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

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Daniela Mardare, Takeo Shigemoto, Krzysztof Matyjaszewski

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Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

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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 POLYDISPERSIONS IN THE RADICAL POLYMERIZATION OF STYRENE IN THE PRESENCE OF STABLE RADICALS

Daniela Mardare, Takao Shigemori and Krzysztof Matyjaszewski*  
Department of Chemistry  
Carnegie Mellon University  
4400 Fifth Avenue  
Pittsburgh PA, 15213

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. One of the approaches is based on the reversible reaction between growing radicals \( (P^-) \) and scavenging radicals \( (R^-) \) to form covalent species \( (P-R) \). The first system of this type was based on dithiocarbamate derivatives. However, in addition to the clean reversible homolytic cleavage of the covalent species, some side reactions, e.g. attack of growing radicals on scavenger species via degradative transfer, and/or slow initiation with \( (\text{RNC}_2\text{S})^+ \) radicals were also reported. These reactions did not allow the formation of well defined polymers with dithiocarbamate derivatives. Apparently, alkoxyamines behave in a more chemoselective way. Nitroxy 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 at temperatures lower than 100°C. With these conditions it is not possible to adopt this system for polymerization of styrene. Well defined polystyrenes can be prepared in the presence of nitroxy radicals at temperatures above 120°C. It has been already reported that in the presence of alkoxyamines prepared by reacting benzoyl peroxide with small excess of 2,2,6,6-teramethylpiperidine-1-oxyl (TEMPO) as scavenging radical, well defined polystyrenes with molecular weights up to \( M_w=10^5 \) could be obtained.

We have previously reported that the spontaneous thermal polymerization of styrene can be controlled in the presence of various stable radicals. 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 depend 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 and with three ULTRASTYRAGEL columns (100 A, 500 A, 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, 0.234 g \((1.5x10^{-3}\text{ mol})\) 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 \((110-130^\circ \text{C})\) for different time periods. After the polymerizations, the contents of the ampoules 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. This was confirmed by trapping experiments with nitroxy radicals. The contribution of the thermal initiation may be decreased in the presence of acids and bases which accelerate concentrations to the inactive dimers. This generally leads to slower polymerization and higher molecular weights. 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 \( k = 10^9 \text{ M}^{-1}\text{s}^{-1} \)). Thus, the onset of styrene polymerization is observed when concentration of radicals decreases from \((\text{TEMPO})=10^{-2} \text{ M/L} \) to \(<10^{-3} \text{ M/L} \) 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 \( M_0=0.01 \) and \( 0.03 \text{ M/L} \) and radical initiators \( \text{BPO} \) and \( \text{AIBN} \). Under these conditions the polydispersities of polystyrenes prepared at various temperatures.

Fig. 1. Kinetics of bulk polymerization of styrene at 120°C with BPO/AIBN & \( \text{[TEMPO]}=0.01 \text{M} \).

Fig. 2. Kinetics of bulk polymerization of styrene at 120°C with BPO/AIBN & \( \text{[TEMPO]}=0.03 \text{M} \).

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.
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. Yield, $Y$, 

\[ Y \approx \frac{M_{\text{pol}}}{M_{\text{init}}} \]

where $M_{\text{pol}}$ is the molecular weight of the polymer and $M_{\text{init}}$ is the molecular weight of the initiator. This can be described either in terms of kinetic parameters or by the slow continuous generation of radicals in the thermal initiation process.

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 $M_{\text{pol}}$ 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 continuous generation of radicals in the thermal initiation process.

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

It seems that the controlled polymerization of styrene in the presence of the 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), by the thermal decomposition of the initiator (AIBN, and also BPO). The amount of the scavenger controls the polymerization rates and molecular weights, especially, $M_{\text{pol}}$ values. On the other hand, the amount of the scavenger regulates the induction periods and if used in the excess over scavenger it also affects $M_n$ but not $M_{\text{pol}}$ 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.

**References**


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