Application of a New Unimolecular Initiator in the Synthesis of (α,ω) Ketone Functionalized Polystyrene in Nitroxide Mediated Polymerization

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ABSTRACT: The ketone functionalized *N*-alkoxyamine, a derivative of 4-oxo-2,2,6,6-tetramethylpiperidin-1-oxyl (4-oxo-TEMPO) was synthesized and applied as an initiator in the nitroxide mediated polymerization of styrene in bulk at 120°C. In the presence of the prepared initiator: 1-phenyl-1-(4-oxo-2,2,6,6-tetramethylpiperidinoxy)propanone polymers with well-defined molecular weight were obtained. By contrast, when an accelerator such as acetic anhydride (10%) was added to the system, lower control of polymerization was observed. Additionally, the functionality of polymers was evaluated on the basis of a quantitative investigation of UV–visible spectra of 2,4-dinitrophenylhydrazone formed from the polymers and the synthesized initiator. The UV–vis spectra of the hydrazone derivatives obtained from polymers by means of 2,4-dinitrophenylhydrazone made it possible to confirm that the polymers prepared in the presence of the ketone functionalized *N*-alkoxyamine retain the ketone functionality on the polymer chain. The functionality for the obtained polymers exceeded 1 significantly. The obtained (α, ω) telechelic polymers are of great importance in the synthesis of new biohybrid materials such as bioconjugates with proteins or peptides as well as new polymer nanostructures. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000:000–000, 2012

INTRODUCTION

The preparation of well-defined polymer nanostructures requires new synthetic methods in order to introduce reactive groups into polymer chains. Living anionic and cationic polymerization are attractive methods to use in the synthesis of end functionalized polymers and (α, ω) difunctionalized polymers (telechelic polymers) with well-defined structures characterized by well-defined and narrow distributions of the molecular weights.[1–4] However, the living anionic (cationic) polymerization has some drawbacks connected with the tolerance of functional groups as well as the reaction conditions. Hence, the living/controlled free radical polymerization is potentially a more powerful process in comparison with ionic polymerization. The wide range of monomers, which undergo living/controlled free radical polymerization in relatively mild experimental conditions that makes this method extremely advantageous.[5]

Nitroxide-mediated radical polymerization (NMRP)[6–13] has become an increasingly common method of controlled free radical polymerization because it enables to synthesize functionalized polymers with narrow distribution of the molecular weight. The

polymer chains, obtained in the NMRP process using alkoxyamine as an initiator,[11,13–17] are capped by the nitroxyl radical from one side, and by the initiating radical derived from alkoxyamine molecules from the other. Hence, the addition of functionalized alkoxyamine to the reacting system allows to synthesize (α, ω) telechelic polymers with a wide range of functional groups. For instance, the functionalized alkoxyamines with carbonyl groups are very promising for the synthesis of biohybrid materials because of their ability to react under mild conditions with peptide and protein molecules containing the amine groups during reductive amination. Additionally, the presence of a reactive carbonyl group in the polymer chain opens up the possibility of modifying the polymer chain by means of many chemoselective reactions.[18] Braslau and coworkers[17] described the synthesis of the ketone functionalized alkoxyamines in the nitroxide part of the molecule and evaluated the new compounds as initiators in NMRP. The formation of the ketone derivative at the nitroxide part of the prepared polymers was confirmed in the reaction with 2,4-dinitrophenylhydrazine (DNPH). Gigmes et al.[18] described the preparation of ketone-terminated polystyrene coupled with DNPH using NMRP.
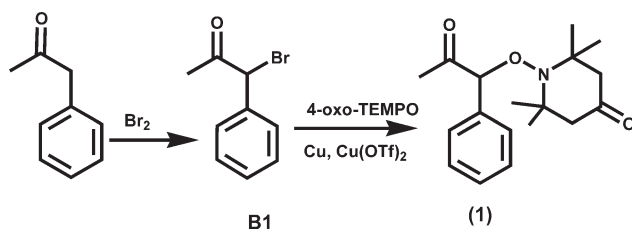
Scheme 1. The scheme of synthesis of initiator (**1**).

