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Nitroxide-mediated Living Radical Polymerization of Styrene with Fluorescent Initiator

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A fluorescence method was used for determination of marked chain ends in polystyrene samples prepared by 4-substituted TEMPO type nitroxide-mediated living free radical polymerization of styrene. 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)-piperidin-4-yl-4-pyren-1-ylbutanoate (PYNOR) was prepared and used as an unimolecular initiator bearing pyrene as a fluorescence mark on mediating nitroxide fragment. The bulk polymerization of styrene at 120°C, in the presence of new unimolecular initiator, was a typical nitroxide mediated living radical polymerization. For comparison, two different molar ratios of initiator and monomer (1:400 and 1:1000 initiator - monomer [I:M]) were used for polymerization. When I:M = 1:400, the obtained polydispersity was 1.12 and maximum molecular weight 27,000 g/mol was obtained at 62% conversion. For ratio 1:1000, slightly higher polydispersity was obtained −1.26 and the molecular weight was 53,000 g/mol at 70% conversion. The content of the polystyrene chains bearing mediating nitroxide fragment was determined by fluorescence spectroscopy. The intensity of pyrene fluorescence decreased as the molar mass, and the conversion increased as well. The extent of the incorporation of chromophore at propagating chain end or "livingness" of polymerization decreased despite the fact that the polydispersity did not change. The extent of side reaction leading to broadening of polydispersity is suppressed due to the high viscosity of the system at higher conversion. A low extent of "livingness" will have a very negative effect on possible preparation of block copolymers.

Keywords: nitroxyl mediated radical polymerization; fluorescence probe; end-capped polystyrene

1. Introduction

At the present time, very intensive research activity is devoted to advanced polymeric materials with controlled molecular structure. The nitroxide-mediated radical polymerization (NMRP) is a very efficient controlled radical polymerization process based on the pioneering work by Solomon (1) and Georges (2). The living polymerization technique was first suggested in 1967 by Borsig et al. used initiators 3,3,4,4-tetraphenyl-hexane and 1,1,2,2-tetraphenyl-cyclopentane, respectively, for polymerization of methyl-methacrylate (3), styrene (4) and for copolymerization of methyl-methacrylate and styrene (5, 6). Similarly, Braun used thermo labile bulky organic alkanes to successfully mediate stable free-radical polymerization of several vinyl monomers (7).

A nitroxide-mediated technique of living polymerization is usually used for styrene-based systems, and it has significant functional group tolerance and enables easy purification of the obtained polymer (8). The first nitroxide-mediated polymerizations were used as an initiation system (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) with benzoyl peroxide (9). Later, Hawker presented the synthesis of an unimolecular initiator based on TEMPO (10, 11) for controlled radical polymerization.

The synthesis of functionalized unimolecular initiators (12) allows the preparation of a wide range of different materials, which are either difficult to achieve or not available via other polymerization processes. For example, the architecture or topology of the polymer (i.e., comb, star, dendritic, etc.) (13), composition of the backbone (i.e., random, gradient, or block copolymer) (14), and inclusion of functionality (i.e., chain-end, site-specific, etc.) (15) can all be readily manipulated using living free radical methodologies, while still retaining a high degree of control over the molecular weight and polydispersity. Polymers containing chromophore units have been used in the last decade to study the structure and properties of different materials. The chromophore can be introduced either into polymer's main chain, or bonded as a side group or eventually just dispersed in polymer matrix. Despite the fact that the last way is the easiest, the preparation of polymers with bonded chromophore is preferred.

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The main difficulty of using the chromophore dispersed in a polymer is to determine the location of the probe in the system and to find out to what extent it may disturb the system. However, it does not mean that the use of chromophore as dopant is not useful. For example, the compounds containing pyrene as chromophore linked to hindered amine stabilizer (HAS) were dispersed in polymer matrix, and their photostabilizing efficiency has been evaluated in photo-oxidation of isotactic polypropylene (16).

A variety of chromophores including pyrene, anthracene and phenanthrene either as dopants, or covalently attached to the polymer as labels, or both, were investigated to characterize the glass transition in thin and ultrathin polymer films (17).

