Synthesis of Polystyrene Oligomers by Nitroxide-Mediated Radical Polymerization Using Diethylketone Triperoxide as a Multifunctional Radical Initiator

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ABSTRACT: Styrene oligomers (M_n, 2500–3000 g/mol) with low polydispersity index and containing peroxidic groups within their structure were synthesized using a novel trifunctional cyclic radical initiator, diethylketone triperoxide (DEKTP), through nitroxide-mediated radical polymerization (NMRP), using OH-TEMPO. During the synthesis of the polystyrene (PS) oligomers, camphorsulfonic acid (CSA) was used to inhibit the thermal autoinitiation of styrene at the evaluated temperatures ($T = 120–130°C$). The polymerization rate, which can be related to the slope of the plot of monomer conversion with reaction time, was monitored as a function of OH-TEMPO, DEKTP, and CSA concentrations. The experimental results showed that all the synthesized polymers presented narrow molecular weight distributions, and the monomer conversion and the molecular weight of the polymers increased as a function of reaction time. Under the experimental conditions, $T = 130°C$, [DEKTP] = 10 mM, and [DEKTP]/[OH-TEMPO] = 6.5, PS oligomers containing unreacted O—O sites in their inner structure were obtained. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1320–1328, 2012

Key words: polystyrene; radical initiator; NMRP; radical polymerization; oligomers

INTRODUCTION

During the past decades, many efforts have been conducted to develop new techniques of living radical polymerization, which can give access to the synthesis of well-defined polymeric structures such as block, star, and comb architectures.[1] One of these techniques, nitroxide-mediated radical polymerization (NMRP), is focused on the use of stable free radicals, such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy).[2,3] Unlike conventional radical polymerization, in which growing radical chains undergo irreversible termination reactions, in NMRP, the polymeric chains are reversibly deactivated by a nitroxide molecule, and when the chain ends are active, they can incorporate more monomer units throughout the polymerization. By means of NMRP, polymers with relatively narrow molecular weight distributions have been synthesized.[4]

The mechanism of NMRP involves a reaction between the active free radicals with a nitroxide molecule, resulting in a dormant species. The chemical bond in the dormant species between the free radical and the nitroxide can be reversible dissociated, allowing more monomer units to be incorporated to the polymer chain.[5]

The concentration of active radicals is controlled by a dynamic equilibrium between the dormant species and the active free radicals. This dynamic equilibrium has to be shifted toward the dormant species so that the concentration of active radicals is reduced to lower values in comparison with a conventional radical polymerization. Because the propagation reaction is of first order with respect to the radicals concentration and the irreversible biradical termination is of second order, a lower radicals concentration reduces the termination rate, preserving the living character of the polymerization.[6] The termination reactions, which lead to dead chain ends and a broadening of the molecular weight distribution, cannot be eliminated, but they are almost suppressed. The termination reactions also can lead to higher nitroxide concentration, which shifts the equilibrium toward the dormant species, thereby lowering the concentration of active radicals and decreases the reaction rate.[7]

In the presence of TEMPO, the polymerization reaction is performed at temperatures of about 125–140°C, where the dissociation of the reversible C—ON bond can occur. In the case of styrene, these temperature conditions result in the occurrence of thermal initiation.[8,9] To suppress the thermal polymerization of styrene, several organic acids have

been used, e.g., camphorsulfonic acid (CSA),[10] which has demonstrated to have an effective control over the thermal initiation of styrene, even in the presence of nitroxides.[11] It has been pointed out that CSA increases the polymerization rate in NMRP while broadening the molecular weight distribution[12]; this effect was attributed to nitroxide consumption as a result of nitroxide disproportionation by the acid molecule, which shifts the equilibrium to the formation of active radicals.[13] In addition, CSA can react with a nitroxide molecule to form hydroxylamine, leading to a poor control over the polymerization and in consequence broadening the molecular weight distribution. This effect is due to fewer TEMPO molecules present during the polymerization, which shifts the equilibrium to the active species.[14]

For the radical polymerization of styrene, benzoyl peroxide (BPO) is one of the most common radical initiator used; but in recent years, there have been several reports in the literature that mention the use of multifunctional cyclic radical initiators for the polymerization of vinyl monomers such as styrene,[15] with the goal of obtaining polymers with high molecular weight (>250,000 g/mol) and high conversion yields.[16,17]

In the particular case of the diethylketone triperoxide (DEKTP), a cyclic trifunctional peroxide initiator, it has been reported for the synthesis of polystyrene (PS) yielding polymers with high molecular weight (250,000–450,000 g/mol, depending on the DEKTP concentration and the reaction temperature used, 120–130°C) at relatively short polymerization times (4–5 h).[18] The radical decomposition mechanism of DEKTP was found to be as complex as the one of a lineal bifunctional initiators, but DEKTP showed greater activity.[19] Two mechanisms have been proposed for the decomposition of DEKTP: a total decomposition of the three O—O groups at a temperature higher than 130°C, and a sequential decomposition of the O—O groups at temperatures between 110 and 130°C. In the last case, Cerna et al.[18] were able to synthesize PS with undecomposed O—O in the polymer backbone.

This study reports the synthesis of PS oligomers by NMRP presenting low molecular weights using DEKTP as radical initiator and OH-TEMPO as nitroxide. In addition, the possibility of introducing peroxidic groups into the polymer structure was also evaluated, because these oligomers could be used as macroinitiators and/or precursors for the synthesis of interpenetrated polymer networks.

