Inhibitor Radicals in Styrene Polymerization

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ABSTRACT: Stable radicals derived from inhibitor molecules were detected in the process of styrene polymerization. *N*-(1,4-dimethylpentyl)-4-nitroso-aniline and 2,4-dinitrophenol inhibitors were shown to produce nitroxyl radicals. Phenoxyl radicals come from 4-benzylidene-2,6-di-*tert*-butyl-cyclohexa-2,5-dienone. The radical structures were determined. The kinetics of radical formation was studied. These radicals can participate in the process of living radical polymerization and significantly affect the kinetics of polymerization. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1599–1603, 2004

Key words: ESR/EPR; radical polymerization; polystyrene

INTRODUCTION

Living free radical polymerization controlled by a stable radical is one of the techniques for producing polymers with well defined microstructures.[1] This type of polymerization does not require highly purified monomers and solvents, which makes it attractive for industrial applications. The technique is based on the reversible trapping of the propagating polymeric chain with a counter radical. The trapping reaction (reversible inhibition) makes the classic termination almost negligible, leading to narrow molecular weight distribution of the polymer. Nitroxyl, phenoxyl, and verdazyl radicals were applied as inhibitor radicals for the reversible trapping of the growing polymeric chains . In recent years, alkoxyamines, which can both initiate polymerization and generate inhibitor radicals, have been widely used in living radical polymerization (see, for example, refs. 2 and 3.) Nevertheless, scientists are still searching for new compounds that are capable of effective participation in living radical polymerization reactions. For this reason, we have performed an ESR study of stable radicals derived from molecules of inhibitors to the process of styrene thermal autopolymerization. We have identified the radicals, studied the kinetics of their formation and followed their evolution with reaction time.

EXPERIMENTAL

Styrene was purified by distillation under vacuum (20 torr) at 44-45°C ($n_D^{20} = 1.5462$). Inhibitors were used without further purification. Each type of inhibitor powder was weighed and put in a vial with styrene solution. The solutions were stirred. After the inhibitors dissolved, ≈0.2 mL of each solution were placed in a glass tube of 3 mm diameter. The solutions were studied both in the presence and in the absence of oxygen. The solutions were deoxygenated by bubbling argon through the solution or by repeated freeze-thaw cycles.. The experimental results did not depend on the method of deoxygenation. The glass tubes were then sealed.

ESR spectra were recorded with an X-band RADIOPAN ESR-spectrometer equipped with a flowing air thermostat-temperature controller. For determination of inhibitor radical concentration, several nitroxyl radical concentration standards were prepared by dissolving known amounts of nitroxyl radical (4-hydroxy-2,2,6,6,-tetramethyl-pyperine-*N*-oxyl) in toluene. The ESR spectra were doubly integrated, and the value of the integral intensity was plotted as a function of concentration. The inhibitor radical concentrations were read from the calibration curve. The same glass tubes were used for recording the ESR spectra of the standard solutions and of the studied solutions. The structures of the three inhibitors studied are given in the Scheme 1.

RESULTS AND DISCUSSION

Inhibitor C [*N*-(1,4-dimethylpentyl)-4-nitroso-aniline]

Nitroso compounds are widely used to trap carbon-centered radicals. The trapping reaction results in the formation of a nitroxyl radical.[4] This nitroxyl radical can take part in living radical polymerization.[5]

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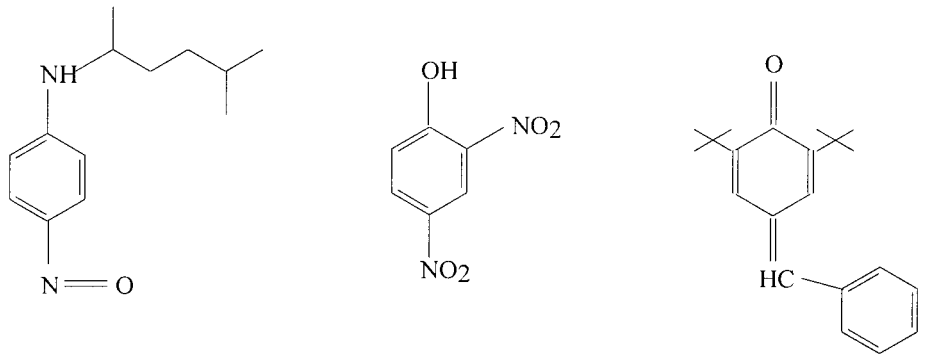