Labeled polymers are useful in studies of various physical properties in thin films, solutions or even in gels using fluorescence techniques. This technique was successfully applied for assessment of intermolecular energy transfer processes using anthracene labeled poly(styrene)-b-poly(ethylene oxide) prepared by living anionic polymerization (18). Photoactive polymers can be considered as valuable candidates to prepare nanomaterial, which are characterized by high sensitivity to environmental influence and response to external stimuli. For example, Goldbach et al. (19) reported that high molecular weight polystyrene and polymethyl methacrylate containing anthracene end groups can undergo end coupling reaction. In this way, block copolymers are formed via cyclodimerization upon UV irradiation above 300 nm.

With pyrene, covalently bonded to polymethacrylic acid, the behavior of the polymer was studied under all pH conditions. This study showed that the pyrene fluorescent probe was a sensitive indicator of the conformational behavior of PMA (20). Chromophore-labeling of polymers has also been utilized in fluorescence studies of the cyclization rates of end-labeled polymers, such as poly(ethylene glycol) and polystyrene, in different organic solvents (21, 22), and in the investigation of the core-corona interface of block copolymer micelles of poly(isoprene) and poly(methymethacrylate) in acetonitrile using time-resolved fluorescence energy transfer spectroscopy (23, 24).

Linear polymers labeled with pyrene were used for evaluation of the extent of termination. For the termination, chain-chain coupling during the living free-radical polymerization was used. The star polymer, with incorporated pyrene units, was formed by the reaction of labeled polymers with multifunctional star polymers and the inclusion of pyrene into the star structure was a direct result of termination by radical coupling (25).

The aim of this work is to prepare polystyrene with fluorescence marked chain ends. Dormant chain population can be characterized and quantified directly by fluorescence spectroscopy. Comparison of fluoresence intensities of the unimolecular initiator solution with polystyrene solutions of the same molar concentration (calculated on the base of molar mass determined by Gel Permeation Chromatography-GPC) give us the extent of livingness of this type of nitroxide mediated living radical polymerization.

2. Experimental

2.1 General Methods

Commercial reagents were obtained from Sigma-Aldrich and used without further purification. Styrene (99% Aldrich) was distilled under reduced pressure. The solvents for UV and emission analysis were obtained from Sigma-Aldrich, 99.5+%, A.C.S. spectrophotometric grade.

Analytical TLC was performed on commercial Merck plates coated with silica gel 60 F_{254} (0.20 mm). For flash chromatography, Merck Silica gel 60 (0.0603–0.200 mm) was employed.

^{1}H-NMR spectra were recorded in solution with a Bruker AC-300P (300.1 MHz) spectrometer, with the TMS as an internal standard. The ^{13}C-NMR spectra were recorded at 75.5 MHz on a Bruker AC-300P with solvent carbon signals as an internal standard.

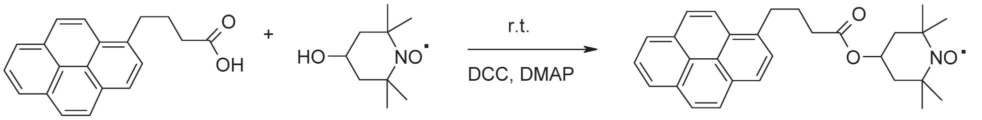
GC-MS mass spectra were recorded on a Agilent Technologies 6890 N network GC System with Agilent 5973 Network Mass Selective Detector. MALDI-TOF mass spectra were recorded on a Kratos Kompact MALDI II. UV-VIS absorption spectra were taken on Perkin-Elmer UV/VIS Lambda 25 spectrometer. Elemental analyses were performed with a Euro Vector EA 3000 Elemental Analyzer. Emission spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer.

The number (M_n) and weight average (M_w), molecular weights and the molecular weight distribution (polydispersity M_w/M_n) of the polymers were determined by GPC under the following conditions: a WATERS 600E instrument equipped with UV and RI detectors, using chloroform containing 0.1 vol% triethanolamine (TEA) as solvent (flow rate: 1.0 ml/min). The samples were measured at 30°C with concentration 2 mg/ml, calibrated with poly(2-vinyl pyridine).