EXPERIMENTAL

Materials

Styrene monomer (Aldrich) was dried over $MgSO_4$ overnight, distilled under vacuum and refrigerated
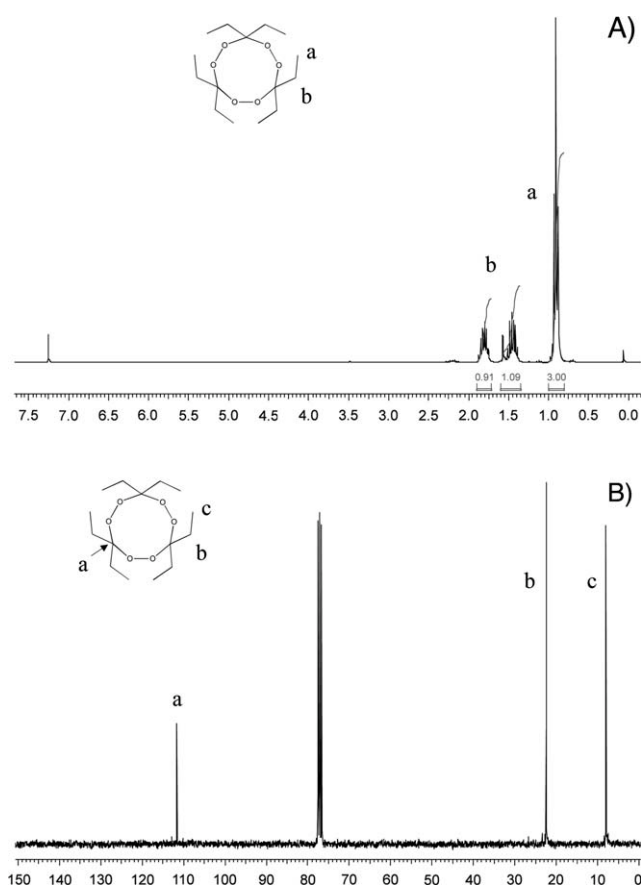
Figure 1 (A) ^{1}H-NMR and (B) ^{13}C-NMR spectra of DEKTP.

before its use. OH-TEMPO and CSA (Aldrich) were used as received.

Synthesis of DEKTP

DEKTP was prepared in a one-step reaction using diethylketone and hydrogen peroxide following the method described by Eyler et al.[20] In a clean round-bottom flask, 4.6 mL (59 mmol) of hydrogen peroxide (H_2O_2 30% v/v), 7.3 mL of sulfuric acid (H_2SO_4 70% v/v), and 5.6 mL (50 mmol) of diethylketone were added. The solution was stirred for 3 h, and the temperature of the reaction was kept at −10°C. The reaction mixture was extracted using petroleum ether and washed with an aqueous solution of ammonium sulfate $((NH_4)_2SO_4)$. Later, the extracted product was dried over magnesium sulfate ($MgSO_4$) for 12 h. Then, the solution was filtered and rotoevaporated, and the remaining product was a mixture of DEKTP and diethylketone diperoxide. Chilled methanol was added to the remaining product to promote the crystallization of the DEKTP because the diperoxide initiator is liquid under these conditions. The purity of the final product was analyzed by nuclear magnetic resonance (NMR). In Figure 1, it can be observed from the ^{1}H-NMR

TABLE I
Experimental Conditions for the Synthesis of PS Oligomers

Reagents	Parameters
[CSA] (mM)	0–3.9–30
[DEKTP] (mM)	5–10–15–20
[OH-TEMPO]/[DEKTP]	1.5–2.5–3.5–4.5–6.5
Temperature (°C)	120–130

spectra, the different signals corresponding to the ─CH$_3$ (δ ppm 0.85, t, 18 H) and to the ─CH$_2$ (δ ppm 1.4, m, 6 H; δ ppm 1.8, m, 6 H), and from the ^{13}C-NMR spectra, the corresponding signals of the ─CH$_3$ (δ ppm 8), ─CH$_2$ (δ ppm 23), and ─C (δ ppm 112), respectively.

Characterization

The NMR characterization was performed on a Varian-Gemini 2000 spectrometer using 5-mm NMR tubes and CDCl$_3$ as solvent at room temperature. For ^{1}H-NMR and ^{13}C-NMR measurements, the magnetic field used was 200 and 50 MHz, respectively.

The molecular weights (M_n, M_w) and the polydispersity index (PDI = M_w/M_n) were determined by permeation chromatograpgy (GPC) in a Hewlett–Packard HP 110 equipped with a HP 1100 UV detector and a HP 1047A RI detector using a set of three columns in series of pore size of 10^5, 10^4, and 10^3, respectively. Tetrahydrofuran (THF; HPLC grade) was used as solvent, and the instrument was calibrated using PS standards.

Synthesis of PS oligomers

The synthesis of PS oligomers was performed by bulk polymerization, using heavy wall ignition Pyrex glass tubes. A solution of styrene monomer, DEKTP, CSA, and OH-TEMPO (see Table I) was added to the glass tubes. The tubes were degassed to remove traces of oxygen and moisture by three cycles of freeze/thaw using liquid N$_2$, and they were flame sealed under vacuum and kept in an oil bath at different temperatures (Table I) for different predetermined periods of time. In each case, the polymer sample was precipitated from methanol and dried under vacuum until constant weight, and the monomer conversion was measured gravimetrically. The molecular weight and molecular weight distribution of the PS were obtained by GPC using THF as solvent. In addition, the different PS samples obtained were analyzed by NMR to detect the presence of unreacted peroxidic O─O groups within the polymer chain.

