

Conditions of microgel formation in homogeneous anionic polymerization of 1,4-divinylbenzene

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SUMMARY:

A kinetic model of the homogeneous anionic polymerization of 1,4-divinylbenzene (1,4-DVB) in dilute solutions with instantaneous initiation and without cyclization and termination reactions is proposed. The monomer and pendant vinyl group conversions, degrees of polymerization of the primary chains and the crosslinking densities were predicted as a function of the reaction time as well as 1,4-DVB and initiator (butyllithium) concentrations. The previous experimental data concerning the formation of the microgels can be explained using the kinetic mechanism of the polymerization reaction and neglecting cyclization. Calculations indicate that reactive 1,4-DVB microgels can be synthesized in the whole concentration range of the initiator.

Introduction

The idea to synthesize reactive microgels has derived from the fact that they are formed as intermediates in monovinyl-divinyl monomer copolymerization reactions¹⁾. The reason for the appearance of the microgels during the network formation processes, long before any macrogelation, is the existence of nonidealities such as unequal vinyl group reactivity and cyclization²⁾. For instance, in styrene-divinylbenzene (S-DVB) copolymerization, the growing chains in the pregel stage are rich in DVB units due to the higher reactivity of the DVB monomer. Furthermore, these chains are highly diluted by the monomer (and solvent) so that cyclization predominates in the early stages of the reaction. As a consequence, the growing chains become internally crosslinked and their structure approaches the microgels. Thus, the appearance of the microgels during the network formation processes can be compared with the formation of primary molecules as intermediates in the classical gelation theories³⁾.

For the synthesis of reactive microgels from 1,4-DVB monomer, three methods have been applied⁴⁾, one is the polymerization in highly dilute solution, in which intramolecular crosslinking is favoured. The second method is the polymerization in an emulsion in which the crosslinking reactions are limited to colloidal particles. The third method, recently developed in our laboratory, is the nonaqueous dispersion polymerization using living soluble polymer chains as an initiator of the reaction and also as steric stabilizers of the phase-separated particles⁵⁾.

Homogeneous anionic polymerization of 1,4-DVB with butyllithium (BuLi) leads to the formation of reactive microgels only under certain conditions. Hiller showed that, depending on the concentrations of 1,4-DVB and BuLi, linear or branched polymers,

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microgels or macrogels can be obtained using this method^{6,7}. His results are collected in Fig. 1(a) showing the dependence of the polymer structure on the reaction conditions. It can be seen that the structure of the resulting polymers changes from a linear to a crosslinked one as the concentration of 1,4-DVB or BuLi increases. (BuLi contents are expressed in mol-% of the initial monomer concentration). Contrary to these results, Burchard et al. could synthesize reactive microgels at very high BuLi concentrations⁸. Fig. 1(b) illustrates their results as the dependence of the molar mass of the polymers on the initial BuLi content. They observed a transition from microgel to macrogel with decreasing BuLi content, i. e., with increasing mole ratio of 1,4-DVB to BuLi. Although the solvents used in both series of experiments are different (tetrahydrofuran and benzene, respectively), the opposite effects of the initiator at low and high concentration ranges need some comments.

Here, we present a simple kinetic model for the homogeneous anionic polymerization of 1,4-DVB to explain the experimental results. Using the kinetic model, the monomer and pendant vinyl group conversions, degrees of polymerization of the primary chains and the crosslinking densities were predicted as a function of the reaction time, 1,4-DVB and BuLi concentrations, and they were compared with the experimental results.

Kinetic mechanism

The initiation mechanism of the anionic polymerization by BuLi is known to be dependent on the structure of the butyl group and on the type of the solvent used⁹. Here, we assume that BuLi dissociates instantaneously in free ion pairs and the

