Influence of the content of n-butanol on the critical conversion of gel formation during "living" three-dimensional radical co-polymerization of styrene and divinylbenzene

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Abstract. In this work, a study was made of the copolymerization of styrene and divinylbenzene in the presence of alkoxyamine synthesized "in situ" from benzoyl peroxide and 2,2,6,6-tetramethylpiperidine-1-oxyl in a solution of n-butanol (50-70 wt.%) at 120 °C. According to the experimental data obtained, the critical gelation conversion lies in the range of 50-75%. A decrease in the critical gelation conversion is also observed when the content of n-butanol 60%, which is accompanied by a separation of the system into two phases, that is, polymer is precipitated. With a lower content of precipitator, the separation of the system into two phases does not occur. It is assumed that in this case the removal of highly branched macromolecules from the polymerizing system occurs as a result of occlusion of "suspended" double bonds that become inaccessible to radicals, but "suspended" double bonds of linear and weakly branched macromolecules remain available for participation in the reaction with growth radicals.

1. Introduction
The synthesis of highly branched and network polymers is often carried out by the method of three-dimensional radical polymerization [1-14]. The fundamental aspects of the synthesis are described in sufficient detail in the reviews [15-20].

A promising way to obtain highly branched polymers of irregular structure is a three-dimensional radical polymerization proceeding in the mode of “living” chains [21]. The theoretical derivation of the dependencies that establish the relationship between the conditions of the process and the molecular mass distribution of macromolecules formed in the pre-gel period of a “living” three-dimensional radical polymerization was carried out in [5, 22]. In [23–26], three-dimensional radical polymerization of vinyl monomers with two or more double bonds was theoretically investigated, proceeding by the classical radical mechanism taking into account quadratic chain breakage or in the presence of inhibitors and chain transfer agents, as well as “living” three-dimensional radical polymerization with reversible inhibition. Using “living” three-dimensional radical polymerization, one can regulate the magnitude of the critical gelation conversion over a wide range by changing the ratio of a polyfunctional monomer with two or more double bonds and a “living” radical polymerization agent [3, 22].

It is known that a polymer product formed during three-dimensional radical polymerization prior to gelation is a mixture of linear, weakly branched and highly branched macromolecules. The theoretical content of highly branched macromolecules consisting of at least seven primary polymer chains does
not exceed ~ 30 wt.%. That is, more than half of the polymeric substance is “ballast” that does not have unique properties [22]. To increase the content of the highly branched fraction, an approach was tested in [7], in which the “living” three-dimensional radical polymerization is carried out in an environment with a worsening thermodynamic quality, which is created as a result of adding a precipitating agent — n-butanol to the mixture. In particular, it is shown that the proportion of the highly branched fraction in the polymer product isolated near the critical gelation conversion increases with the addition of n-butanol up to 50 wt.%. At the same time, the value of the critical gelation conversion also increases. The styrene-divinylbenzene system, including the “living” radical polymerization of a mixture of these monomers, can be considered as a model due to comprehensive study [27–31].

In this work, the “living” polymerization was carried out in the presence of alkoxyamine, synthesized in situ from benzoyl peroxide and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) according to the procedure [32]. The main objective of the work is to study the effect of the content of n-butanol, as a precipitator of polystyrene chains, on the copolymerization process of styrene and divinylbenzene in the presence of alkoxyamine. In particular, the task was to determine the dependence of the experimental critical gelation conversion with an n-butanol content of 50–70 wt.%, Provided that the value of the theoretical critical gelation conversion, calculated without taking into account the influence of the thermodynamic quality of the environment in which branched macromolecules are formed, in all experiments persisted and was equal to 0.5.

2. Materials and Methods

2.1. Materials

Styrene (ST) MM = 104.15 g/mol; \( \rho = 0.906 \) [33].

Styrene was purified from hydroquinone with a 10% aqueous solution of NaOH, washed with distilled water until neutral, dried over calcined CaCl₂, distilled in vacuum, and immediately before the experiment further purified by freezing in high vacuum.

Divinylbenzene (DVB) MM = 130 g/mol; \( \rho = 0.914 \) [34].

Used divinylbenzene technical (80% mixture of isomers) of the company “Aldrich” without additional purification.

2,2,6,6-tetramethylpiperidine-1-oxyl MM = 156 g/mol [35] of the company “Sigma”, 95–98% without further purification, were used as the “living” polymerization agent.

Benzoyl peroxide MM = 242 g/mol and dicumyl peroxide (PC) MM = 270 g/mol [34] were purified by recrystallization from ethanol.

N-butanol MM (N-but) = 84 g/mol; \( \rho = 0.810 \) [33] was purified by fractional distillation [36].

2.2. Methods

The copolymer was obtained by the method of “living” radical copolymerization of styrene and divinylbenzene in the presence of alkoxyamine, synthesized “in situ” from benzoyl peroxide and TEMPO, and high-temperature initiator — dicumyl peroxide, in a solution of n-butanol in sealed glass ampoules with an internal diameter of 5 mm. The content of n-butanol ranged from 50 to 70 wt.%.