RESULTS AND DISCUSSION

Different polymerization conditions were evaluated in the synthesis of PS oligomers. In Table I, the different concentrations of DEKTP initiator, organic acid CSA, and the ratio of OH-TEMPO/DEKTP used are shown. It is worth mentioning that during the different reactions while one variable was evaluated, all the other parameters were kept constant.

Effect of the CSA concentration

The effect of the CSA concentration on the evolution of the molecular weight of the PS and the monomer conversion during the synthesis of PS oligomers was evaluated. For this purpose, different concentrations of CSA (0, 3.9, and 30 mM) were used, whereas the concentration of the other reagents were kept constant [DEKTP] = 5 mM, T = 120°C and [OH-TEMPO]/[DEKTP] = 6.5 mM. A temperature of 120°C was selected taking into account that at this temperature, the DEKTP decomposes preferentially through a sequential mechanism generating biradical species, which can initiate the styrene polymerization.[18] Nevertheless, DEKTP can decompose not only through a sequential mechanism but also following a total decomposition process, resulting in six radical species, so that a ratio of [OH-TEMPO]/[DEKTP] = 6.5 was selected to capped all the free radicals that can be formed from the decomposition of one DEKTP molecule. The excess of [OH-TEMPO] used was to trap the eventually thermal polystyril radicals formed at the temperatures used.

The experimental results for the different concentration of CSA used in the synthesis of PS oligomers are summarized in Table II. From the data in Table II, it can be noted that by increasing the amount of CSA, the molecular weight of the resulting oligomers and the values of monomer conversion are increased, for the same reaction time. This behavior can be explained in terms of a higher rate in the consumption of nitroxide molecules, as it was described by Georges et al.[12]

The higher PDI values with the lower concentration of CSA (3.9 mM), indicates that this concentration is not sufficient to suppress the thermal initiation of styrene, resulting in oligomers with similar molecular weight, molecular weight distribution, and monomer conversion as the series of reactions without CSA. Moreover, the thermal initiation of styrene generates more active free radicals during the reaction that could lead to irreversible termination reactions, broadening the molecular weight distribution and resulting in a poor control over the PDI of the polymer chains. On the contrary, a 10-fold increment in the CSA concentration (30 mM) reduces the PDI to 2 as a consequence of promoting certain control over the reversible termination reactions between the growing radical chains, resulting in higher molecular weights after 10 h of reaction.

Even though the control over the polymerization is poor at high polymerization times (~ 15 h), the

Summary of the Experimental Results of the PS Oligomers Obtained by Bulk Polymerization at 120°C with Different CSA Concentrations at Different Reaction Times ([DEKTP] = 5 mM and [OH-TEMPO]/[DEKTP] = 6.5)

[CSA] (mM)	Time (h)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	Conversion (%)
0	10	1902	6049	3.1	13.8
0	15	2683	10,146	3.7	25.6
0	20	3101	13,414	4.3	35.1
3.9	10	2105	7444	3.5	15.8
3.9	15	3072	12,166	3.9	25.7
3.9	20	2737	14,495	5.2	36.0
30	10	108,869	234,764	2.1	76.2
30	15	119,869	239,808	2.0	84.4
30	20	117,099	241,315	2.0	92.6

molecular weight of the polymer decreased when using [CSA] = 30 mM and/or presented no changes when using [CSA] = 0, 3.9 mM. In a parallel experiment, it was observed that during the first 10 h of polymerization (the data obtained are not included herein), the molecular weight of the polymer increases with time from 409 g/mol (1 h) to 66,200 g/mol (4 h), as a consequence of the presence of OH-TEMPO in the reaction, which shifts the equilibrium to the dormant species decreasing the bimolecular termination reactions.

Effect of the DEKTP concentration

Taking into account the results obtained using different concentrations of CSA, the concentration of 30 mM seems to be the most suitable to obtain PS oligomers at relatively short polymerization times ($\sim$ 1 h). It must be taken into account that at this shorter reaction times, the PS chains thermally produced are almost eliminated, because it required approximately 10 h to obtain a conversion value of 10% for the other two CSA concentrations. Nevertheless, with [CSA] = 30 mM, the molecular weights reported were higher than the ones pretended (M_n = 3000 g/mol or lower). To decrease the molecular weight of the PS chains, different concentrations of DEKTP were evaluated ([DEKTP] = 5, 10 mM), and the molecular weight distribution and conversion values were monitored. Because the control over the polymerization is lost after 10 h of reaction time for the system with 30 mM of CSA (as it can be observed from the values of M_n, Fig. 2), shorter polymerization times were used.