Methanol, cyclohexane and toluene were used as mobile phases for the GPC and as solvents for measurement of absorption and emission spectra of nitroxide derivatives and unimolecular initiator. Toluene, a good solvent for polystyrene, was used for the measurement of fluorescence spectra.

2.1.1 {2,2,6,6-tetramethyl-4-[(4-pyren-1-ylbutanoyl)oxy] piperidin-1-yl}oxidanyl (PYNO)

1-Pyrene butanoic acid (1 g, 3.5 mmol) and 2,2,6,6-tetramethyl-4-hydroxy-piperidin-1-oxyl (4-Hydroxy TEMPO) (0.597 g, 3.5 mmol) were dissolved in dichlormethane (20 ml). Equimolar quantities of N,N′ dicyclohexyl-carbodiimide (DCC) (0.715 g) and 4-dimethylaminopyridine (DMAP) (0.424 g) were added, and the mixture was stirred at room temperature. After three days, the reaction was stopped and the solvent was evaporated under reduced



Sch. 1. Reaction scheme of the preparation of {2,2,6,6-tetramethyl-4-[(4-pyren-1-ylbutanoyl)oxy]piperidin-1-yl}oxidanyl derivates (PYNO).

pressure. The residue was then further purified by flash chromatography (pentane/ethylacetate 9:1 (v/v)) to obtain the product as a red solid substance (1.1 g, 71%) with a 110–112°C melting point (Scheme 1).

^{1}H-NMR (CDCl$_3$): δ (ppm) = 2.27 (t, 2H, CH_2COO), 2.50 (t, 2H, CH_2Ar), 3.47 (m, 2H, CH$_2$CH_2CH$_2$), 7.92–8.35 (m, 9H, Ar).

^{13}C-NMR (CDCl$_3$): δ (ppm) = 25.91 (CH$_2$$CH_2CH_2$), 32.01 ($CH_2Ar, CH_2$COO), 122.45–134.69 (16 C(Ar)).

$C_{29}H_{32}NO_3^{\cdot}$ (442.57): Calcd.: C, 78.70; H, 7.29; N, 3.60: Found: C, 78.79; H, 7.34; N, 3.31.

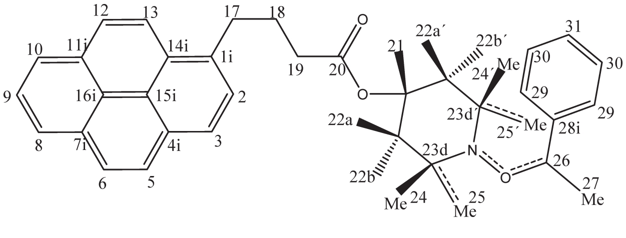
Mass spectrum (ESI): 443.2 $[M+H]^+$, 460.2 $[M+NH_4]^+$, 907.3 $[2\ M+Na]^+$ UV (λ [nm] (log ε) in methanol): 233 (4.98), 242 (5.20), 254 (4.36), 264 (4.73), 276 (5.03), 299 (3.83), 311 (4.35), 325 (4.76), 341 (4.95).

2.1.1 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidin-4-yl 4-pyren-1-ylbutanoate (PYNOR)

Unimolecular initiator was prepared by a reaction of PYNO with styrene according to the literature (26) (Scheme 3). 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidin-4-yl-4-pyren-1-ylbutanoate was obtained as a colorless oil with a yield of 100% (Scheme 2).

^{1}H-NMR (CDCl$_3$): δ (ppm) = 0.64 (s, 25′), 1.11 (s, 24′), 1.25 (s, 24), 1.31 (s, 25), 1.47 (s, 27), 1.48 (s, 22b′), 1.56 (s, 22b), 1.70–1.73 (d, 22a′), 1.82–1.85 (d, 22a), 2.13–2.18 (q, 18), 2.39–2.42 (t, 19), 3.36–3.39 (t, 17), 4.73–4.77 (q, 26), 4.99–5.04 (m, 21), 7.21–7.25 (t, 31), 7.29–7.30 (m, 29 + 30), 7.84–7.86 (d, 2), 7.97–8.00 (t, 9), 8.02 (d, 5 + 6), 8.04 (d, 12), 8.09–8.11 (d, 3), 8.15–8.16 (d, 8), 8.16–8.17 (d, 10), 8.28–8.30 (d, 13).