Alkoxyamine (**1**) is a derivative of 4-oxo-TEMPO nitroxide radical, which has already been successfully used in the controlled polymerization of styrene initiated by means of benzoyl peroxide (BPO) as reported by Schmidt-Naake and Baumann[19] They observed that the use of 4-oxo-TEMPO instead of TEMPO results in the shortening of the induction period and simultaneously increases the conversion of the system. Higher conversions reported for the systems containing 4-oxo-TEMPO under the same reaction conditions were associated with the lower enthalpy of dissociation of the bond between 4-oxo-TEMPO and the growing radical, and can be attributed to thermal decomposition of 4-oxo-TEMPO. However, latest investigations demonstrated that the ketone group in position 4 in the piperidine ring does not affect the stability of the C-ON bond.[20] Thus, the differences between the polymerization of styrene in the presence of TEMPO and 4-oxo-TEMPO cannot be explained on the basis of the differences in the stability of adducts formed between TEMPO (4-oxo-TEMPO) and the growing chain radical.

This article presents the synthesis of the ketone functionalized alkoxyamine in nitroxide and the alkyl fragment of the molecule, and the use of alkoxyamine in the preparation of (α, ω) functionalized polystyrene in control fashion at 120°C. Earlier study in my laboratory revealed that the investigated alkoxyamine has a very short half-time of homolysis of the C—ON bond at 120°C[20] and because of that such an alkoxyamine can be used to provide the initiating radicals and the mediator in the first seconds of polymerization.

EXPERIMENTAL

Materials
4-Oxo-TEMPO was synthesized according to the procedure described in the Ref. 21 from 2,2,6,6-tetramethyl-4-piperidone (95%, Aldrich), mp = 32–35°C (lit. 33–35°C[20]), copper powder (99.5%, Aldrich), 4,4'-di-*tert*-butyl-2,2'-dipyridyl–ditbdpy (98%, Aldrich), copper(II) trifluoromethanesulfonate-Cu(OTF)$_2$ (98%, Aldrich), phenylacetone (99%, Aldrich) were used without further purification. Styrene was purified according to the common procedures and was distilled under reduced pressure over calcium hydride before use. Acetic anhydride was heated with CH$_3$COONa for 2 h and was subsequently distilled in dry oxygen-free argon atmosphere.

Synthesis
Scheme 1 illustrates the particular steps of the synthesis of alkoxyamine (**1**).

The alkoxyamine was synthesized according to the procedure described by Matyjaszewski et al.[22] from the corresponding bromine derivative.

1-Bromo-1-phenyl-2-propanone (B1). Bromine Br$_2$ (8 g, 0.05 mol, 1 equiv.) dissolved in 33 cm^3 glacial acetic acid was added dropwise during a period of 30 min into the mixture of phenylacetone (6.71 g, 0.05 mol) dissolved in 33 cm^3 glacial acetic acid. The mixture was stirred and cooled in an ice bath and then the temperature was allowed to rise until 20°C. The reaction was carried out in the dark. During the addition of bromine the reaction mixture changed its color from cloudy to clear orange-red. When the addition of bromine was completed, a rapid stream of argon was passed through the solution to remove the residues of the fumes of hydrogen bromide. Subsequently, the mixture was washed with NaHCO$_3$(aq) until CO$_2$ stopped evolving. The organic layer was dried over Na$_2$SO$_4$ for 3 h under argon atmosphere and the product (bright green oil) was immediately used as a reagent for the further reaction without any purification. This bright green oil (the product) is extremely reactive and because of that it should be stored in an oxygen-free atmosphere (change of color to emerald green or black was observed after a period of 2 weeks in the presence of atmospheric oxygen). Refractive index B1: n_D^{20} = 1.570 (lit. n_D^{23} = 1.560[23]); ^{1}H NMR spectrum (200 MHz, CDCl$_3$) was in an excellent agreement with the literature data.[23]