In Table III, the experimental values of molecular weight and conversion obtained by varying the concentration of DEKTP are reported. It must be pointed out that the concentration of OH-TEMPO was also varied to keep the ratio of [OH-TEMPO]/[DEKTP] = 6.5 constant. In Figure 3, the plots of ln [M_0]/[M] and M_n as a function of the reaction time

and monomer conversion are shown. From Figure 3, it can be observed that as the concentration of DEKTP increases, a presence of an induction period is noted, which can be interpreted as the time that is required to reach the equilibrium between the dormant and the active species before the polymerization can initiate. In the presence of lower concentrations of [DEKTP], this period is shortened or almost eliminated, as in the case of [DEKTP] = 5 mM. Nevertheless, after the induction period of 1 h with [DEKTP] = 10 mM, it seems that a better control over the propagation is attained, evidenced by lower values of PDI and a linear behavior of the plot of conversion as a function of reaction time, which indicates a better control over the reversible termination reactions. Moreover, the molecular weight plot presents a more linear behavior for the case of using a higher DEKTP concentration and the molecular weight values, as it has been expected within the range of 1000–3000 g/mol.

In the case of the reactions where lower concentration of DEKTP was used, higher molecular weight
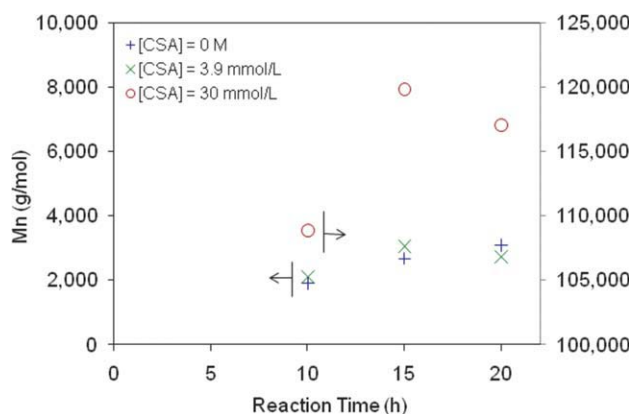
Figure 2 Evolution of molecular weight as a function of reaction time of the different PS oligomers synthesized with different concentration of CSA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

TABLE III
Summary of the Experimental Results of the PS Oligomers Obtained by Bulk
Polymerization at 120°C with Different DEKTP Concentrations at Different Reaction
Times ([CSA] = 30 mM and [OH-TEMPO]/[DEKTP] = 6.5)

[DEKTP] (mM)	Time (h)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	Conversion (%)
5	1	409	457	1.1	4.6
5	2	42,743	88,170	2.0	7.3
5	3	57,306	207,642	3.6	16.0
10	3	307	361	1.1	0.9
10	4	349	414	1.1	2.2
10	5	406	526	1.2	2.9
10	6	1043	1458	1.3	4.6

values were obtained (as expected) together with higher monomer conversion values. This behavior is not common for this type of polymerization, so that to have a better understanding of this unusual behavior, several reactions with different concentrations of DEKTP were prepared for a fixed reaction time of 10 h, using the synthesis conditions shown in Table IV.

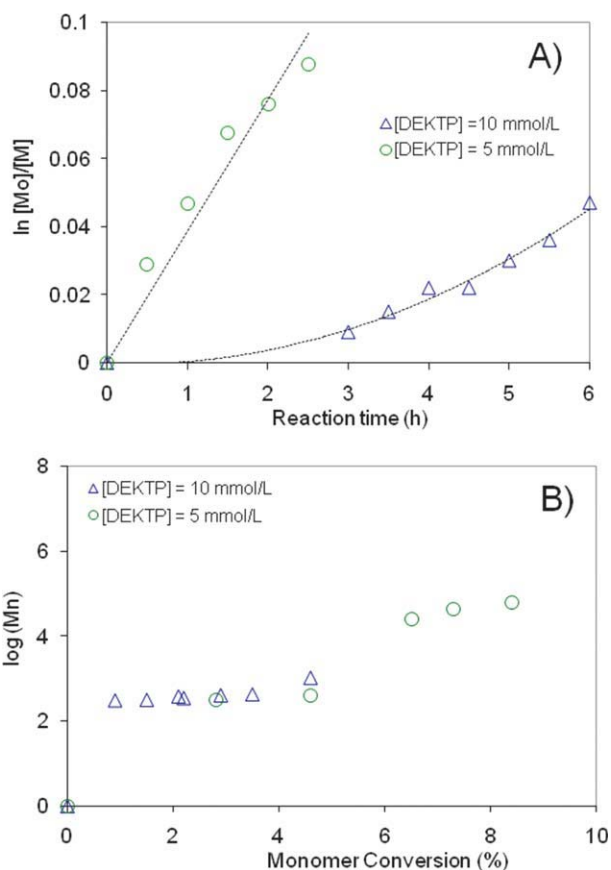The increase in monomer conversion and molecular weight as the DEKTP concentration decreases

Figure 3 Plot of (A) ln [M_o]/[M] with reaction time and (B) log (M_n) as a function of conversion for the PS oligomers synthesized with different concentration of DEKTP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

can be attributed in principle to the catalytic nature of the CSA. Because the amount of CSA used in all the cases was kept constant at 30 mM, the ratio of [CSA]/[DEKTP] differs for each case, being higher for [DEKTP] = 5 mM. In this sense, as the amount of CSA increases, an increase in the polymerization rate and in the PDI values is observed as a result of disproportionation reactions that can undergo the nitroxide in the presence of CSA.[13] This situation shifts the equilibrium between the dormant and the active species to the latter and thus the control over the polymerization is lost. In the same way, the time required to reach the equilibrium differs from one reaction to another, being increased as the ratio of CSA/DEKTP is decreased. It cannot be neglected that the presence of induced transfer reactions of the DEKTP can lead to a decrease, not only of the molecular weight, but also of the overall polymerization rate. The presence of such reactions is being studied in a parallel work.

