Synthesis of di- and triblock-copolymers of vinylic monomers in the presence of high molecular weight nitroxyl radicals formed in situ from N-tert-butyl-C-phenylnitrone

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High molecular weight nitroxyl radicals formed directly in polymerization system (in situ) from N-tert-butyl-C-phenylnitrone are efficient agents for the chain growth control and allow one to perform synthesis of di- and triblock-copolymers based on a number of vinylic monomers (styrene, methyl methacrylate, N-vinylpyrrolidone, and butyl acrylate) under more mild temperature regimes than their low molecular weight analogs. The macromolecular structures synthesized are characterized by GPC, NMR and IR spectroscopy, and MALDI TOF MS method.

Key words: controlled polymerization, vinylic monomers, nitroxyl radicals, block-copolymerization.

Improvement of methods for the preparation of polymer materials, as well as search for efficient ways for control and direction of the chain growth process in order of subsequent synthesis of macromolecules with a pre-set structure and certain complex of properties is among key problems in chemistry and technology of high molecular weight compounds. A possible way for solving the problem indicated above is based on the most dynamically developing in the last years concept of controlled (“pseudoliving”) radical polymerization (CRP), which opens wide, and sometimes unique, perspectives for the direction of the polymeric chain growth under conditions of radical initiation.

Among known methods of CRP, polymerization in the presence of stable radicals, in particular, nitroxyl radicals allowing one to perform synthesis of macromolecules by the nitroxide-mediated radical polymerization, is of special interest. In the polymers obtained by such methods, there are present labile bonds, which makes possible their use in obtaining block-copolymers by addition of new portion of a comonomer to the high molecular weight products. In addition, the formation of block-copolymers under radical polymerization conditions serves as a direct and unambiguous evidence that the mechanism of living chains operates in the process of the macromolecule synthesis.

As it is known, TEMPO was the first nitroxyl radical suggested for CRP, in the presence of which a controlled synthesis of polystyrene was observed only at high enough temperatures (120—140 °C). Later, in a number of works it has been shown that introduction of electron-withdrawing substituents allows one to reduce the temperature of the controlled synthesis. This is clearly seen in the case of N-tert-butyl-N-(1-tert-butyl-2-ethylsulfonyl)-propylnitroxyl and N-tert-butyl-1-[(diethoxyphosphoryl)-2,2-dimethylpropylnitroxyl (also known as SG1), the presence of which makes the polymerization to occur at temperatures below 90 °C. An increase in steric hindrance of the nitroxyl center with bulky substituents has similar effect.

A logical development of studies dealing with reduction of the temperature interval for CRP became an original version suggested in work and consisting in the use of sterically hindered nitroxyl radicals, which contain high molecular weight fragments and are formed directly during synthesis of the macromolecule (in situ) as a result of reaction of growth radicals with a spin trap (Scheme 1).

A polymer-oligomeric fragment creates steric hindrance during recombination of the nitroxyl radical with the second growing radical.

This leads to a significant (by the order of magnitude) decrease in the equilibrium constant of the nitroxide-mediated radical polymerization (Scheme 2) as compared to the analogous value for low molecular weight TEMPO-type nitroxyl radicals, which in the end promotes a reduction of the temperature of controlled polymerization and a significant increase in its rate, as well as allows one to widen the scope of monomers, for which the mechanism of pseudoliving polymerization regulated by nitroxyls operates.

The data on block-copolymerization with the use of high molecular weight nitroxyl radicals formed in situ, are very scarce and are not systematized.\(^2_6\) Formation of block-copolymers, as a rule, was proved indirectly based on the displacement of the GPC-curves of the reaction product mixtures without their preliminary separation and analysis of the composition by physico-chemical methods. At the same time, as it was mentioned above, the possibility of the synthesis of block-copolymers is a direct and irrefutable evidence of the occurring polymerization in the regime of "living" chains.

