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Synthesis of branched polymers via radical copolymerization under oxygen inflow

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ABSTRACT

Branched and highly-branched polymers were prepared through radical copolymerization of styrene (St) and divinylbenzene (DVB) in the presence of dissolved molecular oxygen (AIBN, 95 °C). The gel point (C_g) was found to depend on DVB/St ratio and oxygen concentration in liquid phase ($[O_2]$). Our data of size-exclusion chromatography (SEC) coupled to a multi-angle laser light scattering detector (MALLS) and differential refractive index detector (DRI) suggest that thus synthesized products are a mixture of primary polymer chains (PPCs) and branched macromolecules whose relative amount grows on approaching to C_g. Polymers with a largest amount of highly-branched macromolecules $\omega_{HBP} \approx 40$ wt% were obtained in the vicinity of C_g. Synthesized polymers contain pendant double bonds $[C{=}C] \approx 1 \times 10^{-3}$ mol/g and some amount of peroxide groups $[O{-}O] = (0.1–0.5) \times 10^{-3}$ mol/g.

1. Introduction

In the field of radical polymerization, nowadays much attention is being paid to synthesis of polymers with a complicated topology such as branched and highly branched polymers [1]. For the purpose, most promising seems to be radical copolymerization of monomers containing two and more double bonds. As is known [2], radical polymerization of monovinyl, M_1, and divinyl, M_2, monomers gets started with formation of linear primary polymer chains (PPCs) containing pendant double bonds (Scheme 1). A mean number of the pendant bonds per a primary polymer chain can be expected to increase with a fraction of M_2 in a starting mixture. As the number of PPCs is low (as well as the amount of pendant double bonds), polymer radicals react largely with double bonds in monomers M_1 and M_2. With increasing number of PPCs, the amount of pendant double bonds also grows. Growing radicals can encounter the pendant double bonds more frequently to form links with already existing PPCs and thus to give macromolecules containing two and more PPCs. As a result, the mean molecular weight of newly formed polymer and a mean number of pendant double bonds per a macromolecule tend to increase on approaching to critical conditions of gelation. At typical conditions (initiation rate $W_i \approx 10^{-7}–10^{-6}$ M s) and low concentration of cross-linking monomer, M_2, the gelation happens at a very low extent of conversion. For radical polymerization of styrene with 1 wt% divinylbenzene ($T = 120$ °C, 0.0053 M Trigonox B), the critical conversion at gelation is about 7% [3].

In order to synthesize and then separate branched polymers, the process should be stopped prior to the onset of gelation. In this context, it seems important to find some ways for increasing the critical extent of conversion (gel point) C_g and thus to ensure more or less acceptable yield of desired polymer products. For this role, most promising candidates seem to be radical polymerization in the presence of chain transfer agents [4–7] and living/controlled radical polymerization [8–14].

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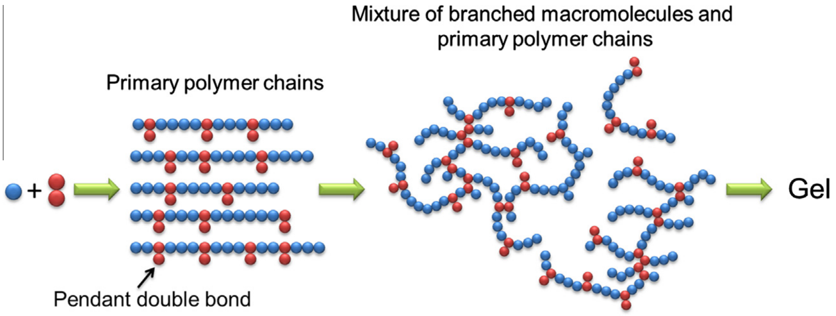

Scheme 1. Formation of branched macromolecules during radical copolymerization of monovinyl and divinyl monomers.