Effect of the [OH-Tempo]/ [DEKTP] ratio

The ratio of [OH-TEMPO]/[DEKTP] is another variable that was manipulated in the synthesis of the PS oligomers to achieve better control over the polymerization, resulting in narrow molecular weight distributions.

Georges et al.[2] reported the use of a ratio of 1.2 when the radical initiator BPO and TEMPO were used in the synthesis of PS, giving a PDI value of 1.2. Because BPO can generate two free radicals as a result of the cleavage of the peroxidic group, it was believed that the amount of nitroxide molecules required to achieve control over the polymerization might be at least half of what is needed to end capped all the free radicals generated from the initiator.

In this study, DEKTP is used as the radical initiator, and it can generate, depending on the temperature range used, six free radicals per initiator molecule that are capable of initiating the polymerization of styrene, because it contains three peroxidic

[DEKTP] (mM)	[CSA]/[DEKTP]	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	Conversion (%)
5	6	41,960	158,039	3.7	88.2
10	3	6713	9256	1.3	15.9
15	2	715	1257	1.7	7.6
20	1.5	547	712	1.3	5.2

groups.[18] Different ratios of [OH-TEMPO]/[DEKTP] were used to attain lower PDI values and to achieve a better control over the polymerization.

In all the different reactions previously discussed, a ratio of [OH-TEMPO]/[DEKTP] = 6.5 mM was used, where this ratio was estimated by taking into account that the three peroxidic groups of the initiator could be susceptible to decomposition, resulting in six free radicals. At the same time, a small excess of OH-TEMPO was used to end capped the PS chains that were autoinitiated because of the high temperature used, even though CSA was used to suppress the thermal initiation of styrene. Because the ratio of [OH-TEMPO]/[DEKTP] can affect directly the rate of polymerization and the induction period in which the equilibrium between the active and dormant species is reached, several PS polymerizations were performed using the synthesis conditions shown in Table V.

From the data shown in Table VI, it is evident that the monomer conversion and the molecular weight decreased when the concentration of OH-TEMPO was increased. This effect is a consequence of a large number of free radicals susceptible of being end capped by nitroxide molecules, which prevents the formation of high–molecular weight polymer. A similar effect can be noted with the PDI values as the concentration of OH-TEMPO is increased, where all the active sites of the growing chains are end capped, resulting in a decrement of the PDI to 1.6.

When the ratios of 1.5 and 2.5 were used, higher conversion values ($\sim$ 98%) were achieved after 15 h, because all the free radicals generated on the DEKTP decomposition and/or the thermally produced PS chains cannot be end capped with nitroxide

molecules. This is the reason why the propagating species propagate as in a classic radical polymerization, achieving high conversion values and high molecular weights produced by means of bimolecular irreversible termination reactions leading, in this case, to a broad molecular weight distribution. Increasing the ratio of [OH-TEMPO]/[DEKTP] to 4.5, the molecular weight and the conversion values are decreased as a consequence of achieving better control over the addition of monomer units to the active sites, because most of them are end capped by nitroxides. The best results were obtained when a ratio of 6.5 mM was used, because the amount of OH-TEMPO used was sufficient to end capped all the active species, shifting the equilibrium toward the dormant state, decreasing the rate of polymerization and resulting in lower PDI values.

After it was established that a ratio [OH-TEMPO]/[DEKTP] of 4.5 and 6.5 resulted in a better control over the polymerization, a series of reactions were performed at lower reaction times, and the results are shown in Table VII.

In each series of polymerizations, the induction period differs with the OH-TEMPO concentration, from 3 h (ratio = 4.5) to 6 h (ratio = 6.5), because it required more time to reach the equilibrium between the active and the dormant species so that the addition of monomer units is delayed. During the induction time, a high concentration of free radicals is presented, which favors primary termination reactions that prevent the growing polymer chains to reach a higher degree of polymerization.

From Figure 4, it can be observed that when a [OH-TEMPO]/[DEKTP] ratio of 4.5 was used, the

TABLE V
Synthesis Conditions for the Synthesized PS Oligomers Using Different Ratios of [OH-TEMPO]/[DEKTP]

Reagents	Parameters
[CSA] (mM)	30
[DEKTP] (mM)	10
[OH-TEMPO]/[DEKTP]	1.5–2.5–4.5–6.5
Reaction time (h)	15
Temperature (°C)	120

TABLE VI
Experimental Results of the PS Oligomers Obtained by Bulk Polymerization at 120°C for 15 h with [CSA] = 30 mM and [DEKTP] = 10 Mm

[OH-TEMPO]/ [DEKTP]	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	Conversion (%)
1.5	90,094	261,315	2.9	98.6
2.5	135,130	328,409	2.4	98.0
4.5	21,745	41,688	1.9	38.1
6.5	4086	6610	1.6	14.5

TABLE VII
Experimental Results of PS Oligomers Obtained by Bulk Polymerization at 120°C with [CSA] = 30 mM and [DEKTP] = 10 Mm

[OH-TEMPO]/ [DEKTP]	Time (h)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	Conversion (%)
4.5	4	3604	7877	2.1	1.5
4.5	6	16,028	27,601	1.7	19.3
4.5	8	17,695	26,101	1.4	28.2
4.5	10	33,768	51,643	1.5	53.2
6.5	4	349	414	1.1	2.2
6.5	6	1043	1458	1.3	4.6
6.5	8	2104	2931	1.3	5.1
6.5	10	3284	4880	1.4	9.7