The purpose of the present work is the synthesis of styrene block-copolymers with the use of high molecular weight nitroxyl radicals formed in situ in the presence of \(N\)-tert-butyl-\(C\)-phenylnitrone (BPN).

### Experimental

Monomers were purified off from stabilizer with 10% aqueous sodium hydroxide, then washed with water, dried, and distilled at reduced pressure, their characteristics agreed with the reference data.\(^2_9\) Azoisobutyric acid dinitrile (AIBN) was purified by recrystallization from ethanol. The BPN samples were synthesized from tert-butylhydroxylamine and benzaldehyde according to the known procedure and purified by recrystallization. Organic solvents were dried with calcium chloride and distilled at atmospheric pressure.

The starting polystyrene containing a nitroxyl fragment was synthesized in the presence of BPN (0.08 mol.%) and AIBN (0.8 mol.%) as initiators, which were dissolved in the monomer. The solution obtained was placed into glass tubes and trice degassed by freezing with liquid nitrogen. Polymerization was performed at 70 °C with the polymerization time of 0.5—5 h. Then the polymer was purified by five-time reprecipitation with isopropyl alcohol from solution in chloroform to remove the residues of initiator, BPN, and monomer.

To perform diblock-copolymerization, a sample of purified polystyrene (10 wt.%) synthesized with the use of BPN according to the procedure described above, was dissolved in comonomer, methyl methacrylate (MMA), \(N\)-vinylpyrrolidone (VP) or butyl acrylate (BA). The solution was placed into glass tubes and degassed by trice freezing with liquid nitrogen. Then the polymerization was carried out (in the case of MMA at 70 °C, in the case of VP and BA at 90 °C). The polymerization products were reprecipitated from solution in chloroform with hexane (in the case of MMA and VP) or methanol (in the case of BA). A mixture of polymers after the reaction was separated by extraction. Polystyrene was extracted with cyclohexane from the mixture using a Soxhlet apparatus, polyMMA with acetonitrile, polyVP with water, polyBA with hexane. The block-copolymer yields \(Q\) were calculated using the following formula:

\[
Q = P[1 - (C + W)/100%],
\]

where \(C\) is the concentration of initiating polymer in the solution of comonomer (wt.%), \(W\) is the mass fraction of polymer of the second monomer in the mixture of polymers after the reaction, isolated by extraction (wt.%), \(P\) is the overall conversion of comonomer (wt.%).

The fraction of active chains \(W_{act}\) in polystyrene was determined using the equation:

\[
W_{act} = 100\% - W_{in}(1 + P/C),
\]

where \(W_{in}\) is the fraction of polystyrene in the mixture of polymers after the reaction (wt.%), isolated by extraction.

To obtain poly(styrene-block-MMA) with low molecular weight, a solution of polystyrene in a mixture of MMA and chloroform (1:1, wt.) was prepared. The weight proportion polystyrene : MMA was 4:1. Further experiment was carried out similarly to that described above.

Triblock-copolymerization was performed in the presence of poly(styrene-block-MMA) purified off homopolymers in styrene or BA (10 wt.%) at 90 °C. After the reaction, the samples were reprecipitated from chloroform with methanol. Homopolymers, polystyrene or polyBA, was washed off from the mixture by extraction in the Soxhlet apparatus with cyclohexane or hexane, respectively. The yield of triblock-copolymer was calculated using formula similar to the Eq. (1).

The polymeric samples obtained were analyzed by GPC, NMR and IR spectroscopy, and MALDI TOF MS. GPC analysis of polymers was performed on a Knauer chromatograph equipped with a differential refractometer (K2301), UV detector (K2501), and a Phenomenex Linear (2) phenogel column (10 μm, 7.8x300 mm). Chloroform was used as an eluent with the rate of 1 mL min\(^{-1}\). The concentration of a polymer in the sample was 10 mg mL\(^{-1}\), the injector loop volume was 20 μL. Polystyrene narrow MWD standard kits with MWF 12600—2570000 Da were used for calibration. Direct calibration was used for block-copolymers.