C
N-(1,4-dimethylpentyl)-4-nitroso-aniline

D
2,4-Dinitrophenol

Q
4-Benzylidene-2,6-di-*tert*-butyl cyclohexa-2,5-dienone

Scheme 1

ESR spectra of inhibitor C radicals in deoxygenated and oxygenated styrene solutions were taken at 110° and 130°C. The ESR spectrum (Fig. 1) consists of three basic spectral components, with a distance between lines of 11.5 G. Additional splitting of the basic components with a distance between lines of 2.5 G is observed as well. This spectrum is typical of aromatic nitroxyl radicals.[6,7] Three lines of the spectrum are due to the interaction of uncoupled electrons with nitrogen nuclei (a_N = 11.5 G). Additional splitting (a_H = 2.5 G) was assigned to the interaction of uncoupled electrons with protons of the aromatic ring and protons of polystyrene macroradicals (R = CH(Ph)-CH_2≈). Approximately the same value for the hyperfine coupling constant has been observed for the α-proton of the nitroxyl radical *t*-Bu(NO ·)-CH(Ph)CH_2≈.[8]

Aromatic nitroxyl radicals are derived from the interaction of inhibitor C with active radicals, R · , involved in the polymerization process. Scheme 2 shows the mechanism of nitroxyl radical formation.

The kinetics of nitroxyl radical formation during styrene polymerization in the presence of inhibitor C are shown in Figure 2. It is important to notice that nitroxyl radicals within the first few minutes of thermal treatment. The radical concentration at a temperature of 130°C is higher than at a temperature of 110°C. The maximum nitroxyl radical concentration at 130°C is approximately 10^2 times less than the initial concentration of inhibitor C in the styrene solution. At the same time, the concentration of the nitroxyl radicals in oxygen-containing samples is approximately two times less than concentration of the radicals in the deoxygenated samples. It seems that nitroxyl radicals are terminated by side reactions in the presence of oxygen.

Nitroxyl radical concentration increases during the first minutes of observation and then varies only slightly. The stationary radical concentration can be explained by the reaction of reversible inhibition (Scheme 3).

The shape of the ESR signal does not change during thermal treatment. This means that only one type of radical, shown in structure **I** of Scheme 2, has been detected.

Note that the reaction given in Scheme 3 is capable of providing living chain styrene polymerization.

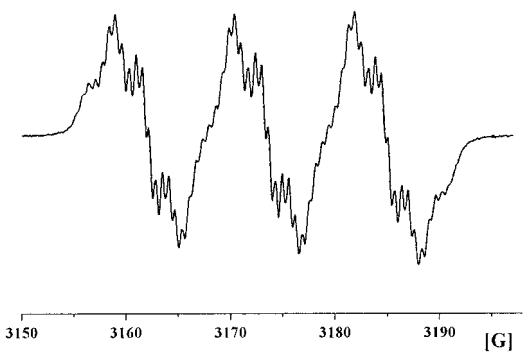
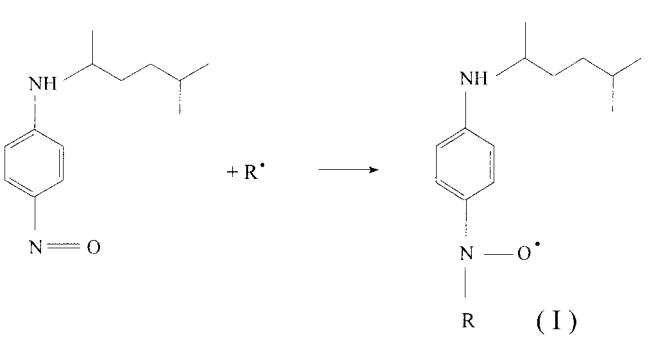


Figure 1 ESR spectrum of nitroxyl radical (**I**) in styrene solution at 110°C. The same spectrum is observed at 130°C.