^{13}C-NMR (CDCl$_3$): δ (ppm) = 21.08 (24, 24′), 23.32 (27), 26.81 (18), 32.71 (17), 34.04 (25′), 34.17 (19), 34.34 (25), 44.60 (22), 44.66 (22′), 59.93 (23d′), 60.17 (23d), 66.76 (21), 83.33 (26),123.33 (13), 124.75 (3), 124.8 (10), 124.91 (8), 124.97 (16i), 125.07 (15i), 125.83 (9), 126.64 (29), 126.70 (6), 126.97 (31), 127.36 + 127.38 (2, 12), 127.48 (5), 128.05 (30), 128.73 (14i), 129.95 (4i), 130.88 (11i), 131.40 (7i), 135.73 (1i), 145.33 (28i), 173.02 (20).



Sch. 2. Structure of PYNOR.

$C_{37}H_{41}NO_3$ (547.31): Calcd.: C, 81.13; H, 7.54; N, 2.56; Found: C, 80.94; H, 7.76; N, 2.50. Mass spectrum (ESI): 548.2 $[M+H]^+$.

UV (λ [nm] (log ε) in methanol): 233 (5.03), 242 (5.25), 254 (4.47), 264 (4.79), 275 (5.08), 298 (3.99), 311 (4.38), 325 (4.81), 341 (4.99).

2.2 General Procedure for the Polymerization of Styrene

Styrene and the pyrene-labeled nitroxide initiator were placed in a Schlenk flask and degassed by three freeze-pump-thaw cycles, the flask was then sealed. The solution was stirred at room temperature for 10 min and placed to oil bath at 120°C. The polymerization was stopped by cooling with liquid nitrogen. The polymer was purified by precipitation in methanol and dried in vacuum to a constant weight. The pure polymer was analyzed by GPC, ^{1}H-NMR and ^{13}C-NMR.

2.3 Fluorescence Measurements

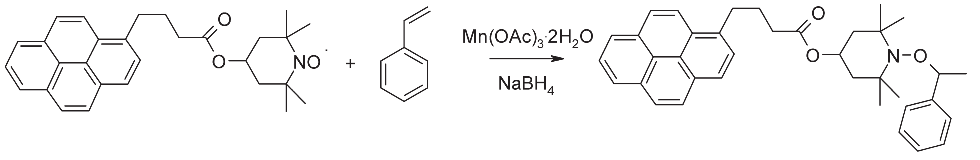
The purified polymer samples were analyzed by GPC. After assignment of exact molar mass, 10^{-6} mol/l solutions in toluene were prepared. Excitation wavelength was 345 nm.

3. Results and Discussion

Alkoxylamine-based unimolecular initiator with chromophore properties was prepared by a reaction of 1-oxy- 2,2,6,6-tetramethyl-4-piperidinylester of 4-(1-pyrenyl)-butyric acid with styrene according to the literature (26) (Scheme 3).

Spectral characteristics (absorption and emission spectra) were measured for all prepared compounds and polymers. Detail descriptions of those spectra were published previously (16, 27).

Two variables, the molar ratio of initiator to monomer and the monomer conversion were examined to determine how the amount of living fluorescence marked polystyrene chain ends varied with increasing of molecular mass and conversion. Two different initiator-monomer ratios I:M (1:400 and 1:1000) were used for polymerization. The dependencies of molecular mass on conversion are shown in Figure 1. Due to the different initiator–monomer ratios, the increase of molar masses is different. Naturally, the initial rather linear part of the curve is much steeper for the ratio 1:1000 than for the 1:400 one. The molar masses increased with the conversion roughly linearly for the initiator-monomer ratio I:M = 1:400. There is some deviation between the theoretical



Sch. 3. Preparation of unimolecular initiator PYNOR with pyrene as chromophore.

and experimental molar masses. In some cases, experimental molar mass is higher than the theoretical one. In the case of I:M = 1:1000, the molar mass of the polymers was close to the theoretical molar mass till 50% conversion. After, there is a small increase of molar mass, despite the conversion increasing, causing high deviation. Polymerization of styrene is mediated by new unimolecular initiator and revealed quasi living character.