1-Phenyl-1-(4-oxo-2,2,6,6-tetramethylpiperidinoxy)propanone (1). The compound (**1**) was obtained in the reaction carried out for 24 h at 60°C. The crude product was purified by column chromatography: adsorbent: Al$_2$O$_3$ (neutral, activity I), eluent: cyclohexane/ethyl acetate (1/1). The product was a yellow oil (yield 30%) from which a white precipitate was formed in a freezer. The obtained white solid was in turn recrystallized from methanol and white crystals, mp. 81.5–83°C were collected.

^{1}H NMR(500 MHz, CDCl$_3$): δ 0.82 (bs, 3H); 1.16 (bs, 3H); 1.25 (bs, 3H); 1.30 (bs, 3H); 2.16 (s, 3H); 2.1–2.23 (m, 2H); 2.48–2.66 (m, 2H); 5.24 (s, 1H); 7.37–7.40 (m, 5H).

^{13}C NMR (125 MHz, CDCl$_3$): δ: 207.67; 206.40; 137.33; 128.98; 128.519; 127.01; 96.22; 63.23; 53.84; 33.61; 33.18; 25.52; 22.11.

MS with m/z by electrospray TOF-MS ES + with Na$^+$ observed 326.2 and calculated 326.2.

Polystyrene Synthesis. Polymerizations of styrene (according to Scheme 2) in the presence of the initiator (**1**) applied in a molar ratio 300 : 1 (concentration of the dissolved initiator 32 mmol/dm^3) were carried out in bulk at 120°C in glass ampules degassed by pump-freeze-thaw cycles repeated three times and sealed under dry oxygen-free argon. The ampules were then immersed in an oil bath preheated to 120°C. For kinetic analyses, the samples were removed from the oil bath after scheduled time and cooled in ice-cold water. The content of the ampules was dissolved in THF at room temperature and precipitated by the addition of chilled methanol. The precipitated polymers were dried at 40°C under reduced pressure to constant mass to afford polymers in the form of white powder. The monomer conversions were determined gravimetrically.

Molecular Weight Determination and Distribution
The experimental molecular weights were determined by means of size exclusion chromatography (SEC) using polystyrene standards and the SEC Instrument LabAlliance equipment, a
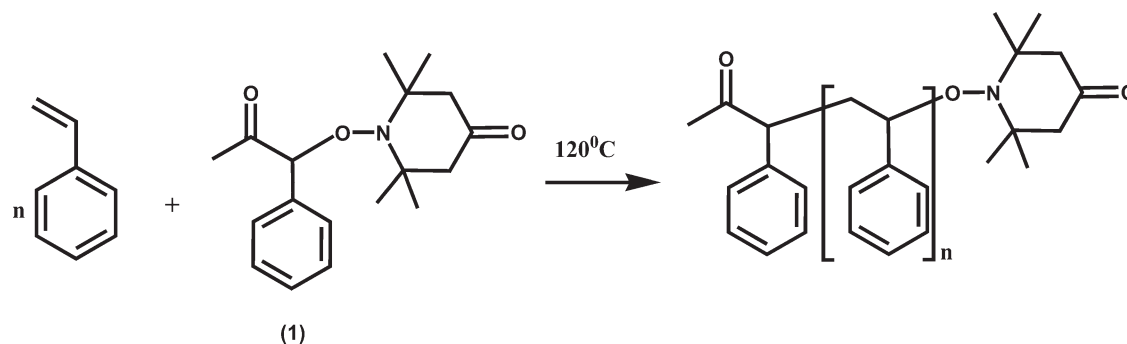
Scheme 2. The scheme of synthesis of ketone functionalized polystyrene.

Jordi Gel DVB Mixed Bed SEC Column (250 × 10 mm²), a DRI detector and Agilent DAD VL+ 1260 detector (35°C), eluent CHCl₃, 1 mL/min.