TABLE VIII
Experimental Results of the PS Oligomers Obtained by Bulk Polymerization at Different Reaction Times Using [CSA] = 30 mM, [DEKTP] = 10 mM, and [OH-TEMPO]/ [DEKTP] = 6.5

Temperature (°C)	Time (h)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	Conversion (%)
120	4	349	414	1.1	2.2
	6	1043	1458	1.3	4.6
	8	2104	2931	1.3	5.1
130	4	2553	3840	1.5	15.8
	6	5055	8999	1.7	25.4
	8	9131	14,380	1.5	34.6

plot does not adjust to a straight line as well as when a ratio of 6.5 is used. This suggests that the number of active radicals varies during the polymerization, which means that not all the free radicals produced are being end capped by nitroxide molecules, resulting in the presence of termination reactions. This behavior can also be attributed to undecomposed peroxidic groups within the polymer backbone, which can be cleaved during the polymer-

ization and generate new active sites, which in turn can initiate the styrene polymerization. In the case of a [OH-TEMPO]/[DEKTP] ratio of 6.5, the behavior adjust better to a straight line, indicating that the amount of OH-TEMPO is sufficient to end capped all the free radicals produced during the reaction, leading to a better control of the polymerization, although the monomer conversion values are relatively low at the polymerization times evaluated.

Effect of the temperature

All the reactions that have been discussed previously were conducted at 120°C, where the best results were the synthesis of PS oligomers with a PDI = 1.3 but low monomer conversion values (5% at 6 h). To increase the monomer conversion, several polymerizations were performed at a higher reaction temperature, 130°C, because at this temperature, the initiator can be decomposed through a combination of sequential and total decomposition pathways.[18] In Table VIII, the experimental results of these reactions and the comparison with the reactions conducted at 120°C are summarized.

The experimental data obtained for the reactions at 130°C evidenced higher molecular weights and conversion values in comparison with the reactions at 120°C. Because the reversible bond between the nitroxide and the free-growing radical (NO—C) is weakened as a consequence of an increase in the reaction temperature, the overall polymerization rate is increased allowing the addition of more monomer units to the active chain. On the other hand, the PDI values were increased in both cases, probably due to the presence of fewer initiator molecules that have not been decomposed. As the reaction takes place, new free radicals from the initiator can be generated following a sequential decomposition mechanism, resulting in polymers chains with higher molecular weight and higher PDI. To corroborate the sequential decomposition of DEKTP, which means undecomposed peroxidic O—O groups in the polymer backbone, the PS oligomers were characterized by NMR.
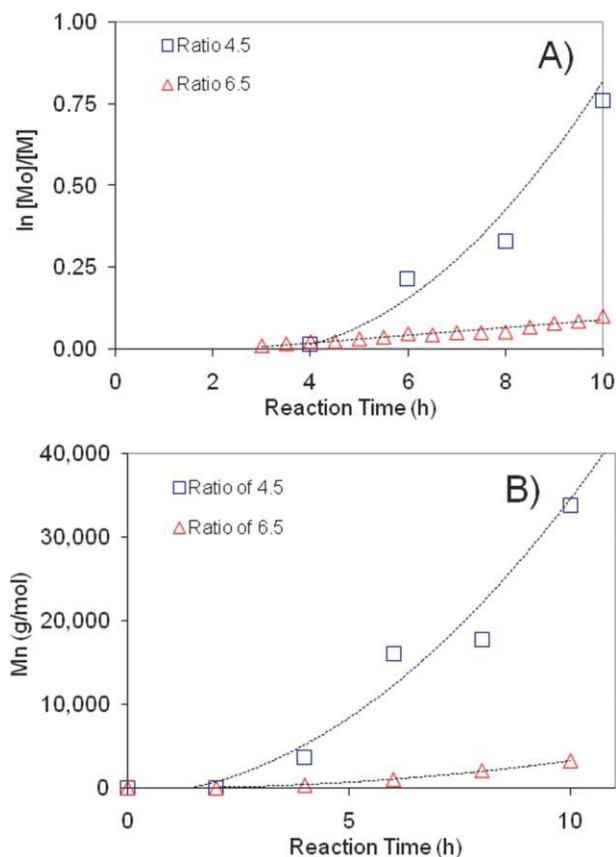
Figure 4 (A) ln $[M_o]/[M]$ and (B) M_n as a function of reaction time for the PS oligomers synthesized with different [OH-TEMPO]/[DEKTP] ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
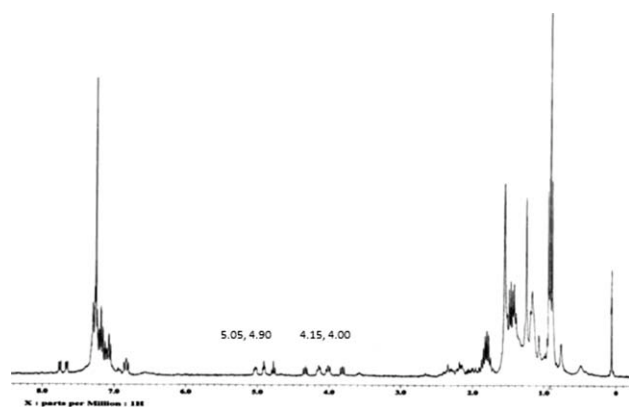
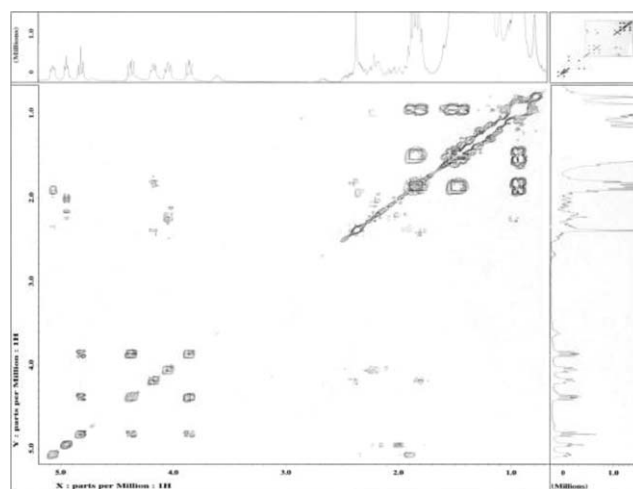**Figure 5** ^{1}HNMR spectra of the PS oligomers obtained, [DEKTP] = 10 mM, [CSA] = 30 mM, [OH-TEMPO]/[DEKTP] = 6.5 mM, T = 130°C, and reaction time = 2 h.