Figure 2 shows the changes of polydispersity during polymerization. The plot has two different regions for both different ratios I:M. Polydispersity is very broad in the first stage of polymerization. It seems that the production of growing radicals due to the thermo initiation is very high. Concentration of free nitroxide radicals, due to initiator disproportionation is too low to control this spontaneous polymerization mechanism. But as the polymerization proceeds, the polydispersity drops and it means that the nitroxide radical concentration reaches the level capable of controlling the process under living character. In the case of lower I:M ratio 1:400 (Table 1), the first measured polydispersity after $1\frac{1}{2}$ h of polymerization was 1.42 for 8.2% conversion, and it dropped down to the value 1.17 after 13 h at 51% conversion. For the I:M ratio 1:1000 (Table 2), the first measured polydispersity 1.66 at 9.4% conversion after 1 h of polymerization decreased to the value 1.37 after 3 h to reach the constant value 1.22 after 6 h at 50% conversion. Dependence of conversion on the time of polymerization is shown in Figure 3. At both molar ratios of initiator to monomer, the conversion increased in the first 12 h almost linearly and reached the value 60% for I:M ratio 1:1000 and 50% for ratio 1:400. Further extension of polymerization time resulted just in the very modest increase of conversion.

The changes of fluorescence intensity were observed during the polymerizations. In both ratios of initiator to monomer, the fluorescence intensity of solutions prepared from precipitated polystyrenes was less intensive than the intensity of pure initiator solution despite the same molar concentration was used as is shown on Figure 4 for the ratio I:M = 1:400. Molar concentration of polystyrene solutions was calculated on the base of molar masses obtained from GPC measurements. In the active stages of polymerization, the free nitroxide radical is formed by decomposition of the unimolecular initiator. This radical is able to quench excited state of chromophore–pyrene. The quenching resulted in the decreasing of emission intensity in comparison with the intensity of the original unimolecular initiator. But the dissociation equilibrium constant K_d for nitroxide radical and dormant adduct is for TEMPO 7×10^{-12}. On the assumption that the value for prepared 4-substituted TEMPO is similar, the concentration of NO-radical is extremely small and cannot be responsible for fluorescence decrease. Moreover, the fluorescence was measured from PS samples after precipitation, which removed free low molecular NO-radical. Figure 5 shows the changes of livingness expressed as the ratio X/X_0 during the polymerization. X represents the values of fluorescence intensity of polystyrenes obtained at given time of polymerization and X_0 is the fluorescence

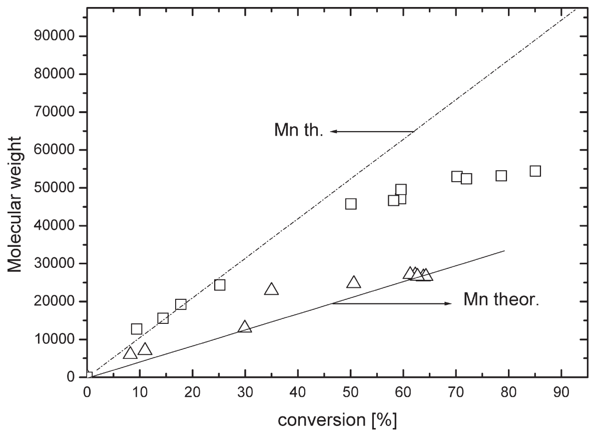


Fig. 1. Dependence of M_n on the monomer conversion for the bulk polymerization of styrene at the ratio [I:M]: [1:400] 8 and [1:1000] ∀.