2,4-Dinitrophenylhydrazone Synthesis and UV–Vis Studies. The synthesis of the ketone derivatives in the reaction with DNPH leading to appropriate hydrazones is well studied and straightforward.[24] Dinitrophenylhydrazones have intense molar absorptivities and because of that a quantitative analysis of the functionalized polymers can be performed by means of UV spectroscopy.

The Synthesis of the Hydrazone Derivative of the Initiator (1). A solution of 8 mg of (1) dissolved in 1 mL of ethanol was added to 0.6 mL of DNPH solution (2.145 g of DNPH dissolved in 7.5 mL of H₂SO₄, 10 mL H₂O, 35 mL ethanol). The yellow crystals were collected after 10 min and washed twice with chilled methanol, mp = 119–121.5°C, IR (in KBr 1 : 300): 3431, 3423, 1618, 1594, 1518, 1425, 1338, 1313 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): 11.2, 11.0 (1H s N—NH), 9.13 (1H, m, Ar—H, meta NH, ortho dinitro), 8.98 (1H, d, Ar—H, meta NH, ortho nitro J = 10 Hz), 7.99, 7.97 (1 H, m, Ar—H, ortho NH), 7.37–7.40 (m, 5H, Ar), 5.64 (1H, s, CH—Ar); 2.15–2.19 (m, 2H); 1.67 (bs, 2H), 1.26, 1.24, 1.23,1.22 (methyl groups in piperidine).

The Synthesis of the Hydrazone Derivative of Polymers
A solution of the polymer (10 mg dissolved in 20 cm³ tetrahydrofurane) with 0.160 g of trichloric acid and 11 mg DTNPH

was stirred at room temperature for 24 h. After that the polymer was isolated from the reaction mixture by means of the addition of chilled methanol and subsequent filtration. The obtained product was dried at 40°C until it attained constant weight. Finally, the hydrazone derivative of the polymer was obtained as a yellow powder.

The UV–visible absorption spectra for the synesized derivatives were recorded on a Cary 50 Varian spectrophotometer.

RESULTS AND DISCUSSION

The compound (1) was successfully employed as a unimolecular initiator in a series of polymerizations of styrene. Selected samples of the prepared polymers were analyzed by means of SEC method. The characteristics of the selected polymers obtained from SEC measurements are presented in Table I, whereas SEC chromatograms for these samples are presented in Figure 1. The obtained molecular weight distributions are narrow and polydispersity indexes are below 1.3. The results reveal that the molecular weight distribution is very narrow for the short time of polymerization (P1 and P2). However, if the time of polymerization is longer, the weight distribution broadens on the side of high molecular weights. Such an observation can be explained as a consequence of the increase of contribution of the autopolymerization process. Hawker and coworkers[25] found that the addition of acylating agents such as acetic anhydride during the polymerization of styrene mediated by TEMPO

Table I. Time of Polymerization (t), Average Molecular Weight Number and Weight (M_n), (M_w) and Polydispersities Index PDI from SEC Analyses, Percent of Conversion (% conv), Average Number of C=O Group for the One Polymer Chain from UV–Vis Measurements (DF) for the Chosen Probes of Polystyrenes Obtained in Polymerization with (1) as Unimolecular Initiator (32 mmol/L) P1–P5 and with Addition of Acetic Anhydride as Accelerator (PA), Theoretical Targeted Molecular Weight M_n = 27.1 × 10³ (Da) for 100% of Conversion