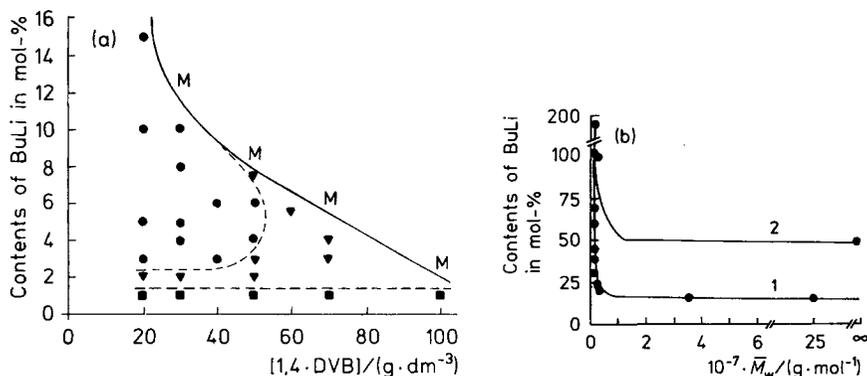


Fig. 1. Experimental results of microgel synthesis in homogeneous anionic polymerization of 1,4-divinylbenzene (1,4-DVB) with butyllithium (BuLi). (a): Dependence of the polymer structure on the initial contents of BuLi (in mol-% of the monomer) and the initial concentration of 1,4-DVB. Data were obtained by Hiller and Funke^{6,7}. Symbols represent linear (■), branched (▼), microgel (●) and macrogel (M) structures. (b): Dependence of weight-average molar mass of the polymers \bar{M}_w on the initial BuLi contents. Initial monomer concentration = 2,5 g/100 mL (1) and 5 g/100 mL (2). Data from Eschwey, Hallensleben and Burchard⁸

concentration of ions does not change during the reaction (termination-free system). Furthermore, the primary chains formed under the conditions of microgel synthesis are too short for the formation of tension-free rings and therefore, cyclization reactions can be neglected. A further assumption is that the reactivities of pendant vinyl groups and the living ends are independent of the size of molecules to which they are attached.

In the kinetic analyses that follow we consider as "primary chains" the polymer chains which would result if all crosslinks were severed³⁾. Furthermore, the terminology of Mikos et al. is used for the description of the reaction steps¹⁰⁾. The symbol $P_{p,c}$ is used for the primary chains with p pendant vinyl groups and c crosslinked units (see Fig. 2). Thus, $P_{0,0}$ represents the butyl anions. All possible reaction steps are shown schematically in Fig. 3. Based on this scheme, the reactions can be formulated as

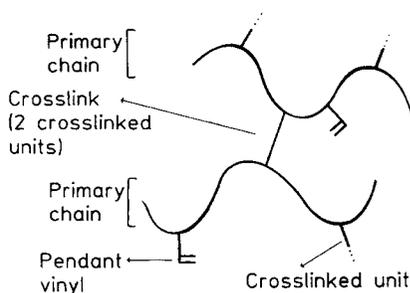


Fig. 2. Schematic illustration of a network structure formed in the polymerization of 1,4-divinylbenzene monomer

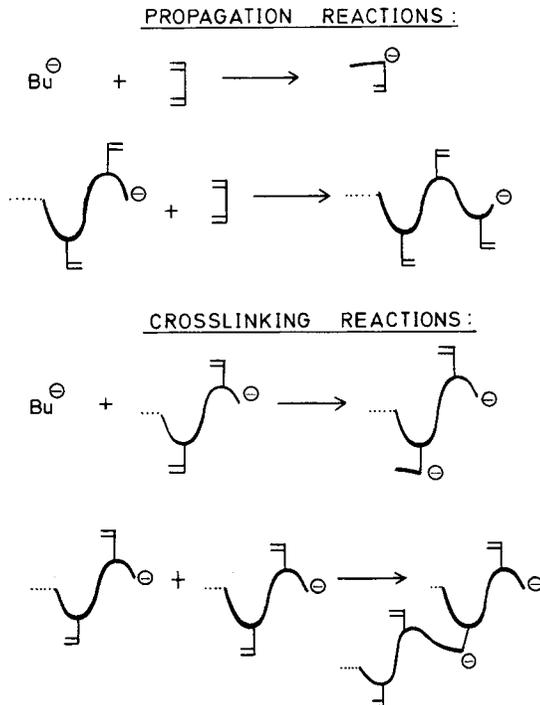
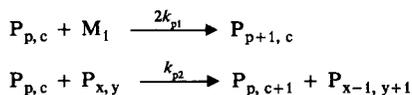


