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CONTROL OF MOLECULAR WEIGHTS AND POLYDISPERSITIES IN RADICAL POLYMERIZATION OF STYRENE IN THE PRESENCE OF STABLE RADICALS

by

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Radical polymerization of styrene was investigated by initiation with benzoyl peroxide and AIBN, in the presence of nitroxy-based stable radical scavengers. The effects of the concentration of the nature and concentration of nitroxy radicals and the nature and concentration of the radical initiators on the kinetics, evolution of molecular weights and polydispersities of polystyrenes prepared at various temperatures are also discussed.

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CONTROL OF MOLECULAR WEIGHTS AND POLYDISPERSITIES IN THE RADICAL POLYMERIZATION OF STYRENE IN THE PRESENCE OF STABLE RADICALS

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Introduction

Control of molecular weights, polydispersities and terminal functionalities can be accomplished in radical polymerization in systems with the equilibration between active and dormant species[1]. One of the approaches is based on the reversible reaction between growing radicals (P_n^*) and scavenging radicals (R^*) to form covalent species (P_n-R). The first system of this type was based on dithiocarbamate derivatives[2]. However, in addition to the clean reversible homolytic cleavage of the covalent species, some side reactions, e.g. attack of growing radicals on covalent species via degradative transfer, and/or slow initiation with $R_2NCS_2^*$ radicals were also reported[3,4]. These reactions did not allow the formation of well defined polymers with dithiocarbamate derivatives. Apparently, alkoxyamines behave in a more chemoselective way. Nitroxyl radicals do not initiate polymerization of alkenes and the contribution of side reactions is less important. Alkoxyamines have been used successfully in the synthesis of well defined oligomers based on acrylic monomers[5] at temperatures lower than 100°C. Under these conditions it is not possible to adopt this system for polymerization of styrene. Well defined polystyrenes can be prepared in the presence of nitroxyl radicals at temperatures above 120°C. It has been already reported that in the presence of alkoxyamines prepared in situ by reacting benzoyl peroxide with small excess of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as scavenging radical, well defined polystyrenes with molecular weights up to $M_n=100,000$ could be obtained[6].

We have previously reported that the spontaneous thermal polymerization of styrene can be controlled in the presence of various stable radicals[7]. Initially, polymerization is inhibited by these radicals and it starts after an induction period, when nearly all stable radicals are consumed. The induction period and the rate of the subsequent controlled propagation depends on temperature and concentration of the scavengers. Molecular weights are controlled by the amount of the scavenger and polydispersities are relatively low ($M_w/M_n<1.3$). In this paper we present results of additional studies on the effect of the concentration of the nature and concentration of nitroxy radicals and the nature and concentration of the radical initiators on the kinetics, evolution of molecular weights and polydispersities of polystyrenes prepared at various temperatures.

Experimental

Styrene (Aldrich), was passed through a short column of neutral alumina, then fractionally distilled under reduced pressure. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) was purified by sublimation. Polymerization initiators (benzoyl peroxide, BPO, and 2,2'-azobis(2-methylpropionitrile), AIBN) were purified by recrystallization from methanol/chloroform, and diethyl ether, respectively. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC), using a Waters 510 pump equipped with a 410 differential refractometer and photodiode array UV detector, using THF as eluent with a flow rate of 1.0 mL·min^{-1} and with three ULTRASTYRAGEL columns (100 Å, 500 Å, and Linear) in series. The molecular weight calibration curve was obtained using polystyrene standards.

Polymerizations

All polymerizations were carried out in sealed vials, under argon. In a typical procedure for the thermal polymerization of styrene in the presence of 0.1M TEMPO, 0.234g (1.5×10^{-3} moles) TEMPO were dissolved in 15 mL freshly distilled styrene, under argon. Then, aliquots (3 mL) were removed and added to ampoules which were sealed. The mixtures were polymerized at the desired temperature (110-130°C) for different time periods. After the polymerizations, the contents of the ampoule were first diluted with small amounts of tetrahydrofuran, then poured into methanol. The precipitated polymers were filtered and dried *in vacuo* overnight. Small portions were then analyzed by GPC.