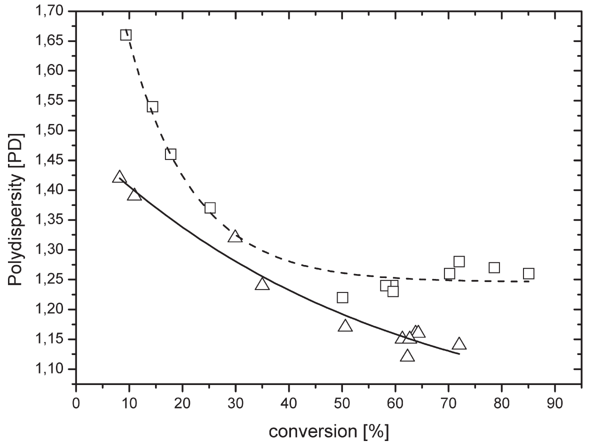


Fig. 2. Dependence of conversion on polydispersity of polystyrenes prepared at different ratio [I:M]: [1:400] 8 and [1:1000] ∀.

Table 1. Block polymerization of styrene with PYNOR. Initiator to monomer ratio [I:M] = [1:400]

Time (hour)	Mn-GPC (g/mol)	Mn theor.	Conversion (%)	Polydispersity	Fluorescence integral	Ratio X/X_0
1.5	6009	3461	8.2	1.42	13013	0.79
2	7072	4643	11.0	1.39	11903	0.72
5	12970	12620	29.9	1.32	10520	0.64
9	18960	14772	35.0	1.24	9428	0.62
13	24700	21357	50.6	1.17	10017	0.61
24	26990	26295	62.3	1.12	10023	0.61
33	26500	26928	63.8	1.16	10045	0.61
39	26580	27139	64.3	1.16	9502	0.58
48	27100	25873	61.3	1.15	9170	0.56
58	26670	26464	62.7	1.15	7821	0.47
84	27060	30389	72.0	1.14	5781	0.35

X – fluorescence intensity of bonded initiator on polystyrene chain, X_0 – fluorescence intensity of free initiator at the beginning of polymerization. 10^{-6} mol/l solutions in toluene.

intensity at the beginning of polymerization – the solution of pure initiator. Molar concentrations of pure initiator and polystyrene solutions were identical for all samples – 10^{-6} mol/l. The amount of polystyrene was calculated on the base of molar mass from GPC measurements. Therefore, the ratio X/X_0 represents a fraction of the polystyrene molecules with fluorescence probes at the chain ends (Scheme 4) or the extent of livingness of the process at different stages. There is a continuous decrease of fluorescence intensity indicating the decrease of polystyrene molecules with fluorescence probe at the chain ends during polymerization. This means that the probability of the cyclic dissociation process of dormant species, insertion of some monomer units to active polystyrene radical and reversible coupling with nitroxide back to dormant species depends on the polymerization time. This process is obviously dependent on conversion, molar mass of produced polymer and most probably on the system viscosity. TEMPO derivative bearing fluorophore was used by Priddy (28) and Hawker (29). Priddy used phenyl-azo-phenyl and Hawker used pyrene as chromophore. High levels of propagating and chain end incorporation were achieved just for a very low molecular mass (<10,000). In another work, Hawker (30) used a more efficient TIPNO (2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy skeleton) instead of TEMPO. Pyrene and dimethylamino-naphthylsulfone were used as chromophore. This type is a better regulator for NMRP than the TEMPO type and it works well in the polymerization of acrylates as well. In this case, the change end functionality calculated on the base of extinction coefficient of fluorescence was very high, 85–90% even for high conversion.

Figure 6 depicts the influence of the extent of livingness on molar mass. These courses show three different stages for polymerizations under both different ratios of initiator to monomer. After an initial decrease of the value of the ratio X/X_0, there some type of plateau appears, and finally decreases sharply. The ratio $X/X_{0,}$ as the extent of livingness at the second stage of more or less constant values, depends

Table 2. Block polymerization of styrene with PYNOR. Initiator to monomer ratio [I:M] = [1:1000]