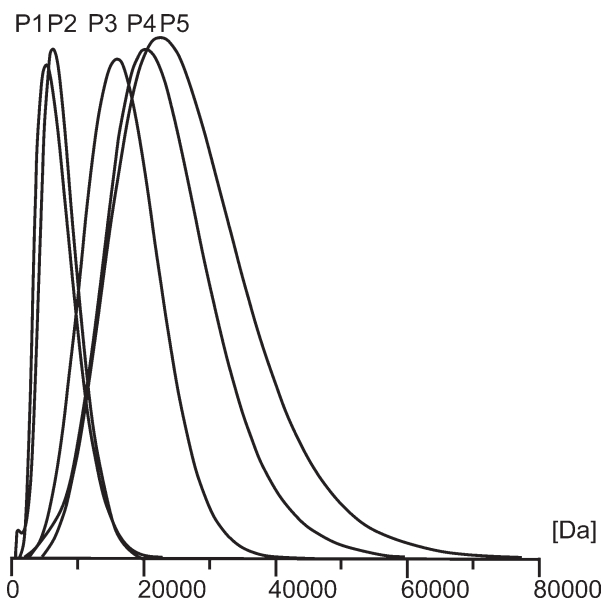| Polystyrene	t (h)	$\bar{M}_n \times 10^3$ (Da)	$\bar{M}_w \times 10^3$ (Da)	PDI	% Conv.	DF
P1	1	4.51	5.65	1.15	7.60	1.98
P2	3	5.86	6.79	1.16	21.6	1.50
P3	4	11.8	15.0	1.20	32.9	1.40
P4	24	16.8	20.3	1.20	80.9	1.20
P5	24.5	19.1	23.0	1.22	91.9	1.20
PA2	2	9.22	15.8	1.46	32.1	0.59
PA4	4	16.1	23.5	1.71	60.3	0.18

Figure 1. The weight distribution curves for polymerization of styrene with (**1**) as unimolecular initiator (molar ratio 300 : 1) at 120°C obtained from size exclusive chromatography analyses. Time of polymerization and % of conversion are shown in Table I.

results in a significant acceleration of the polymerization rate and leads to greater control of the polymerization process. Such a phenomenon is attributed to autopolymerization, which is lower when the reaction time is shortened. In consequence the additive, i.e., 10% (wt) of acetic anhydride to the polymerization system was used. Figure 2 presents the obtained plots depicting time versus conversion. For both systems, either without the acetic anhydride additive or containing the acetic anhydride, an excellent linear relationship between conversion and time was obtained for the conversions of polymerization below 80%. In this range a linear relationship between $\ln([M]_0/[M])$ and the reaction time can be observed (Figure 3), which indicates that the polymerization process follows the first-order kinetics with respect to the monomer and the radical concentra-
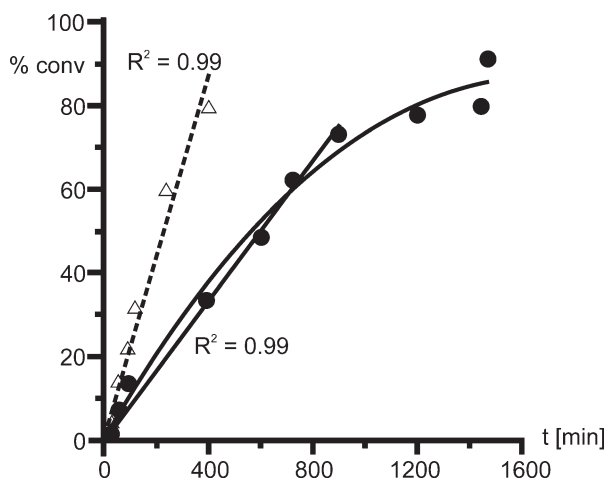

Figure 3. Kinetics of polymerization in the range 0–60% monomer conversion: $\ln[M_0/M]$ versus reaction time [circf] without acetic anhydride, [trio] with 10% (v/v) additive of acetic anhydride.

tion remained constant. For a higher degree of polymerization above 80% the rate of polymerization decreases because the monomer concentration decreases and simultaneously irreversible termination reactions occur to a greater extent and control of the polymerization is significantly lower. Figure 4 illustrates dependence of molecular weight experimental (Mn from SEC) and theoretical (Mn, theor) expected on the basis of molar ratio of styrene to the initiator (**1**) on conversion. For a lower degree of polymerization theoretical and experimental molecular weights are close but at higher degree of polymerization experimental molecular weights are significantly lower in comparison with theoretical because auto-initiation processes occur to a greater extent.