Scheme 2

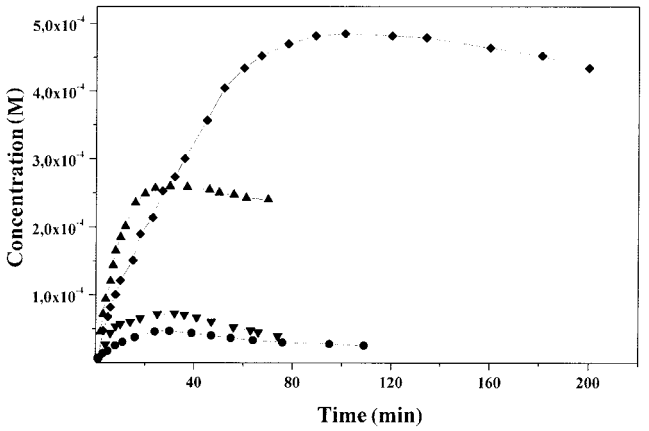


Figure 2 Kinetics of nitroxyl radical (**I**) formation in styrene solution: (●) in the presence of oxygen at 110°C, with inhibitor C concentration of $4.5 \times 10^{-3}M$; (▲) in the presence of oxygen at 130°C, with inhibitor C concentration of $3.19 \times 10^{-2}M$; (▼) in the presence of oxygen at 110°C, with inhibitor C concentration of $3.19 \times 10^{-2}M$; (♦) in the absence of oxygen at 130°C, with inhibitor C concentration of $2.42 \times 10^{-2}M$.

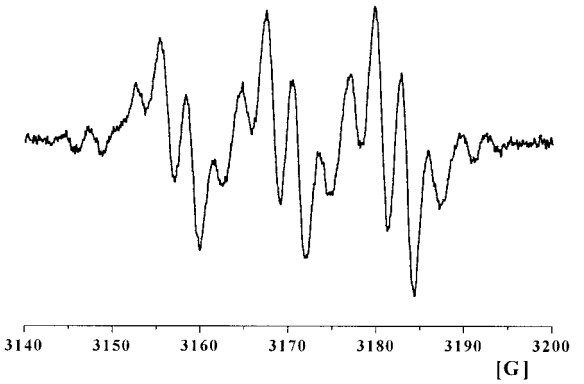


Figure 3 ESR Spectrum of nitroxyl radical (**II**) in styrene solution at 130°C.

Inhibitor D (2,4-Dinitrophenol)

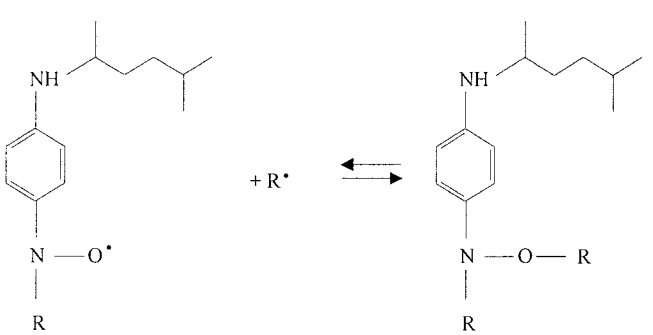
ESR spectra of inhibitor D radicals in deoxygenated and oxygenated styrene solutions were taken at 130°C. The ESR spectrum (Fig. 3) consists of three basic spectral components with a distance of 12.3 G between the lines. Each spectral component splits into several lines with a distance between lines of 2.8 G. This spectrum is typical of an aromatic nitroxyl radical. Three lines of the spectrum are determined by the interaction of uncoupled electrons with nitrogen nuclei (a_N = 12.3 G). Additional splitting (a_H = 2.8 G) is apparently due to the interaction of uncoupled electrons with protons of the aromatic ring and protons of polystyrene macroradicals. A possible scheme of nitroxyl radical formation is presented in Scheme 4 below.