Results and Discussion

Thermal polymerization of styrene is initiated by the reactive intermediates generated by the Diels-Alder dimerization[8]. This was confirmed by trapping experiments[9] with nitroxy radicals. The contribution of the thermal initiation may be decreased in the presence of acids and bases which accelerate isomerization to the inactive dimer. This generally leads to slower polymerization and higher molecular weights[10]. Nevertheless, the thermal initiation cannot be suppressed completely. Polymerization in the presence of large excess of scavenging radicals cannot occur because they react very rapidly with propagating radicals (with diffusion controlled rate constants $k \approx 10^9$ mol[-1]·L·s^{-1})[11]. Thus, the onset of styrene polymerization is observed when concentration of radicals decreases from [TEMPO]$\approx 10^{-2}$ mol/L to $<<10^{-3}$mol/L and initially orange solution becomes nearly colorless. The consumption of TEMPO can be accomplished either by adding the sufficient amount of the radical initiators such as AIBN or BPO or by simple thermal process. Figures 1 and 2 show the kinetics of polymerization of styrene in the presence of [TEMPO]$_0$=0.01 and 0.03 mol/L and radical initiators [BPO]$_0$=0.01 and 0.03 mol/L, [AIBN]$_0$=0.01 and 0.03 mol/L, as well as in the absence of the initiator (pure thermal initiation). Induction periods clearly depend on the amount of the initiator but the slopes of the stationary periods depend only on the initial concentration of the scavenger. If the concentration of the initiator is higher than that of TEMPO, no induction period is observed during which excess of radicals is terminated. Next, is the stationary period in which controlled polymerization occurs. If concentration of radicals generated by the initiator is lower than [TEMPO]$_0$ or no initiator is added, the induction period is observed, during which spontaneous thermal initiation must generate the amount of radicals comparable with [TEMPO]$_0$. Nevertheless, after the stationary conditions are reached, rate of polymerization is the same regardless the concentration of initiator.
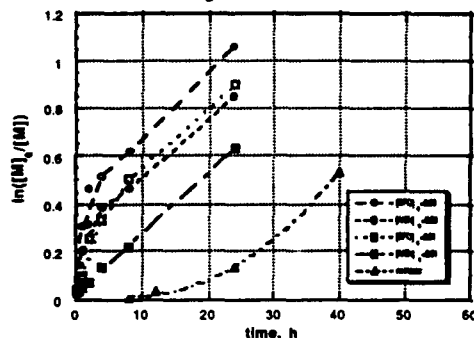

Fig. 1. Kinetics of bulk polymerization of styrene at 120°C with BPO/AIBN & [TEMPO]$_0$=0.01M.
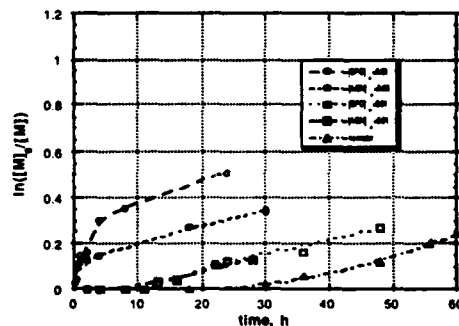

Fig. 2. Kinetics of bulk polymerization of styrene at 120°C with BPO/AIBN & [TEMPO]$_0$=0.03M.

Molecular weights of polymers prepared with higher concentration of TEMPO (0.03 M) grow linearly with conversion, and regardless of the presence and/or nature and the concentration of the initiator correspond to the number of chains equal to the concentration of the scavenger.
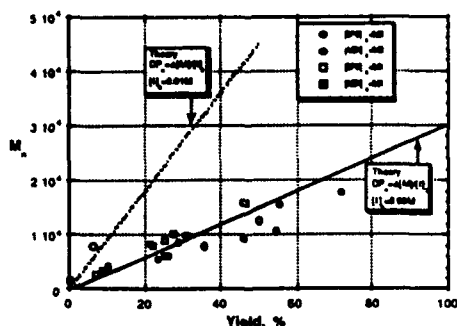
Fig. 3. M_n values in the bulk polymerization of styrene at 120°C with BPO/AIBN & [TEMPO]$_0$=0.03M.

The amount of BPO equimolar to TEMPO produces an excess of radicals, as observed in the initial fast step in Fig.2. Apparently, the efficiency of initiation with BPO is higher than with AIBN and exceeds 50%. During this first non-stationary period, the free radicals propagate fast but must still exchange efficiently with dormant species because molecular weights at the initial stages are much lower than those in a purely thermal process (M_n=200,000). The products from the first non-stationary stage have higher molecular weights. The value of molecular weights at the peak maximum in this system initially increases fast but then reaches asymptotically the theoretical dependence.