Fig. 3. Propagation and crosslinking in the anionic polymerization of 1,4-divinylbenzene (1,4-DVB). (Bu): butyl, ([]): 1,4-DVB, ([]): pendant vinyl, (~): backbones of the primary chains

follows:



where M_1 is 1,4-DVB monomer, k_{p1} and k_{p2} are the rate constants for propagation and crosslinking reactions, respectively. The reaction rate for 1,4-DVB monomer can thus be written as follows:

$$d[M_1]/dt = -2k_{p1} \cdot [P] \cdot [M_1] \quad (1)$$

where $[M_1]$ is 1,4-DVB concentration and $[P]$ is the concentration of total living species, i. e.,

$$[P] = \sum_{p=0}^{\infty} \sum_{c=0}^{\infty} [P_{p,c}] \quad (2)$$

and, according to the assumptions, it is equal to the initial BuLi concentration in the reaction batch. The rate equations for pendant vinyls and crosslinked units can be given as:

$$d[M_2]/dt = 2k_{p1} \cdot [P] \cdot [M_1] - k_{p2} \cdot [P] \cdot [M_2] \quad (3)$$

$$d[M_3]/dt = 2k_{p2} \cdot [P] \cdot [M_2] \quad (4)$$

where $[M_2]$ and $[M_3]$ are the concentrations of pendant vinyls and crosslinked units, respectively. The factor 2 enters in Eq. (4), because two crosslinked units are involved in each crosslink, namely, the one originally bearing the pendant double bond and the other one formed as a result of the reaction of a growing chain with a pendant double bond (see Fig. 3).

The number-average degree of polymerization of the primary chains \bar{y}_n and the average number of crosslinked units per primary chain, called crosslinking density, ν_e can be calculated as:

$$\bar{y}_n = ([M_2] + 0,5[M_3])/[P] \quad (5)$$

$$\nu_e = [M_3]/[P] \quad (6)$$

It must be pointed out that Eq. (5) defines \bar{y}_n from the point of view of molecular weight of the primary chains. Therefore, each crosslinked unit contributes in Eq. (5) only one half to the monomeric units of the primary chains.

Furthermore, the monomer conversion x and the fraction of units with pendant vinyls f are given by:

$$x = 1 - [M_1]/[M_1]_0 \quad (7)$$

$$f = [M_2]/([M_2] + 0,5[M_3]) \quad (8)$$

where $[M_1]_0$ is the initial monomer concentration.

During the anionic polymerization of 1,4-DVB, the living end of a growing chain may contain a pendant vinyl group or a crosslinked unit. As was found by Worsfold¹¹⁾, the reactivity of the growing chains is independent of the type of their living ends. Moreover, he found in anionic S-DVB copolymerization an approximately tenfold greater rate constant for propagation compared to that for crosslinking reactions. In the following calculations, Eqs. (1) to (8) were solved for $k_{p2} = 0,1 k_{p1}$ and the reaction times are expressed in units of $k_{p1} \cdot t$, where t is the actual reaction time.

The number of crosslinked units per primary chain reaches the value 2 at the incipient macrogel formation (gel point). Consequently, if cyclization is disregarded, $\nu_e = 2$ represents the critical condition for microgel-macrogel transition. Furthermore, polymers with ν_e values between 0,1 and 1 are called branched chains and those with $\nu_e < 0,1$ are denoted as linear chains.

Results and discussion

The calculated monomer and pendant vinyl conversions, x and f , respectively, together with the degrees of polymerization of the primary chains \bar{y}_n are given in Fig. 4 as a function of the reaction time. The calculations were performed for an initial

