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Influence of intramolecular crosslinking on gelation in living copolymerization of monomer and divinyl cross-linker. Monte Carlo simulation studies

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ARTICLE INFO

ABSTRACT

The effect of intramolecular crosslinking (IC) (cyclization) on gelation was studied using Monte Carlo simulations. The consumption of crosslinker in the IC process is proposed as one of the main reasons of significant overestimation of the gel point by Flory-Stockmayer theory. The system under study is atom transfer radical polymerization (ATRP) of a monomer and bifunctional (e.g. divinyl) crosslinker. The simulation method is based on dynamic lattice liquid algorithm (DLL) and reproduces changes of the system dynamics during polymerization. The effect of cyclization on gel point for various reagents ratios and dilutions was investigated. It is shown that intramolecular crosslinking does not change significantly the gel point in condensed systems (no solvent or below 10%). By contrast, it significantly increases gel points in diluted systems (40—90% of the solvent).

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1. Introduction

Polymer gels are a class of branched and cross-linked materials with a numerous applications involving cosmetics (e.g. ointments and beauty products), medical systems (e.g. drug delivery and cell culture growing) and surface coatings (e.g. lubricants and sealing pasts) [1—3]. They are obtained mainly by (i) crosslinking of linear polymers by multifunctional vinyl compounds or (ii) copolymerizing mixture of mono-functional and multi-functional monomers (*in situ* gelation). The latter may be done by applying radical-based processes such as free radical polymerization (FRP), reversible deactivation radical polymerization (RDRP) or even polycondensation [4]. Among these, the RDRP, and especially the Atom Transfer Radical Polymerization (ATRP) [5,6], are the only processes that allow to control the distribution of crosslinks and homogeneity of the structure of gel due to suitable relation of fast initiation to much slower propagation during polymerization [7].

The development of RDRP methods is undeniably one of the most intensely explored areas of research in polymer science. Due to fast initiation and relatively slow chain propagation, the growth of polymer chain follows the first-order kinetics and leads to precise control over molecular weights and their distribution and the structure of obtained chains [8].

During the last two decades, the RDRP methods were successfully applied in syntheses of many interesting materials, previously impossible to obtain by classical FRP. Among these novel polymeric materials one can distinguish: (i) ideally alternating copolymers [9], (ii) block copolymers [10], (iii) tapered and gradient materials [11], (iv) polymers grafted from the surface of inorganic materials [12], (v) cyclic polymers [13], (vi) star-shaped polymers [14] and many others.

During the copolymerization of a mixture of mono-functional and multi-functional monomers gelation should occur at specific conversion of monomers, independently on the temperature of reaction, amount of the catalyst used or relations between addition rates of the components of mixture [15]. The probability of creation of continuous, covalently bounded network with sufficient number of chain branches that ensures the "infiniteness" of the network emerges clearly from: (i) the functionality of monomers [16], (ii) the amount of solvent in the system during gelation [17] and (iii) exact moment of addition of cross-linking agent [14]. These

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considerations are included in the classical theory of gelation described by P. Flory [15,16] and W. Stockmayer [18,19] in 1940's and developed later for chain reactions by Dusek and coworkers [20]. The main drawback of their insights into gelation is the lack of consideration of the cyclization effect on the point of gelation. In classical gelation theory, the topology (e.g. presence of macro-cycles) of the growing macromolecule is neglected and does not contribute to the gelation process. In the frames of this theory the most significant impact on gelation is attributed to initial ratio of cross-linker to monomer. These limitations may render serious deviations between experimentally observed gel points and calculated by equations derived from Flory-Stockmayer theory. The experimental distinction between intra— and intermolecular cyclization is difficult. Rosselgong and Armes made such quantifi-cation using NMR spectroscopy. They found that fraction of cross-links used for intramolecular crosslinking increases with increasing dilution and can exceed 90% [21]. Li at all studied effect intra-molecular crosslinking branched polymers for high dilutions which favor cyclization and found a strong decrease of the fraction of branched polymers with increasing dilution [22,23]. Johnson and coworkers identified intramolecular crosslinks using their network disassembly spectrometry (NDS) concept, consisting in site selec-tive cleavage of bonds in a gel using cleavable and isotope labeled units in macromonomers [22,24].