The addition of acetic anhydride to studied polymerization system increased the conversion from 5 to 13%/h. However, molecular weight distribution for polymers obtained after the addition of acetic anhydride is significantly broader (Figure 5) and

Figure 2. Kinetics of polymerization: monomer conversion versus reaction time: [circf] without acetic anhydride, [trio] with 10% weight of acetic anhydride.
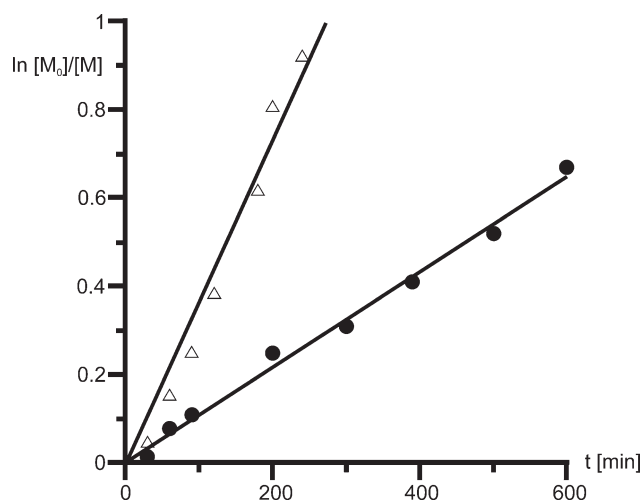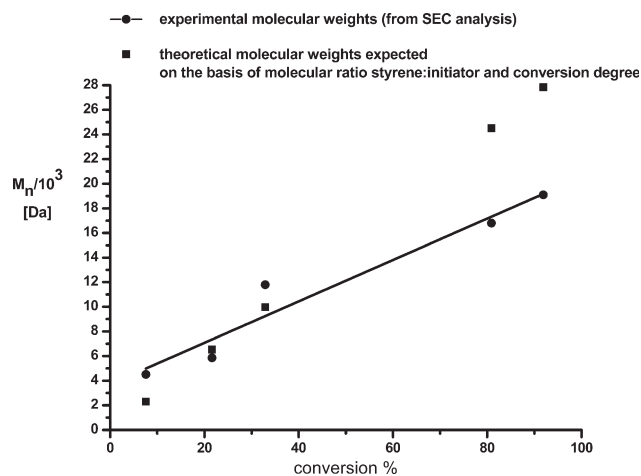

Figure 4. The dependence between conversion and experimental molecular weight (M_n from SEC) and theoretical ($M_{n,}$ theor) expected on the basis of molar ratio of styrene to the initiator (**1**).
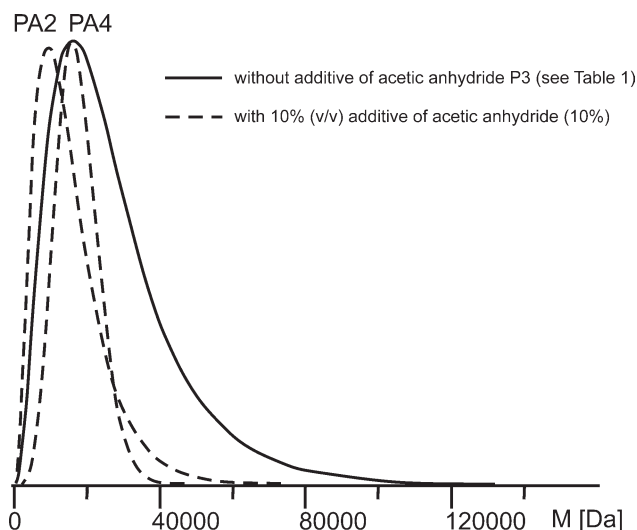
Figure 5. The weight distribution curves for polymerization of styrene with (**1**) as unimolecular initiator without the addition of acetic anhydride and with the addition of 10% (v/v) acetic anhydride obtained from SEC analyses. Time of polymerization and % of conversion are shown in Table I.

polydispersity indexes are above 1.5 (Table I). Hence, the control of the polymerization in a system containing acetic anhydride is lower.

