeric vinyls around the polymer
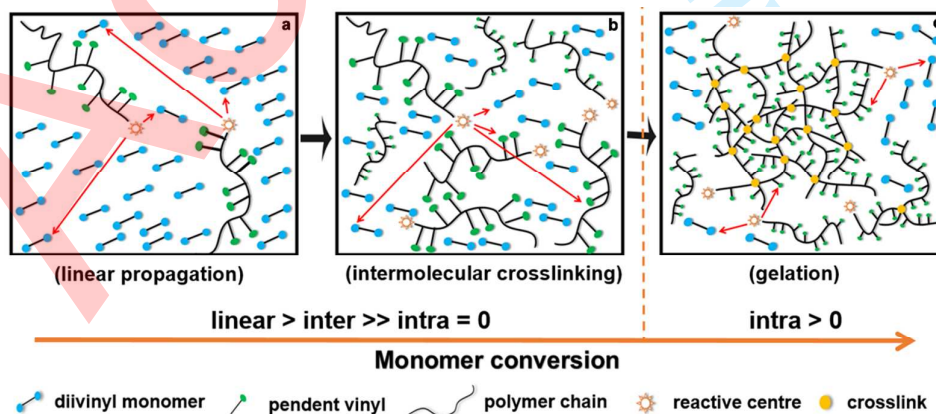

Figure 8 Illustration of the three polymerization stages in FRP of MVMs. (a) linear propagation; (b) intermolecular crosslinking; (c) gelation.

(low monomer conversion at this stage) is much larger than that of the pendent vinyls within the same chain, which indeed results in much bigger probability of linear reaction at the beginning. (2) With the progress of linear growth, the number of long chains and pendent vinyl groups in the system gradually increased (intermolecular crosslinking, Figure 8b). Therefore, in addition to linear growth, the reaction with other chain pendent vinyls begins to occur. But given that the fraction of pendent other chain vinyls around the polymer chains is much larger than that within the same chain, the radicals have much bigger probability to react with the pendent vinyls on other chains (intermolecular crosslinking) than to react (cyclize) with the pendent vinyls on their own chain (intramolecular cyclization). (3) Gelation (Figure 8c). Due to the rapid intermolecular crosslinking reaction, most of the long chains in the system are bounded to big macromolecules with numerous active radical species and pendent double bonds. Here, the probability of intramolecular cyclization is hence dominated.

5   Conclusions

Two kinetic models of Monte Carlo simulations were used to study the FRP of MVMs and the FRcP of monovinyl monomers and divinyl crosslinkers. The first simulation is based on a **wo.c.** model simplified by omitting the intramolecular cyclization corresponding to the F-S theory, while the second simulation is the **w.c.** model in which the intramolecular cyclization is statistically considered. The simulated gel points and polymerization processes under various conditions were compared to the experimental gel point obtained in the experiments (ref. [26]) and the calculated gel points based on F-S theory. It was found that the gel points obtained using the two kinetic models are in agreement with the experiments and F-S theory, demonstrating the successful prediction of the gel points of FRP/FRcP of MVMs from both kinetic models. Before the gel point, the polymerization process was correctly presented in both cases, showing the typical features of FRP/FRcP of MVMs, such as rapid increase of the degree of polymerization at the beginning and the abrupt increase of P_w and $Đ$ resulted from a rapid and uncontrolled crosslinking process. With the polymerization proceeding, oligomers in the system are combined together to form a giant macromolecule containing the pendent double bonds and active radicals. Then, the intramolecular reaction within the giant macromolecule are favored. Therefore, beyond the gel point, the **wo.c.** model cannot faithfully reflect the polymerization process due to the ignorance of intramolecular cyclization, while the prediction of **w.c.** model is much closer to the real situation of the reaction. In summary, the effect of cyclization is negligible before the gel point, thus it proves that F-S theory can provide a

successful interpretation of the polymerization process and F-S theory is suitable for the prediction of the gel point in FRP/FRcP of MVMs. The considerable effect of intramolecular cyclization on FRP/FRcP only occurred after the gel point.

Conflict of interest   The authors declare that they have no conflict of interest.

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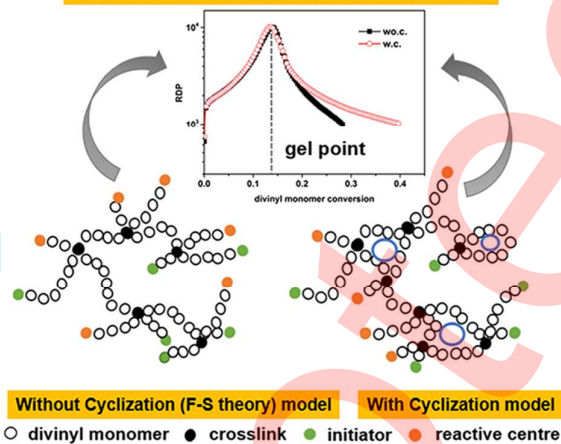
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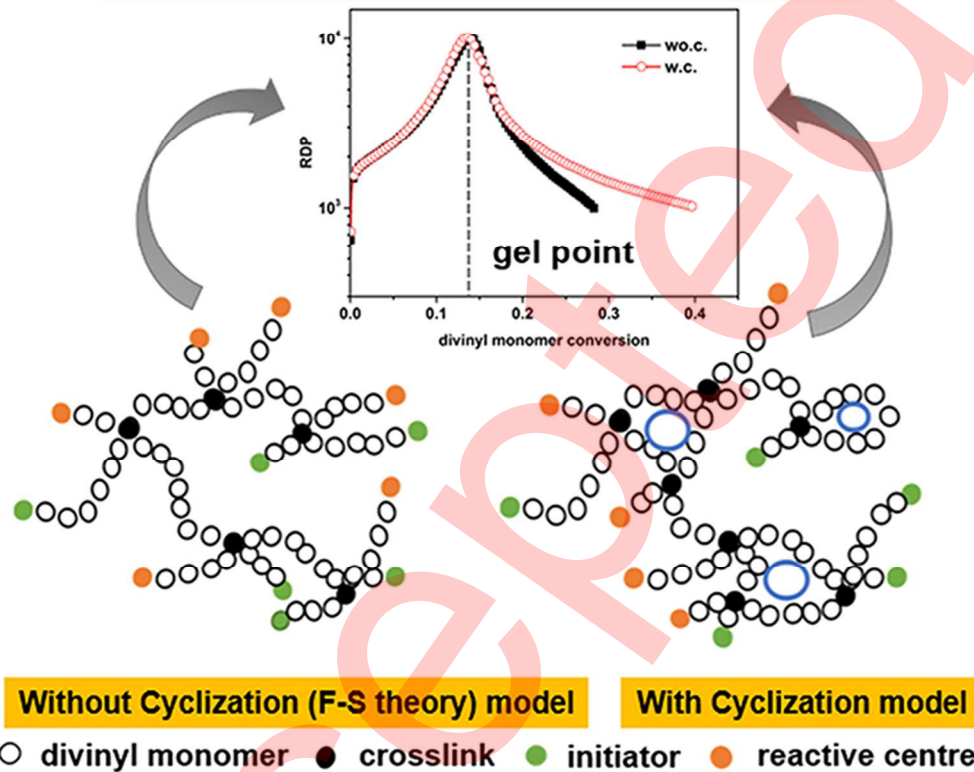
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