Computer simulations have been successfully used to study ef-fect of various properties of polymer systems including the gelation process [17−19]. In particular the Dynamic Lattice Liquid model (DLL) used in our previous work was successful in analyzing copolymerization processes in various systems [25−27], because it reproduces quite well the influence of the increasing chain length and complexity of the system during polymerization, especially at high concentrations (in dense systems). In our previous paper we compared the results of simulations using DLL and FS models with experimental results [28]. We have shown that DLL method re-produces much better the experiment as it takes into account the intramolecular crosslinking. In this work our aim is to investigate the effect of intra-molecular cyclization on the gel point and ki-netics of gelation in the DLL simulations. We will compare two extreme cases where intramolecular crosslinking is allowed (as in the previous work) or it is not allowed (Scheme 1).

Of course, in the real system some intramolecular crosslinking must take place as the active center "does not know" if a distant crosslinker belongs to the same or another molecule. However,

total exclusion of internal crosslinking will provide the upper limit on the contribution of such reactions. We investigate the effect of cyclization on gel point for various reagents ratios and dilution. It should be noted that although intramolecular crosslinking does not contribute to gelation it has an influence on gel structure and its swelling properties.

1.1. Simulation method

The simulation method is based on the dynamic liquid model described in detail in our previous papers [29,30]. The reacting molecules are represented by beads placed on the *fcc* lattice (12 equivalent nearest neighbors). All lattice centers are occupied (dense system). An attempt to move vector is selected at random for each bead and only when these vectors make a closed loop, the moves of all involving beads are performed (excluded volume principle). In the case of polymer molecules, such cooperative move must not break bonds in the chain. This algorithm has been shown to be ergodic and reproduce well static and dynamic properties of polymer systems [31].

In the simulations of ATRP polymerization, each bead represents one of the species appearing in the system, such as initiator, monomer, crosslinker, chain unit, active center, solvent etc., ac-cording to the detailed reaction scheme presented in Ref. [28]. Reaction between an active center and monomer, crosslinker or partially reacted crosslinker takes place when these molecules are close neighbors, with a probability of 0.0051, equal for all reactions. The choice of this probability is a compromise between the relation between the diffusion and reaction constants in ATRP and computation time. No termination reaction is assumed (ideal living polymerization). In the present simulations of gelation the simu-lation box (100 × 100 × 100 beads) contained at the beginning an initiator, crosslinker, monomer and the solvent in proportions corresponding roughly to the experiments reported in Ref. [28]. Two sets of simulations were performed: (i) − (w.c) no limits on reaction (with cyclization, intramolecular crosslinking allowed) (ii) − (wo.c) without cyclization, intramolecular crosslinking not allowed.

Parameters such as weight average degree of polymerization P_w etc. have their usual meaning. Conversion of the monomer and crosslinker is defined as incorporation of vinyl units into a chain, as determined by the decrease of the free monomer or crosslinker concentration in the system. Reduced degree of polymerization
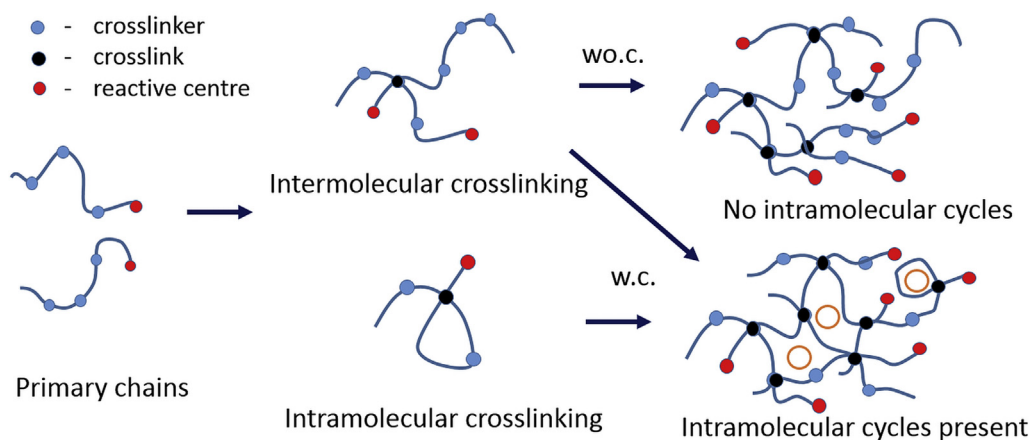
Scheme 1. Schematic presentation of the simulated ATRP copolymerization. Crosslinker units (circles) connected by short monomer chains can react with active centers forming branched macromolecules and finally gel. In the case when intramolecular crosslinking is allowed (w.c., lower part) the macromolecules contain closed circles (loops) marked by open circles. If intramolecular crosslinking is not allowed cycles are not formed (wo.c.) and all crosslinks contribute to gel formation.