The length of the primary polymer chains was regulated by the calculated concentration of TEMPO [37].

The reaction mixture with a known composition was poured into pre-weighed glass ampoules with an inner diameter of 5 mm. The oxygen dissolved in the monomer solution was removed on a vacuum unit with multiple repetitions of the freeze-thaw cycle in liquid nitrogen to a residual pressure of 0.01 mm Hg. The ampoules were unsoldered and placed in a WLM WS 100 heat treatment cabinet (T = 120 °C) and a DAK-1-1 microcalorimeter. The polymerization was carried out until the moment of gelation, the time of occurrence of which was determined by the moment of loss of the system fluidity, then the critical gelation conversion was determined using the kinetic curves obtained by the calorimetric method. The polymerization of the copolymers used in further studies was stopped for 15 min until the loss of system fluidity.
The contents of the ampoules of the obtained copolymer were removed in a Petri dish and dried from the volatile residual product at room temperature in a fume hood for 24 hours and in a vacuum oven at room temperature to constant weight.

The kinetics of radical polymerization were studied by the calorimetric method on a differential automatic microcalorimeter DAK-1-1 in the mode of direct recording of the heat release rate dQ/dt under isothermal conditions.

The molecular-mass characteristics of branched polymers obtained near the gelation, were determined by size exclusion chromatography on a gel chromatograph "Waters", equipped with a differential Refractometer, the eluent tetrahydrofuran, (T=35°C), elution rate 1 ml/min, consisted of two connected in series columns Plgel 5 µm MIXED-C.

3. Results and discussion

In all experiments, the ratio of styrene and divinylbenzene was the same [ST]₀: [DVB]₀ = 100: 1.17. The synthesis conditions are shown in table 1.

| № experience | ω_n-but, wt.% | [n-but]₀, mol/l | [TEMPO]₀, mol/l | [PB]₀, mol/l |
|--------------|---------------|----------------|----------------|--------------|
| 1            | 50            | 5.780          | 0.023          | 0.020        |
| 2            | 55            | 6.322          | 0.021          | 0.017        |
| 3            | 60            | 8.856          | 0.019          | 0.015        |
| 4            | 70            | 9.714          | 0.014          | 0.012        |

Figure 1 shows the kinetic curves of "living" radical copolymerization of styrene and divinylbenzene. Due to the introduction of a high-temperature initiator (dicumyl peroxide) the polymerization rate reduced to the current concentration of monomers remains constant throughout almost the entire process and almost does not depend on the dilution of the system with n-butanol.

In figure 2 shows the dependence of the experimental critical gelation conversion on the n-butanol content in the mixture of polymerizing comonomers. It can be seen that there is a sharp drop in gelation at 60% of the precipitant content, which may be caused by the separation of the system into two
phases, which is also observed at 70% of the content. Taking into account the fact that when the content of n-butanol is up to 50 wt.%, the critical gelation conversion, on the contrary, increased with an increase in the proportion of precipitator [7] and, accordingly, with the deterioration of the thermodynamic quality of the medium, this experimental fact is very interesting from the point of view of the mechanism of the "living" three-dimensional radical polymerization in the boundary conditions with the separation of the system into two phases.

When the precipitator content is less than 60%, the system is not divided into two phases. It is assumed that in this case the removal of highly branched macromolecules from the polymerizing system occurs as a result of occlusion of "suspended" double bonds that become inaccessible to growth radicals, but "suspended" double bonds of linear and weakly branched macromolecules remain available for participation in the reaction with growth radicals.

Figure 3 shows chromatograms of polymer products isolated near the gel point (for the conversion of monomers smaller by ~ 2% of the experimental critical conversion of gelation). From figure 3 shows that the highest content of the highly branched fraction with the highest molecular weight is formed in experiments in which the separation of the system into two phases is not observed.

4. Conclusion
Copolymers of styrene and divinylbenzene in the presence of 50, 55, 60 and 70 wt.% n-butanol were obtained by the method of three-dimensional radical polymerization in the mode of "living" chains. The values of the critical gelation conversion, which lies in the range of 50-75%, are determined.

Analyzing the results obtained, it can be said that highly branched macromolecules emerge from the polymerizing system due to the process of occlusion of "suspended" double bonds, which makes it impossible for the growth radicals to interact with these macromolecules. At the same time, this
process does not interfere with the interaction of linear and weakly branched macromolecules with the radicals of other macromolecules, and allows them to continue to grow to a highly branched state, thereby increasing the yield of high-molecular product. In other words, there is a dependence of the rate constant of the reaction of radicals with “suspended” double bonds on the degree of branching of the macromolecule, which gives an advantage in the growth of molecular weight to weakly branched polymer chains. However, this process is possible only when no interphase separation occurs in the system, that is, the concentration of precipitant should not exceed 60% by mass.

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