Time (h)	Mn-GPC (g/mol)	Mn theor.	Conversion (%)	Polydispersity	Fluorescence integral	Ratio X/X_0
1	12740	9841	9.4	1.66	13273	0.81
1.5	15550	15076	14.4	1.54	12117	0.74
2	19230	18636	17.8	1.46	12024	0.73
3	24350	26383	25.2	1.37	10277	0.62
8	45760	52453	50.1	1.22	8957	0.54
11	47130	62295	59.5	1.24	8588	0.52
13	46680	60934	58.2	1.24	8616	0.52
14	49580	62399	59.6	1.23	9100	0.55
24	53000	73497	70.2	1.26	7302	0.44
34	52370	75382	72.0	1.28	7106	0.43
60	53160	82292	78.6	1.27	6616	0.40
124	54450	89097	85.1	1.26	5399	0.33

X –fluorescence intensity of bonded initiator on polystyrene chain, X_0 – fluorescence intensity of free initiator at the beginning of polymerization. 10^{-6} mol/l solutions in toluene.

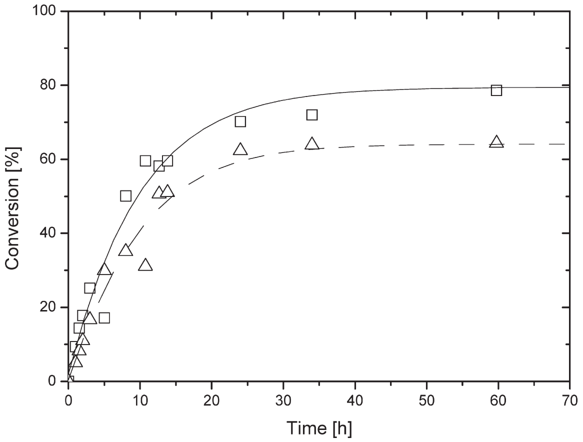


Fig. 3. Kinetic plot of the NMRP of styrene using the prepared unimolecular initiator PYNOR. [I:M] = [1:400] □ and [I:M] = [1:1000] Δ.

on the starting concentration of unimolecular initiator. It is about 0.6 for the lower ratio I:M = 1:400 and 0.5 for ratio I:M = 1:1000. Reflections of these differences are lower values of polydispersity of polystyrenes prepared at I:M = 1:400, PDI about 1.15, in comparison with PDI of polystyrenes prepared at I:M = 1:1000 which have PDI about 1.25. The final stage of sharp decreasing is due to the long thermal treatment of final products. Molar mass, as well as conversion (Fig. 3) does not change. After dissociation of some dormant species to a growing radical and nitroxide bearing fluorescence probe, there is neither insertion of monomers nor reversible reaction, so the number of polystyrenes without fluorescence probes at the chain ends is increasing. Most probably, the disproportionation process is operative, which results in production of a double bond on the end of the polystyrene chain. Hydroxylamine is simultaneously produced, however, it is removed from the system by precipitation and consequently, the fluorescence intensity of the polystyrene solution of the same concentration decreases. Due to the high viscosity, the side reactions, as for example, recombination, do not take place in this stage and the molar mass, as well as the polydispersity, does not change. A low extent of "livingness" will have a very negative effect on the possible preparation of block copolymers especially by using polymers obtained at higher conversions.

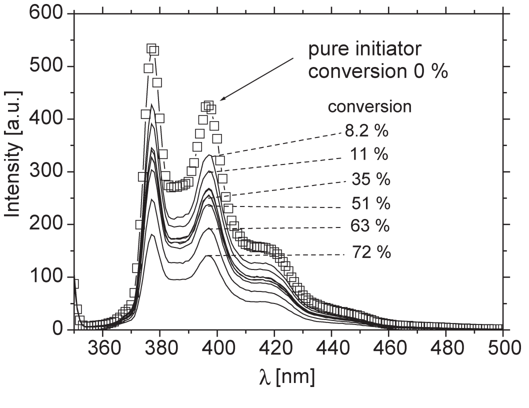


Fig. 4. Changes of fluorescence intensity of polystyrenes at different conversions. Block polymerization with ratio [I:M] = [1:400]. 10^{-6} mol/l solutions in toluene.

