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New difunctional mediators based on 4-amino-TEMPO derivatives for controlling free radical polymerization of styrene

Summary — The free radical polymerization of styrene in the presence of a number of freshly newly synthesized bifunctional mediators differing in the number of methylene groups serving as a link between two functional 4-amino-TEMPO radicals has been investigated. It was found, that the activity of a nitroxide group in the biradicals in controlling radical polymerization of styrene differs from that of the TEMPO radical. Mediators with a lower number of connecting methylene groups between the two TEMPO rings give a higher conversion in the same reaction time. However, no simple correlation between the number of methylene groups in spacer chain and polymerization rate was observed, namely unexpectedly, high rate of polymerization was found for $^{\bullet}C_4^{\bullet}$. The formation of single-arm (P) and double-arm (P-P) macromolecules containing binitroxide at the core was observed.

Keywords: nitroxide mediated polymerization (NMP), TEMPO radical, biradical metiators, methylene linking groups, styrene.

NOWE DWUFUNKCYJNE MEDIATORY NA PODSTAWIE POCHODNYCH 4-AMINO-TEMPO REGULUJĄCE PRZEBIEG RODNIKOWEJ POLIMERYZACJI STYRENU

Streszczenie — Porównano aktywność grup nitroksylowych w szeregu homologicznym nowych dwufunkcyjnych mediatorów (regulujących przenośników) różniących się liczbą grup metylenowych (0, 2, 3, lub 4) w łańcuchu łączącym dwa rodniki 4-amino-TEMPO [wzory (I)—(IV)] w regulowaniu przebiegu rodnikowej polimeryzacji styrenu, stwierdzając występowanie różnic tej aktywności. Liniowy charakter zależności indeksu konwersji styrenu od czasu polimeryzacji (rys. 1) wskazuje na pierwszorzędowość reakcji względem monomeru w odniesieniu do wszystkich badanych dirodników pochodzących z mediatora. Najszybciej polimeryzacja przebiega pod wpływem dirodnika $^{\bullet}C_0^{\bullet}$, a najwolniej wobec $^{\bullet}C_3^{\bullet}$, jednakże nie zaobserwowano prostej zależności pomiędzy liczbą grup -CH_2- w mediatorze a szybkością polimeryzacji. Scharakteryzowano widma ESR polimerów (rys. 3) oraz szczegółowo omówiono wyniki ich badania metodą GPC (rys. 2, 4 i 5 oraz tabela 1). W wyniku polimeryzacji powstają polimery o jedno- i dwuramiennych łańcuchach, prawdopodobnie zawierających centralny fragment dinitroksylowy. Rozkład ciężarów cząsteczkowych (*M*) produktów ma charakter bimodalny a wzajemny stosunek wartości *M* obydwu frakcji wynosi w przybliżeniu 2:1.

Słowa kluczowe: polimeryzacja regulowana rodnikami nitroksylowymi (NMP), rodnik TEMPO, regulatory dwurodnikowe, metylenowe grupy łączące, styren.

The use of nitroxides as mediators for *controlled radical polymerization* (CRP) for the polymerization of a number of monomers, including styrene [1] and its derivatives [2—6] has attracted much interest recently. The generally accepted mechanism of *nitroxide-mediated radical polymerization* (NMRP) involves the dynamic equilibrium formed between the activated and the deactivated (dormant) polymer chains employing stable radicals:

$$P-T \overset{K}{\rightleftharpoons} P^{\bullet}\circlearrowleft_{k_p} + T^{\bullet} \qquad (1)$$

where: *P*• — *growing macroradical, T*• — *2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO), K — equilibrium constant,* k_p *— rate constant of preparation.*

The application of nitroxyl stable free radicals such as TEMPO in the bi-component initiating system and alkoxyamines as unimolecular initiators allows for the synthesis of homopolymers with a low dispersity index

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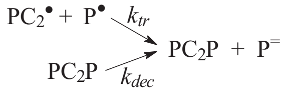
and a controlled architecture as well as the design of copolymers according to specific requirents [7—9].

Not much has been done comparatively on dinitroxide radicals as mediators. GPC studies of polystyrene synthesized in radical polymerization using dinitroxides as mediators and benzoyl peroxide (BPO) as initiator revealed a shoulder developing on GPC curves at high conversions of styrene resulting in a bimodal distribution of the molecular weights [10—12].

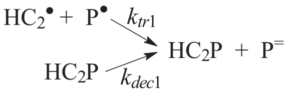
Huang *et al.* [10] propose that major reactions in the NMRP using biradicals, for example, dinitroxide $^\bullet C_2^\bullet$, proceed according to the following equations:

$$PC_2P \overset{K}{\rightleftharpoons} PC_2^\bullet + P^\bullet \circlearrowleft_{k_p} \qquad (2)$$

$$P^\bullet + P^\bullet \xrightarrow{k_t} P\text{—}P \qquad (3)$$



$$\begin{array}{l} PC_2^\bullet + P^\bullet \xrightarrow{k_{tr}} \\ PC_2P \xrightarrow{k_{dec}} \end{array} PC_2P + P^{=} \qquad (4)$$



$$\begin{array}{l} HC_2^\bullet + P^\bullet \xrightarrow{k_{tr1}} \\ HC_2P \xrightarrow{k_{dec1}} \end{array} HC_2P + P^{=} \qquad (5)$$

where: *P-P — dead polymer (saturated), P= — dead polymer (unsaturated),* k_t *— rate constant of termination by combination,* k_{tr} *— rate constant of termination by disproportionation,* k_{dec} *— rate constant of decomposition.*

Resent discussions in the literature on the role of conformational structure of bisnitroxides emphasize importance of some geometrical parameters for NMRP [13, 14].