Note that R · represents an active radical involved in the process of styrene polymerization.

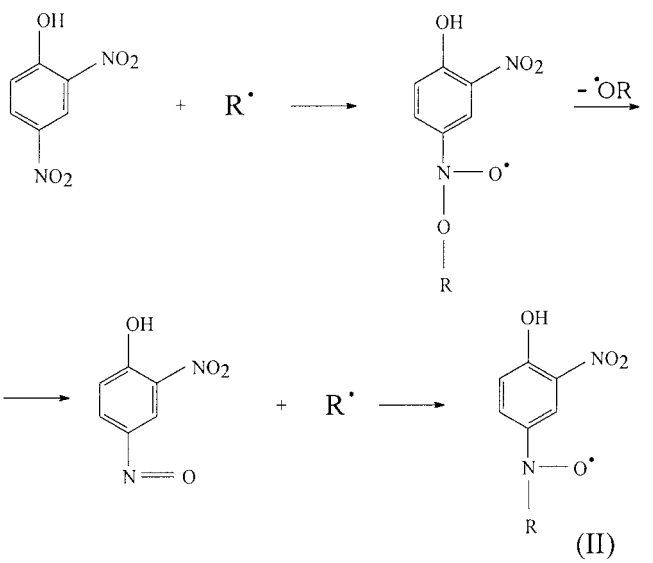
A similar scheme of reaction for active carbon-centered radicals with nitrocompounds has been proposed in another paper[9] and discussed in detail in the literature.[10,11] The active radical R · can react with either *para*- or *ortho*-groups of 2,4-dinitrophenol, leading to the formation of nitroxyl radicals.

The kinetics of nitroxyl formation at 130°C are presented in Figure 4. Notice that nitroxyl radical concentration in styrene solution increases with the increase of 2,4-dinitrophenol concentration in the solution. However, the maximum nitroxyl radical concentration is almost 10^4 times less than the initial 2,4-dinitrophenol concentration in the solution. Nitroxyl radical concentration in deoxygenated solution differs slightly from the concentration in oxygenated solutions. Nitroxyl radical concentration increases during the first few minutes of thermal treatment and then decreases slowly. It is possible to assume that nitroxyl radicals can take part in the reversible inhibition presented in Scheme 5.

The shape of the ESR signal does not change during thermal treatment. This means that only one type of



Scheme 3



Scheme 4

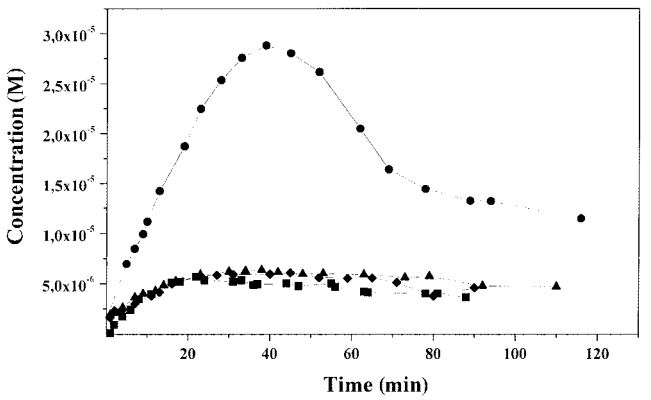


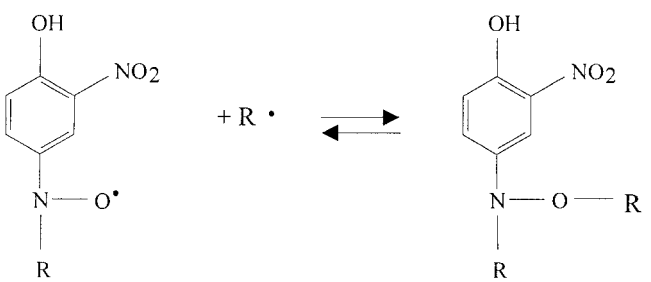
Figure 4 Kinetics of nitroxyl radical (**II**) formation in styrene solution at 130°C: (●) in the presence of oxygen, with inhibitor D concentration of $1.38 \times 10^{-1}M$; (▲) in the presence of oxygen, with inhibitor D concentration of $4.12 \times 10^{-2}M$; (■) in the absence of oxygen, with inhibitor D concentration of $4.34 \times 10^{-2}M$; (♦) in the absence of oxygen, with inhibitor D concentration of $4.57 \times 10^{-2}M$.

radical, showin in structure **II** of Scheme 4, has been detected.