PS oligomers functionalized with peroxidic groups within the polymer chain

Once the reaction conditions at which it is feasible for the synthesis of PS oligomers with narrow molecular weight distributions and low molecular weights was established, the presence of peroxidic groups in the polymer chains, which are unreacted sites remaining from the initiator, was evaluated. The time at which all the O—O groups from the radical initiator (DEKTP) are almost completely decomposed cannot be higher than 8 h, because the half-life of this initiator at 120°C is 1 h.[18]

In the ^{1}H-NMR spectra (Fig. 5) of the PS oligomers obtained with the synthesis conditions of DEKTP = 10 mM, CSA = 30 mM, [OH-TEMPO]/[DEKTP] = 6.5 mM, T = 130°C, and reaction time of 2 h, different backbone structures could be identified. These systems are independent because it can be observed from the corresponding COSY NMR (Correlation spectroscopy) correlation (Fig. 6). On the other hand, two of these systems are associated with species that are connected to heteroatoms and one of them is associated to a symmetric species (Fig. 7) that has been labeled as symmetric, because it presents an identical structure in both sides of the O. radicals, which have equal reactivity and were obtained as a consequence of the total initiator decomposition or as a product of the homolytical cleavage of a peroxide bond of this molecule.

However, the amount of these products obtained at the temperature evaluated (130°C) was not quantitative, and it was not possible to isolate them for characterization to determine the —CH$_3$:—CH ratio from the corresponding attached initiator fragment and monomer, which would correspond to the biradical produced from the total cleavage of the initiator (3 : 1) or to the fragment obtained through the unimolecular cleavage (9 : 1).

Figure 6 COSY spectra for the PS oligomers obtained. [DEKTP] = 10 mM, [CSA] = 30 mM, [OH-TEMPO]/[DEKTP] = 6.5 mM, T = 130°C, and reaction time = 2 h.

^{1}H COSY NMR correlation NMR spectra was used to demonstrate the presence of the symmetric species, which represent the unimolecular homolytic cleavage of the initiator molecule during the preparation of styrene oligomers.

From ^{1}H COSY NMR spectrum (Fig. 6), it can be observed that the presence of diastereotopic protons, signals at δ = 5.05 and 4.90 ppm (m), corresponding to the proton next to the oxygen atom of the nitroxyl fraction, which displays a broad signal because it is related to a quiral carbon atom. On the other hand, it can also be noted from the same figure, that the correlation between diastereotopic proton and the methylene group from the first styrene molecule, which must be located in the complex signals shown
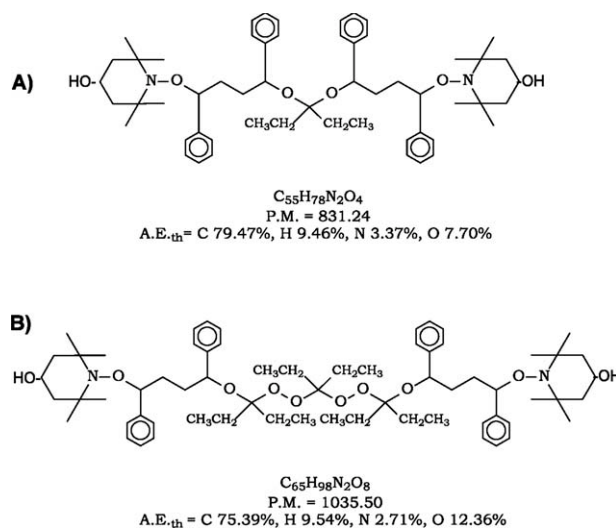
Figure 7 Symmetric products: (A) total dissociation and (B) unimolecular cleavage of the initiator molecule obtained in the PS oligomer synthesis using the TPDEC/TEMPO/CSA system.
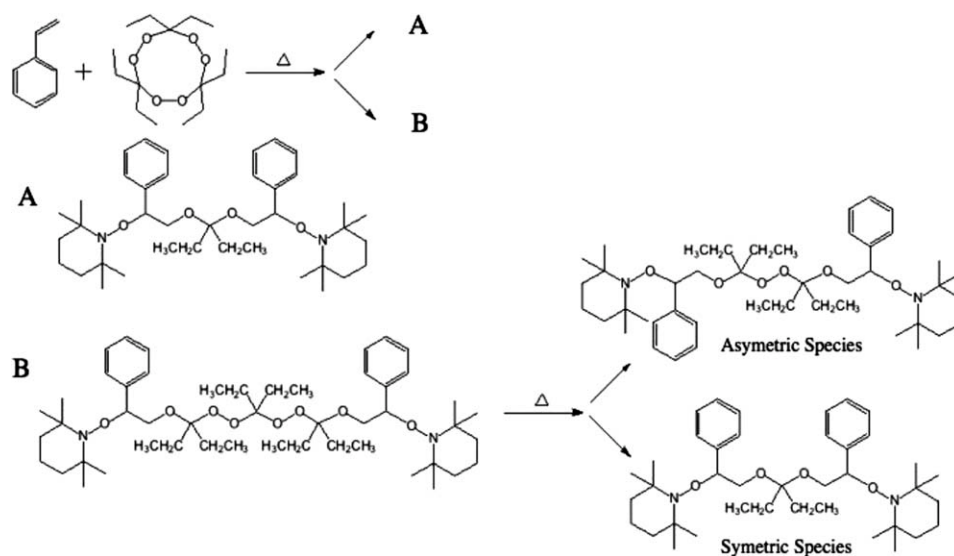
Figure 8 Route for the proposed sequential decomposition of DEKTP initiator: generation of asymmetric species with no peroxide remnant groups and symmetric species with at least one peroxide group remaining in the polymer chain.[18]