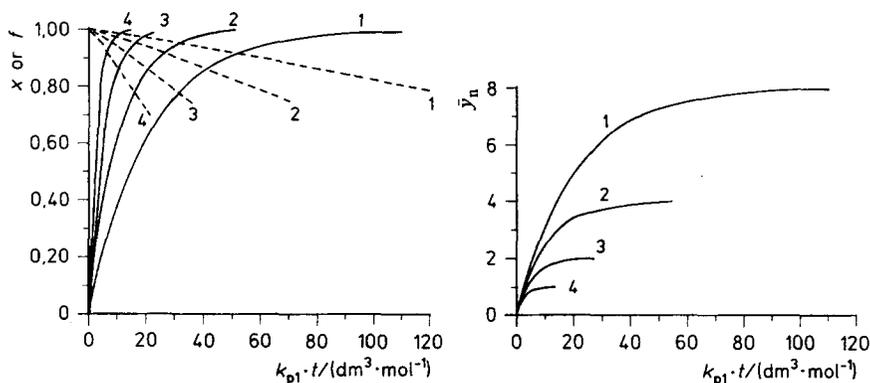


Fig. 4. Calculated monomer conversion x , fraction of units with pendant vinyls f (dashed curves) and the number-average degree of polymerization of the primary chains \bar{y}_n shown as a function of the reaction time expressed in units of $k_{p1} \cdot t$ (in $\text{dm}^3 \cdot \text{mol}^{-1}$). Initial monomer concentration = 2,5 g/100 mL. Mole fraction (in %) of butyllithium: 12,5 (1), 25 (2), 50 (3), and 100 (4)

monomer concentration of 2,5 g/100 mL and for different BuLi concentrations. The time scale is in units of $k_{p1} \cdot t$. The rate of monomer and vinyl group conversions increases and the degree of polymerization of the primary chains decreases with increasing BuLi concentration. Furthermore, at total conversion of 1,4-DVB, 80 to 90% of the DVB units contain pendant vinyl groups. Such a high degree of residual

unsaturation originates from the tenfold greater rate constant of propagation compared to that of the crosslinking reactions in the anionic 1,4-DVB polymerization*).

In Fig. 5, the crosslinking density of polymers v_e is plotted against monomer conversion x . The crosslinking density increases only slightly during the course of monomer conversion and thus, almost linear or branched polymers must be formed

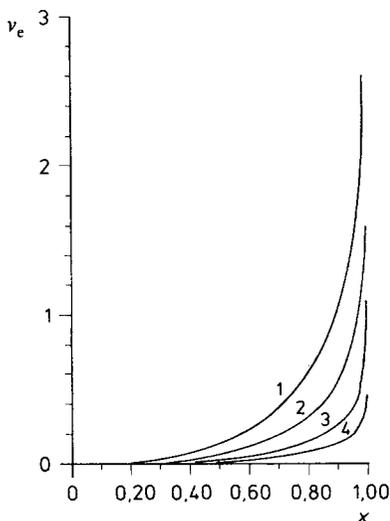


Fig. 5. Dependence of crosslinking density v_e on monomer conversion x for an initial monomer concentration of 2,5 g/100 mL and at various mole fractions (in %) of butyllithium: 12,5 (1), 25 (2), 50 (3), and 100 (4)

during the polymerization process. Batzilla also found experimentally the formation of soluble poly(4-vinylstyrene) chains in the anionic 1,4-DVB polymerization up to 80% monomer conversion¹²⁾, which is in accordance with the present results. Furthermore, the crosslinking density increases abruptly towards the end of monomer conversion and leads to a macrogelation in the reaction batch when its value reaches two. Fig. 6 shows the dependence of the crosslinking density on BuLi contents for a fixed reaction time and for various initial monomer concentrations. As the BuLi contents increases, the crosslinking density increases abruptly due to the increasing rates of reactions, passes through a maximum and then decreases, due to the decreasing length of the primary chains which limits the number of crosslinked units per chain (v_e). There seem to be two opposite effects of the initiator on the crosslinking density of the polymers, namely the effect on the rate of crosslinking reactions and that on the length of the primary chains. As the BuLi contents increases, the first effect tends to

*) The reason for a high degree of residual unsaturation was found from calculations. Residual unsaturation increases as the k_{p2}/k_{p1} ratio decreases, i. e., as the rate constant of crosslinking reactions decreases.