Notice also that the ESR spectra of the radicals were not detected at 130°C in toluene solutions of 2,4-dinitrophenol. This result confirms the theory that the stable nitroxyl radical (structure **II**) is formed by the reaction of 2,4-dinitrophenol with active radicals involved in styrene polymerization.

Inhibitor Q (4-benzylidene-2,6-di-*tert*-butyl-cyclohexa-2,5-dienone)

ESR spectra of inhibitor Q radicals in deoxygenated and oxygenated styrene solutions were taken at 130°C (Fig. 5). The ESR spectrum obtained is a combination of the ESR spectra of different radicals. During the first stage of the polymerization process (up to 80 min), at 130°C, the ESR spectrum one of radicals dominates. This ESR spectrum corresponds to the phenoxyl radical (structure **III**, Scheme 6). The reaction of phenoxyl radical (structure **III**) formation is presented in Scheme 6.



Scheme 5

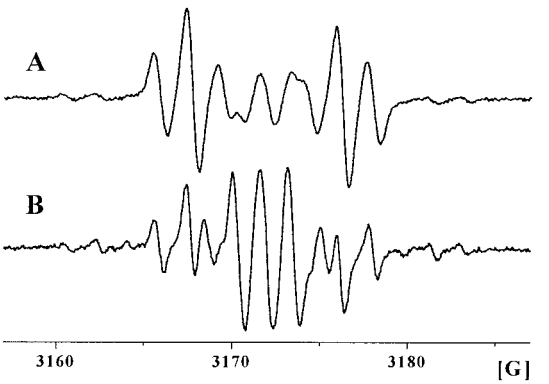
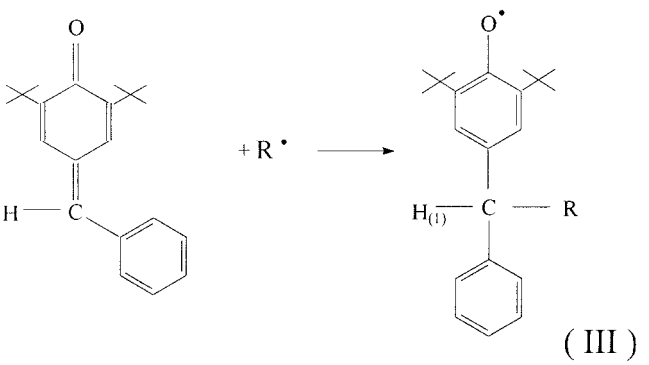


Figure 5 ESR spectra of radicals derived from inhibitor Q in styrene solution at 130°C for (A) 20 min and (B) 150 min.



Scheme 6

Note that R · represents an active radical involved in process of styrene polymerization.

Hyperfine structure constants determined from ESR spectra [Fig. 5(a)] are as follows: $a_{H(1)} = 8.5$ G, $a_{H(2)} = 1.8$ G. The constant $a_{H(1)}$ is due to the interaction of uncoupled electrons with hydrogen atom H(1). The constant $a_{H(2)}$ is determined by the interaction of un-