The presence of the non-stationary period for systems with higher concentration of initiators leads also to higher polydispersities which decrease with the reaction progress. On the other hand, the polydispersities of polymers prepared with less than equimolar amount of radicals increase slightly with conversion to the value of M_w/M_n =1.3. This can be ascribed either to small proportion of transfer or to the slow continuos generation of radicals in the thermal initiation process.
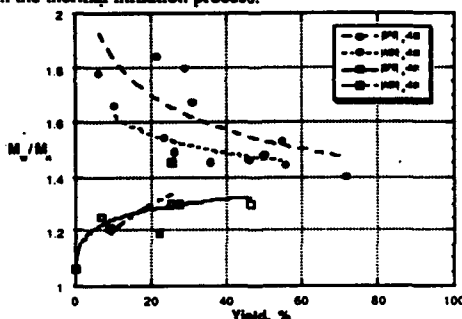

Fig.4 Polydispersities in the bulk polymerization of styrene at 120°C with BPO/AIBN & [TEMPO]$_0$=0.03M.

Polymerizations performed in the presence of lower concentration of TEMPO are not as well controlled and provide additional information on the behavior in this system. In the presence of the excess of radical initiator, M_n values no longer correspond to the number of scavenger molecules but to the total number of chains generated from radical initiators. The efficiency of initiation is approximately 50%, as estimated from the values of M_n, although kinetics (Fig. 1) gives evidences for the more pronounced non-stationary initial period than in Fig. 2.
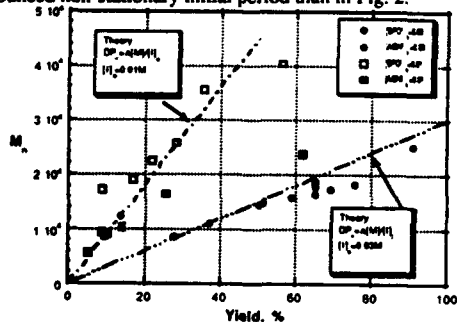

Fig. 5 M_n values in the bulk polymerization of styrene at 120°C with BPO/AIBN & [TEMPO]$_0$=0.01M.

Nevertheless, the number of the growing chains, both in the dormant and active form is defined by the concentration of the scavenger. This is shown below by the increase of the M_{peak} values with conversion. Chains produced in excess to scavenger have been terminated early during the process and only those capped in the form of alkoxyamines can be reversibly activated to grow. Some deviations from the theoretical behavior can be ascribed to the fast non stationary period, transfer and to the slow continuos generation of radicals in the thermal initiation process.
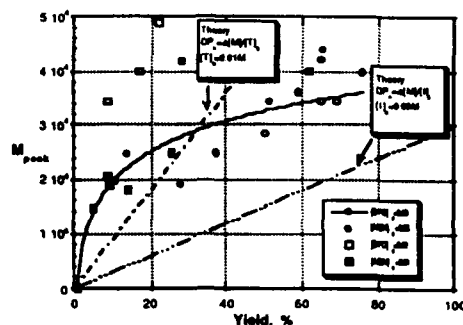

Fig. 6 M_{peak} values in the bulk polymerization of styrene at 120°C with BPO/AIBN & [TEMPO]$_0$=0.01M.

At lower concentration of TEMPO, polydispersitiesare are higher because of the stronger deviations from the ideal system.

It seems that the controlled polymerization of styrene in the presence of nitroxyl radicals occurs regardless of the source of the radicals. Radicals may be formed by the spontaneous thermal initiation, by the redox process (BPO, this is less important at 120°C), or by the thermal decomposition of the initiator (AIBN, and also BPO). The amount of the scavenger controls the polymerization rates and molecular weights, especially, M_{peak} values. On the other hand, the amount of the initiator regulates the induction periods and if used in the excess over scavenger it also affects M_n but not M_{peak} values. Polydispersities remain relatively low and in some cases they decrease with conversion indicating that the exchange reactions are slow in comparison with propagation. These exchange reactions may include both unimolecular and bimolecular processes. It seems that reactions at lower temperatures provide polymers with higher polydispersities because the exchange reactions are not fast enough. On the other hand, at higher temperatures the spontaneous initiation and transfer reactions may play more important role. It is important to accelerate the exchange reactions by modification of the structure of nitroxyl radicals, additives, solvents and to control spontaneous thermal initiation process.

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