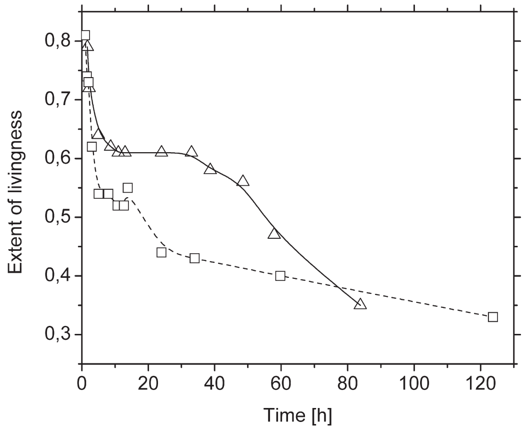
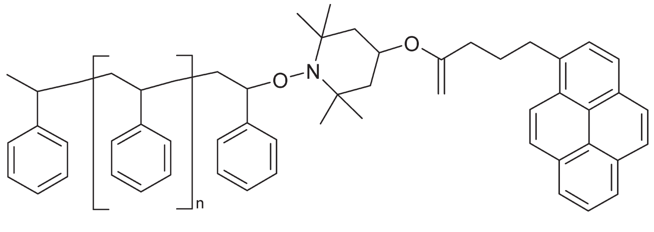


Fig. 5. Changes of extent of "livingness" (ratio X/X_0) during polymerization. [I:M] = [1:400] □ and [I:M] = [1:1000] Δ.



Sch. 4. Structure of polystyrene end-capped with the fluorescence probe.

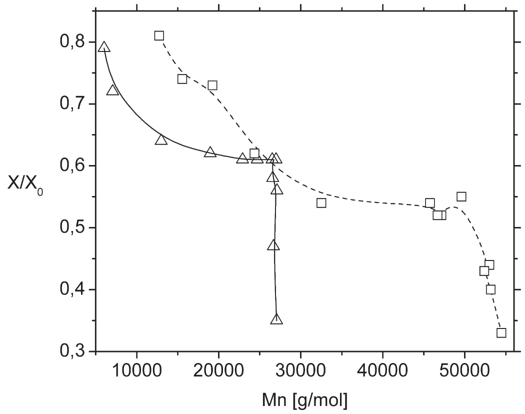


Fig. 6. Dependence of molecular weight on ratio X/X_0 ([I:M] = [1:400] □ and [I:M] = [1:1000] Δ).

4. Conclusions

An initiator of the TEMPO type containing a fluorescence probe was prepared and used as a mediator for the block polymerization of styrene at 120°C. Covalently bonded pyrene was used as the fluorescence probe. For comparison, two different molar ratios of initiator to monomer [I:M] were used ([I:M] = 1:400 and [I:M] = 1:1000). At both I:M ratios, the molar mass, as well as the conversion increased in the first 13 h, almost linearly. Conversion reached 60% for the I:M ratio 1:1000 and 50% for the ratio 1:400. The fluorescence intensity of all polymer samples, in both initiator/monomer ratios, was lower than the intensity of a pure initiator for the solutions of the same molar concentration. Molar concentration of polystyrenes was calculated on the base of molar mass measured by GPC. The ratio of fluorescence intensities of polystyrene samples to the intensity of pure initiator (X/X_0) represents the extent of livingness of polymerization process. Incorporation of terminating fragments into the polymer chain ends decreased during the polymerization under both molar ratios of initiator to monomer. The extent of livingness at 60% conversion was a little higher in the case of a higher initiator to the monomer ratio. The value X/X_0 was 0.6 and 0.5, respectively. This means that each second polymer chain is terminated with nitroxide bearing a fluorescence mark. Despite the consecutive decrease of livingness, the polydispersity did not change and kept the value ca 1.15 and 1.25 for higher and lower concentrations of initiator. This means that the side reaction resulting in the broadening of polydispersity did not take place under these conditions. Most probably, a high increase of viscosity at the higher conversions suppressed these side reactions. Despite the fact that polydispersity of polymers at higher conversions is very low, the use of these polymers for subsequent preparation of block copolymers will be questionable.

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