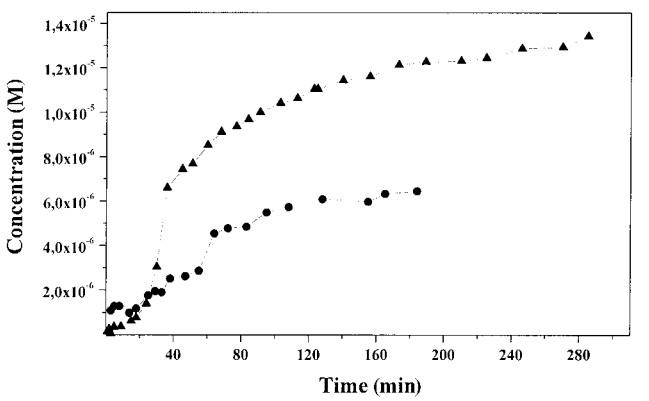
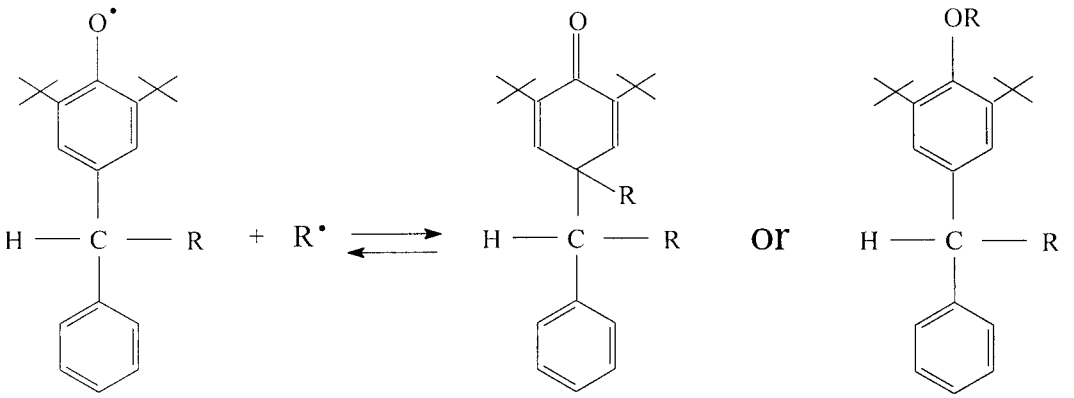


Figure 6 Kinetics of radical formation in styrene solution at 130°C: (●) in the presence of oxygen, with inhibitor Q concentration of $4.95 \times 10^{-2}M$ and (▲) in the absence of oxygen, with inhibitor Q concentration of $4.09 \times 10^{-2}M$.



Scheme 7

coupled electrons with hydrogen atoms of the phenyl ring. The ESR spectra of phenoxyl radicals have been studied extensively.[7,12] Values of the hyperfine structure constants allow us to determine the radical structure (**III**) uniquely.

The initial ESR spectrum transforms during thermal treatment at 130°C. The signal intensity of radical (**III**) decreases, and at the same time the signal intensity of a secondary stable radical increases [Fig. 5(b)]. This means that the radical (**III**) concentration decreases, and at the same time the concentration of secondary radical increases. It is important to notice that the concentration of secondary stable radicals is high at a later stage (300 min) of the process. The structure of the secondary radical is not defined uniquely. The secondary radical can be a result of the isomerization of radical (**III**) or of the reaction of radical (**III**) with styrene monomer. Additional investigations are needed to clarify the structure of this radical.

The kinetics of radical formation at 130°C are presented in Figure 6. Notice that the stable radical concentration is approximately 10^3 times less than the concentration of inhibitor Q in styrene solution. The concentration of radicals in the presence of oxygen is significantly less than the radical concentration in the absence of oxygen. This can be explained by the fact that phenoxyl radicals are usually unstable in the presence of oxygen. After 140 min of thermal treatment at 130°C, radical concentration varies insignificantly. It seems that reversible inhibition takes place (Scheme 7).[13]

Thus, the phenoxyl radical (**III**) is formed from inhibitor Q in styrene solution at 130°C. This radical can disappear partially or can turn into another stable radical with a structure that cannot be defined uniquely from this investigation.

CONCLUSIONS

Results presented in this study show that stable radicals are derived from inhibitor molecules in the process of styrene polymerization. *N*-(1,4-dimethylpentyl)-4-nitroso-aniline and 2,4-dinitrophenol inhibitors produce nitroxyl radicals. Phenoxyl radicals come from 4-benzylidene-2,6-di-*tert*-butyl-cyclohexa-2,5-dienone.These radicals can participate in the process of living radical polymerization and significantly affect the kinetics of polymerization.

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