between 1.7 and 2.5 ppm. Similar situation is shown by the diasterotopic proton at δ = 4.15 and 4.0 ppm, which also exhibits correlation with methylene protons from the styrene fraction on the other side of the polymer chain. The additional signals located between 3.8 and 5.0 ppm can be attributed to the proton of the carbon atom bearing the hydroxyl group of the hydroxy-TEMPO molecule. The symmetrical products describe herein agree with that proposed by Cerna et al.,[18] in the proposed sequential decomposition route of DEKTP initiator shown in Figure 8.

CONCLUSIONS

PS oligomers with low molecular weight and containing peroxidic groups in their inner structure were synthesized using a novel cyclic radical initiator (DEKTP) by NMRP, in the presence of OH-TEMPO. The concentration of CSA presented an important role during the polymerization, because CSA can increase the rate of polymerization while broadening the molecular weight distribution. A [OH-TEMPO]/[DEKTP] ratio of 6.5 proved to be the most efficient among the different ratios evaluated, resulting in the lowest PDI values with an induction time of 3 h. On the other hand, reducing the concentration of OH-TEMPO resulted in an induction time of 1 h, but the control over the polymerization was lost. The sequential decomposition of the initiator DEKTP was corroborated by NMR characterization of the PS oligomers. By means of COSY, the existence of symmetrical species was confirmed.

References

1. Matyjaszewsky, K.; Xia, J. Chem Rev 2001, 101, 2921.
2. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 2987.
3. Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Pat. 4,581,429 (1986).
4. Gaynor, S.; Greszta, D.; Shigemoto, T.; Mardare, D.; Matyjaszewski, K. Polym Prepr 1994, 35, 585.
5. Hawker, C.; Bosman, A.; Harth, E. Chem Rev 2001, 101, 3661.
6. Cunningham, M. F.; Tortosa, K.; Lin, M.; Keoshkerian, B.; Georges, M. K. J Polym Sci Part A: Polym Chem 2002, 40, 2828.
7. Georges, M. K.; Odell, R. P.; Veregin, R. P. N.; Keoshkerian, B. Polym Prepr 1997, 38, 721.
8. Flory, J. P. J Org Chem 1937, 59, 247.
9. Mayo, F. J Org Chem 1953, 75, 6133.
10. Buzanowski, W. C.; Graham, J. D.; Priddy, D. B.; Shero, E. Polymer 1992, 33, 14.
11. Georges, M. K.; Kee, R. A.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. J Phys Org Chem 1995, 8, 301.
12. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. Macromolecules 1994, 27, 7228.
13. Veregin, R. P. N.; Odell, P. G.; Michalak, L.; Georges, M. K. Macromolecules 1996, 29, 4161.
14. Greszta, D.; Matyjaszewski, K. Macromolecules 1996, 29, 7661.
15. Villalobos, M. A.; Hamielec, A. E.; Wood, P. E. J Appl Polym Sci 1991, 42, 629.
16. Meijer, J. US Patent 1990, No. 5,932,660.
17. Yoon, W. J.; Choi, K. J. J Appl Polym Sci 1992, 46, 1353.
18. Cerna, J.; Morales, G.; Eyler, G. N.; Cañizo, A. I. J Appl Polym Sci 2002, 83, 1.
19. Mateo, C. M.; Eyler, G. N.; Alvarez, E. E.; Cañizo, A. I. Información Tecnológica 1998, 9, 19.
20. Eyler, G. N.; Cañizo, A. I.; Alvarez, E. E.; Cafferata, L. F. R. Tetrahedron Lett 1993, 34, 1745.