Han et al.[26] described the polymerization of styrene initiated by BPO in the presence of 4-oxo-TEMPO at 135°C in bulk. The obtained polydispersity indexes were higher than those reported in this article, so in the investigated system better control of the polymerization reaction is provided.

The aim of this work was to obtain (α, ω) telechelic polystyrene in a control fashion. The presence of the carbonyl groups in polymer chains was confirmed by the synthesis of hydrazone means of DNPH. Initially, a model compound was prepared by the formation of 2,4-dinitrophenylhydrazone with the initiator (**1**) by the conventional method. FTIR spectra were recorded for the initiator and the hydrazone of the initiator. The IR spectra of the hydrazone initiator reveal the presence of characteristic bands (1518, 1338 cm^{-1} for N=O in NO$_2$ 1618 cm^{-1} for C=N) and the absence of characteristic and very strong bonds
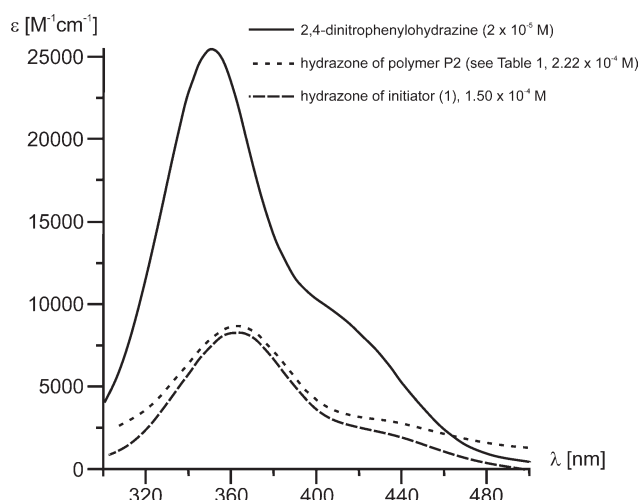

Figure 6. Absorption spectra of 2,4-dinitrophenylhydrazine, selected hydrazone of the polymer (see Table I) and hydrazone of the initiator (**1**) in tetrahydrofuran solutions.

for both carbonyl groups. Additionally, NMR spectra confirm that both carbonyl groups in the initiator molecules undergo a reaction with DNPH. The hydrazones of the polymers were prepared according to the procedure described earlier. Absorption spectra of DNPH, selected hydrazone of the polymer and hydrazone of the initiator (**1**) are presented in Figure 6. Because the hydrazone chromophores are the same in the hydrazone formed from the initiator (**1**) and hydrazones formed from polymers, so their molar extinction coefficients are very similar (see Figure 6). Hence, the calibration curve (the relationship between concentration and absorption at 363 nm) was prepared for the hydrazone of the initiator and used for determination of the concentration of chromophores in the solution of hydrazone of polymers.

The degree of functionalization was calculated next according to the equation:

$$DF = \frac{N_{C>O}}{N_{polym}} \qquad (1)$$

where $_{DF}$ is the degree of functionalization; $N_{C>O}$ is the number of carbonyl groups responsible for the respective absorbance

Table II. The Comparison of Results of SEC–RI and SEC–UV Analyses: Average Molecular Weight Number and Weight (Mn), (Mw) and Polydispersity Index PDI for Polystyrenes P1 and P2 (See Table 1) and Their Hydrazones HP1, HP2, Respectively, Polystyrenes Obtained in Polymerization Process with Acetic Anhydride Addition PA2, PA4 (See Table 1) and Their Hydrazones: HPA2, HPA4, respectively

