



Irregular polystyrene peroxides – a promising macroinitiators synthesized by radical polymerization under oxygen inflow

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ARTICLE INFO

Keywords:

Oxidative polymerization
Styrene
Oxygen
Polystyrene peroxide
Macroinitiator
Methyl methacrylate

ABSTRACT

Polystyrenes with different content of peroxide groups – from polystyrene with the peroxide group content of $[O-O] = 1.7 \times 10^{-3}$ mol/g to alternating copolymer of styrene with oxygen (polystyrene peroxide (PSP)) $[O-O] = 6.6 \times 10^{-3}$ mol/g – are synthesized by radical polymerization in the presence of oxygen. The composition and structure of the polymers are investigated by size exclusion chromatography (SEC), elemental analysis, TGA-DSC, IR and NMR spectroscopy. The synthesized polymers are tested as macroinitiators for radical polymerization of methyl methacrylate (MMA). The MMA polymerization kinetics is studied by isothermal calorimetry. It is found that the polymerization rate increases with the decrease of peroxide group content in the macroinitiator. It is shown that the macroinitiators may be used to obtain block copolymers.

1. Introduction

A block copolymer is two or more polymer fragments (blocks) linked together by a covalent bond. Each of the blocks differs from the others by its chemical composition or chain structure. The thermodynamic incompatibility common to the majority of polymers leads to phase separation of copolymer blocks. The covalent bond between the blocks prevents separation at the macrolevel. As a result, the separation occurs at the microlevel. This leads to the formation of ordered structures with a domain size of about 10–100 nm. Generally, in bulk, diblock copolymers can microphase separate into a variety of morphologies, including spheres, cylinders, bicontinuous gyroids, and lamellae [1]. The morphological variety of multiblock copolymers is much greater [2]. Block copolymers attracts the attention of researchers because of the possibility to control the material structure at the nanolevel [3]. For instance, block copolymers are used as templates for synthesis of nanoparticles [4], membranes [5] or nanoporous materials [6]. Block copolymers containing electron-donor and electron-withdrawing groups are used in photovoltaic [7] and light-emitting devices [8]. Furthermore, block copolymers are surface-active agents for polymer mixtures [9]. The most famous example is high impact polystyrene obtained by the polymerization of the butadiene solution in styrene [10]. Thin films formed by ordered block copolymers are promising materials for nanoscale lithography [11]. In solvents, selectively dissolving one of the blocks, block copolymers form micellae. The latter are used as carriers of functional compounds [12] or nanoreactors [13]. The detailed information on block copolymers and their application are contained in reviews [14].

There are two main approaches to the synthesis of block copolymers: coupling of two appropriately end-functionalized chains [15], and initiation by a macroinitiator. In the latter approach, the macroinitiator can be obtained by addition of polymer chains to easily decaying groups [16], for example, to azo-group, or by various chain polymerization processes such as living ionic

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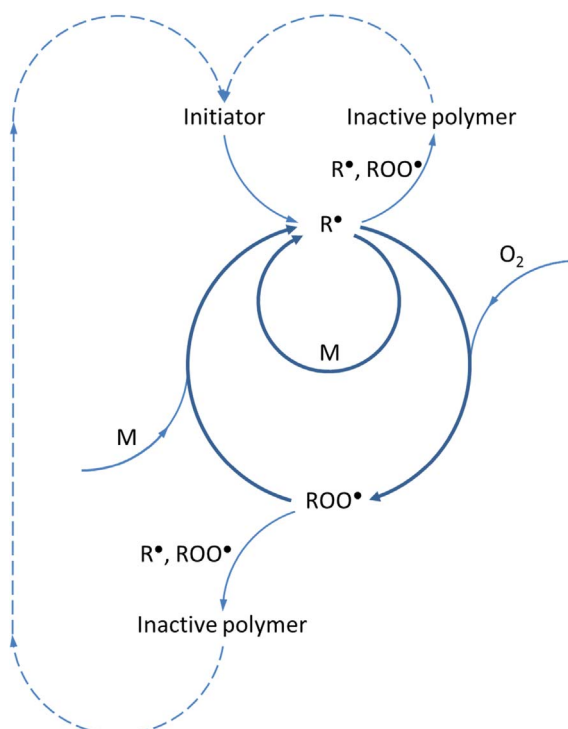
polymerization [17], reversible-deactivation radical polymerization (ATRP [18], RAFT [14b, 19], NMP [20]), and ring-opening metathesis polymerization (ROMP) [21]. The main advantages of living ionic and controlled radical polymerization are precise control of copolymer composition, narrow disperse polymers, as well as possibility to obtain multiblock copolymers (up to 12 blocks [22]). However, these processes require application of expensive compounds that are not available on industrial scale yet. Thus, a vital task is to find approaches for block copolymer synthesis which does not require the use of specially synthesized compounds.

Radical polymerization in the presence of molecular oxygen is of interest for the synthesis of block copolymers. The mechanism of monomer M polymerization in the presence of oxygen is shown in Scheme 1. Radicals formed by decay of the initiator may react with the monomer M (“small” cycle in Scheme 1) or oxygen O₂ (a “large” cycle in Scheme 1). At relatively high oxygen concentration (10⁻²–10⁻³ mol/l) – close to solution saturation – the reaction proceeds only with formation of peroxide radical [23] (“large” cycle). It is associated with the high reactivity of oxygen. The rate constant of reaction of oxygen with a carbon-centered radical (10⁷–10⁹ l/mol s⁻¹) is commensurate with a rate constant of two radicals’ recombination [24]. The main product of the reaction in this case is polyperoxide – an alternating copolymer M with oxygen – [M–O–O]_n–. Polyperoxides of the majority of vinyl and vinylidene monomers can be obtained using free radical polymerization in the presence of oxygen [25].

As oxygen concentration decreases, the contribution of the “small” cycle (Scheme 1) into the polymerization process increases. Irregularities – a few M units in a row – appear in the polyperoxide chain. Polymer chain mainly consisting of monomer units with small number of peroxide groups can be obtained at low concentrations of oxygen. As it can be seen from the Scheme 1, “inactive” polymers formed by chain termination are able to initiate polymerization by peroxide group decay (dash line in Scheme 1). This reaction is classified as a degenerated branching of kinetic chain. Thus, the oxidative polymerization mechanism itself indicates the possibility of using the resulting polymers as macroinitiators.

Block copolymers of styrene with methyl methacrylate were obtained by using polystyrene peroxide (PSP) as a macroinitiator [26]. First, PSP was used as a macroinitiator for styrene polymerization. As a result, the reactive block copolymer PSP-PSt-PSP was obtained. Then methyl methacrylate (MMA) was polymerized in the presence of the reactive block copolymer. PMMA-PSt diblock copolymer was obtained as a result of polyperoxide block decay and polymerization of MMA.

We also suggest using macroinitiators obtained by oxidative polymerization for block copolymer synthesis. The difference of our approach is the use of macroinitiators containing a small amount of peroxide groups instead of polyperoxides. The present work is devoted to the study of styrene radical polymerization with continuous bubbling of gas mixtures of oxygen and nitrogen with an oxygen content less than 10 vol.%, the investigation of the composition and structure of the polymers and the study of their initiating ability.



Scheme 1. Mechanism of oxidative polymerization.

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