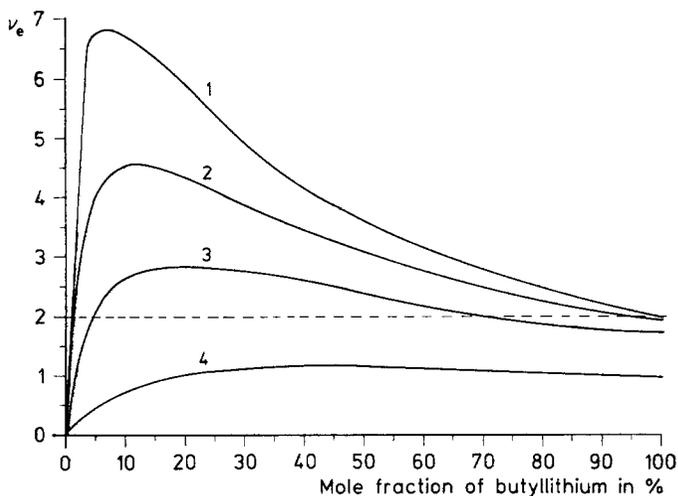


Fig. 6. Dependence of crosslinking density ν_e on mole fraction (in %) of butyllithium. Reaction time = $100 k_{p1} \cdot t$ (in $\text{dm}^3 \cdot \text{mol}^{-1}$). Initial concentration of monomer 1,4-divinylbenzene 6 (1), 4 (2), 2,5 (3), 1 g/100 mL (4). The dashed line represents the microgel-macrogel transition region

increase the crosslinking density due to Eq. (4), whereas the second effect limits its value due to Eq. (6). Thus, for a given reaction time, the combination of these two effects determines the crosslinking density of the polymers.

Depending on the crosslinking density of polymers, the regions for the formation of linear or branched polymers (I and II in Fig. 7, respectively), microgels (III), and macrogels (IV) are given in Fig. 7 for a fixed reaction time. The solid and dashed curves represent the transition regions between these structures. A comparison of Figs. 1 and 7 shows that the results of the kinetic analyses are in good agreement with both series of experiments. The shape of the experimental curve in Fig. 1(a) at the microgel-macrogel region (solid curve) is the same as that calculated from the kinetic model. In the low-concentration range of the initiator, because the reactions are slow and the reaction time is limited, the crosslinking density cannot exceed the critical value 2 if the concentrations of 1,4-DVB and BuLi are chosen in the regions I to III as shown in Fig. 7. Furthermore, a transition from the microgel to the macrogel region takes place with increasing concentrations of 1,4-DVB or BuLi due to acceleration of the reactions. On the other hand, in the high-concentration range of the initiator, the polymerization and crosslinking reactions are very fast, but the length of the primary chains limits the crosslinking density of the polymers. Thus, in this region, a microgel-macrogel transition occurs with decreasing BuLi contents due to the increasing length of the primary chains.

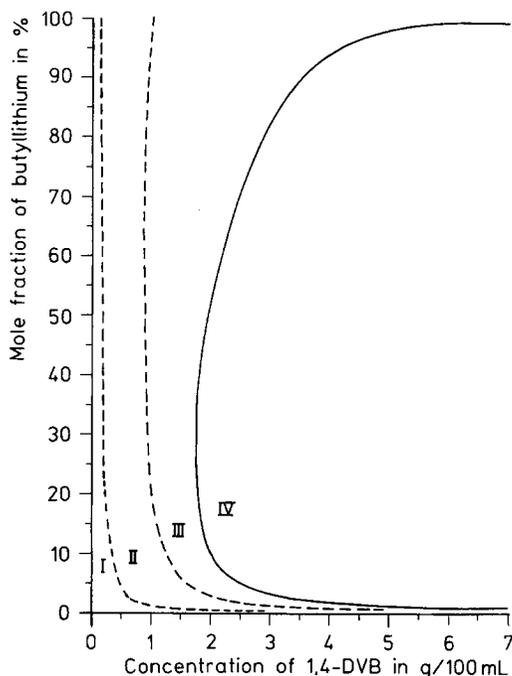


Fig. 7. Calculated dependence of polymer structure in 1,4-divinylbenzene (1,4-DVB) polymerization on the initial 1,4-DVB and butyllithium concentrations. Reaction time = $100 k_{p1} \cdot t$ (in $\text{dm}^3 \cdot \text{mol}^{-1}$). Numbers I to IV represent the regions for the formation of linear, branched, microgel and macrogel structures, resp. The solid and dashed curves represent the transition regions between these structures

Conclusion

1) In the homogeneous anionic polymerization of 1,4-DVB in dilute solutions almost linear or branched, i.e. soluble poly(4-vinylstyrene) chains are formed during the course of monomer conversion. The formation of microgels or macrogels starts towards the end of monomer conversion.

2) Reactive 1,4-DVB microgels can be synthesized on the whole concentration range of the initiator. The limiting factors preventing a macrogelation in the reaction batch are:

- a) the rate of crosslinking reactions at low BuLi contents, and
- b) the length of the primary chains at high BuLi contents.

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