We suggest an alternative approach to the problem: radical copolymerization in the presence of molecular oxygen. In this case, the reaction of dissolved oxygen with growing polymer radicals is known to yield $RO_2^{\cdot}$ radicals [15]. Peroxyl radicals (as well as carbon-centered ones) are capable of taking part in all elementary stages of the polymerization process. Participation of $RO_2^{\cdot}$ radicals in propagation reactions result in appearance of peroxide groups in polymer chains. At high values of $[O_2]$ when all carbon-centered radicals convert into peroxyl ones, we can expect for formation of polyperoxide consisting of alternating monomer units and peroxide groups [16]. Meanwhile, $RO_2^{\cdot}$ radicals can also take part in chain-transfer reactions, the reactivity of peroxyl radicals being higher than that of carbon-centered ones. Upon variation in $[O_2]$, we could change the length of PPCs within wide limits [17]. In this way, we could regulate the amount of pendant double bonds in PPCs and also in produced branched macromolecules and thus to affect C_g without variation in relative amounts of M_1 and M_2 monomers in starting mixture.

Much attention has already been given to high-yield preparation of branched polymers [4,5,7,9,11] with special emphasis on optimization of process conditions (relative amounts of monomers, amount of chain length regulator) toward complete conversion of monomers. However, thus synthesized polymers not always show a high extent of branching. It has been reported [10,18] that most branched polymers are only formed in the vicinity of the gel point. The products prepared far from C_g contain largely linear PPCs and low-branched macromolecules formed by a few PPCs [18,19]. It follows that proper selection of synthesis conditions far below C_g can be expected to result in synthesis of low-branched polymer product.

In this work, we explored the formation of branched polymers within the pre-gelation period of radical copolymerization of styrene (St) with divinylbenzene (DVB) under oxygen inflow.

2. Experimental

2.1. Materials

Commercially pure styrene (St) was purified from hydroquinone with 10% NaOH solution in water, washed with deionized water until neutral reaction, dried over calcined $CaCl_2$, and distilled under reduced pressure. Commercially pure divinylbenzene (DVB) (Aldrich, 80 wt% DVB isomers and 20 wt% ethylvinylbenzene) was used without any further purification. The initiator—2,2′-azo-*bis*-(isobutyronitrile), AIBN—was purified by recrystallization from ethanol. Reagent grade *o*-xylene was used after distillation. Commercially pure oxygen (99.7% by volume) and O_2—N_2 mixtures (5 vol% O_2) were used as bubbling gases.

2.2. Experimental procedures

Aliquot amounts of St and DVB (overall concentration of monomers around 3.4 M) were dissolved in *o*-xylene (79.29 g) and the solution (150 ml) was placed in a 500-ml three-neck flask with a reflux condenser open to atmospheric environment. An aliquot amount of AIBN (1.23 g) was added to the solution and stirred until dissolution. Then the mixture was saturated with oxygen by bubbling through a 1-mm steel capillary for 5 min, after which the flask was put on a silicon oil bath held at 95 ± 1 °C. During the entire process, oxygen gas was supplied to the flask at bubbling rate V_{O2} monitored with a rotameter and the solution was agitated with a two-blade Teflon stirrer driven by IKA RW14 Basic at 750 rpm.

Caution!!! At high oxygen bubbling rate, the formation of polyperoxide is possible. It decomposes vigorously and can explode when heated over 100 °C.

Monomer conversion *C* was determined gravimetrically [20] at a 5% accuracy. The moment of gel formation, t_g, was fixed by the event of formation of macro-gel over the entire mixture. The transition from solution to gel is very rapid and takes around 1 min. Subsequently, extrapolation of the kinetic data to t_g allowed us to determine the critical conversion of gelation (C_g). Note that here the critical conversion of gelation is the conversion of monomers *C*. The discrepancy between *C* and the conversion of double bonds $C_{\text{d.b.}}$ is within experimental error so far as

$$C = C_{\text{d.b.}}\left(1+\frac{1-C_{\text{d.b.}}}{1+\frac{[M_1]_0}{[M_2]_0}}\right), \quad \text{for } r_1 = r_2 = 1. \tag{1}$$

The discrepancy is

$$\frac{C - C_{\text{d.b.}}}{C_{\text{d.b.}}} \times 100\% = \frac{1 - C_{\text{d.b.}}}{1+\frac{[M_1]_0}{[M_2]_0}} \times 100\%.$$

Molecular weight distribution of polymers was determined by size-exclusion chromatography (Waters Alliance GPCV 2000 apparatus: two consecutive PLgel