	P1	HP1	P2	HP2	PA2	HPA2	PA4	HPA4
				PDI				
SEC-RI	1.15	1.16	1.16	1.15	1.46	1.46	1.71	1.73
SEC-UV (363 nm)		1.16		1.14		1.32		1.43
SEC-UV (420 nm)		1.16		1.15		1.33		1.45
				$M_n/M_w \times 10^3$ Da				
SEC-RI	4.51/5.65	4.51/5.65	5.86/6.79	5.86/6.73	9.22/15.8	9.22/15.8	16.1/23.5	17.5/24.1
SEC-UV (363 nm)		4.93/5.72		6.53/7.44		9.13/12.07		14.65/21.0
SEC-UV (420 nm)		4.93/5.72		6.53/7.44		9.07/12.07		14.42/21.0

determined on the basis of concentration of chromophores in the hydrazone solution; and N_{polym} is the number of polymer chains calculated from the number average molar mass (from SEC measurements) and the amount of the hydrazone of polymer in the solution.

The calculated degrees of functionalization of the ketone group DF are shown in Table I. The degree of functionalization exceeds 1, which corresponds to the amount of the carbonyl group that exceeds 1 per one chain. However, for the long-time polymerization the decrease of the parameter can be observed, being close to 1 when the conversion rate attains 80%. It has been reported in the literature that 4-oxoTEMPO undergoes thermal decomposition and forms compounds without the carbonyl group.[27,28] As a result the long-time polymerization minimizes the chance of (α, ω) ketone functionalized polystyrene to synthesize with 4-oxo-TEMPO derivatives. The mechanism of thermal decomposition of 4-oxo-TEMPO was proposed in the Ref. 27.

Additionally, the formation of well-defined functionalized polystyrenes has been confirmed by SEC-RI-UV analysis. Table II presents the comparison of the results of SEC analysis of polymers with the help of RI- and UV-detector after treatment with DNPH. SEC chromatograms for hydrazones of polystyrenes were recorded at 363 nm (maximum absorbance) and also at 420 nm. These measurements confirmed the complete removal of the excess of DNPH during the purification process. For polymers P1 and P2 polydispersity indexes obtained from SEC-RI and SEC-UV are very similar although the average molecular weights obtained from SEC-UV are slightly higher. This indicates that the functionalization is homogenous for these polymers and longer chains are functionalized in the greater degree.

The presence of acetic anhydride in the polymerization system caused a lower control and a significant decrease of the degree of functionalization (see PA1 and PA2 in Table I). Possibly, the increase in the conversion rate from 5 to 13%/h, results in a major contribution of polymer chains in the termination processes. This is in line with the results described by Guillaneuf and coworkers.[29] They observed an increase of the kinetic and loss of control of TEMPO mediated styrene polymerization and proposed that this should be due to a dipole-dipole interaction.

The significant decrease of the degree of functionalization (below one) for polymers obtained in polymerization process in the presence of acetic anhydride can be explained by heterogeneity of polymer chains. For polymers PA2 and PA4 results from SEC-UV and SEC-RI are significantly different (see Table II). The polydispersity indexes obtained from SEC-UV are lower because significant part of polymer chains does not contain the chromophores, mainly those with higher molecular weights, so average molecular weights obtained from SEC–UV are lower in comparison with obtained from SEC–RI analysis.

CONCLUSION

The ketone functionalized *N*-alkoxyamine was synthesized and examined as a new initiator for the nitroxide mediated polymerization of styrene. The results of polymerizations carried out in the presence of the synthesized initiator indicate that good control of the polymerization was achieved. The presence of carbonyl groups in polymer chains was demonstrated by derivatization of polymers by means of DNPH. Quantitative analysis of the functionalized derivatives was performed by measuring the absorptivity of the hydrazone of polymers and the hydrazone of the synthesized initiator. The number of (α, ω) functionalized chains in the obtained polystyrenes were equal to 95% if the value of conversion rate was less than 20%. For other samples the degrees of functionalization were smaller but still exceeded 1 per one polymer chain.

The presence of acetic anhydride in the polymerization system caused an increase in conversion rate from 5 to 13%/h, which immediately resulted in lower control of polymerization and a significant decrease of the degree of ketone functionalization.

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