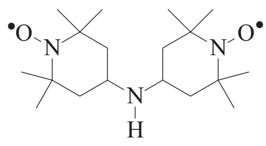
In our previous work, a homologous series of di-TEMPO biradicals was investigated by means of the electron spin resonance (ESR) spectroscopy [15]. The electron coupling between two nitroxyls was found to be transmitted directly through-space. Higher coupling constants *J* and more effective spin—spin interactions were observed for longer chains separating both TEMPO nitroxyls. However, influence of the size of the biradical on NMRP has not been investigated yet.

The main goal of the present study, therefore, was to assess the importance of the distance between two TEMPO nitroxyl groups in difunctional mediators for the controlled radical polymerization of styrene (St). For thus purpose, a homologous series of di-TEMPO biradicals made up of two 4-amino-TEMPOs linked by -$(CH_2)_n$- (n = 2, 3, 4) and also *N,N'*-bis[4-(2,2,6,6-tetramethylpiperidin-1-yloxyl)]amine (mimicking first homolog of the series with n = 0) was applied for NMRP.

EXPERIMENTAL

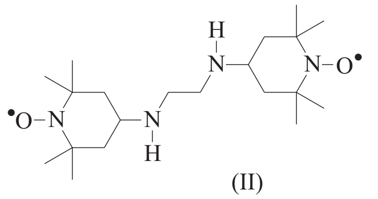
Materials

— *N,N'*-bis[4-(2,2,6,6-tetramethylpiperidin-1-yloxyl)]amine $^\bullet C_0^\bullet$ (I) was prepared according to the procedure given by Rosen [16].

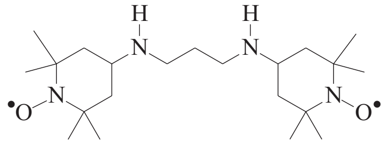


(I)

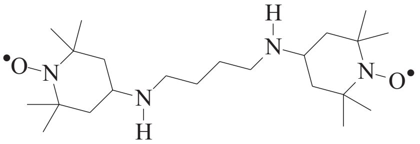
— *N,N'*-bis[4-(2,2,6,6-tetramethylpiperidin-1-yloxyl)]diaminoethane $^\bullet C_2^\bullet$ (II)[*)], *N,N'*-bis[4-(2,2,6,6-tetramethylpiperidin-1-yloxyl)]-1,3-diaminopropane $^\bullet C_3^\bullet$ (III) and *N,N'*-bis[4-(2,2,6,6-tetramethylpiperidin-1-yloxyl)]-1,4-diaminobutane $^\bullet C_4^\bullet$ (IV) were prepared [15] according to the adapted procedure of Nakatsuji *et al.* presented in [10], using corresponding diamine.



(II)



(III)



(IV)

— 4-Oxo-2,2,6,6-tetramethylpiperidin-1-yloxyl (oxo-TEMPO), necessary to synthesize the desired dinitroxyl diamines, was prepared as described by Rosen [16].

Mass spectroscopy, ^1H NMR and ^{13}C NMR data (spectra registered after reduction with phenylhydrazine [17]) revealed the appropriate structures of received products.

The other reagents were obtained from commercial vendors. Benzoyl peroxide (BPO, 97 % purity) were used as obtained from Aldrich.

Styrene was purified according to standard procedures.

Polystyrene synthesis

Polymerization reactions of styrene initiated with BPO in the presence of synthesized biradicals were carried out in glass ampoules degassed in three-fold pump-freeze-thaw cycles and sealed under dehumidificed oxygen-free argon. The ampoules were heated for

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[*)] Some date concerning $^\bullet C_2^\bullet$ will be published elsewhere.

a specific period in an oil bath at 135 °C. For kinetic analyses, the samples were cooled in ice-cold water and its contents dissolved in THF. The unreacted styrene and THF were removed by evaporation in vacuum at 45 °C to a constant weight. The monomer conversion was determined gravimetrically.

Methods of testing

Molecular weight and its distribution

Molecular weights (M) of the obtained polymers were determined by gel permeation chromatography (GPC) [LabAlliance, column Jordi Gel DVB Mixed Bed (250 mm × 10 mm), refractometry detector, detection temperature 35 °C, chloroform as solvent, flow rate — 1 cm^3/min, calibration — polystyrene]. Molecular weight distribution (polydispersity, PD) was analyzed using commercial statistical software OriginPro 7.0.

ESR spectra

The ESR spectra were recorded using ESR Bruker ELEXYS 500 system at room temperature. Polystyrene samples separated from the polymerization mixture were dissolved in toluene. The solution was placed in ESR quartz tubes with ϕ = 4 mm, degassed in repeated pump-freeze-thaw cycles and sealed under oxygen-free dry argon atmosphere.

RESULTS AND DISCUSSION

Polymerization

The influence of the [mediator]/[initiator] ratio on polymerization was investigated for all biradicals at ratios of 0.3 and 0.5. Linear plots of ln ($[M_0]/[M]$) *vs.* polymerization time for all the compounds revealed first-order kinetics with respect to the monomer (Figure 1).

The highest polymerization rate was observed for ${}^\bullet C_0{}^\bullet$ the biradical while ${}^\bullet C_3{}^\bullet$ exhibited the lowest rate. However, no simple correlation between the number of methylene groups in spacer chain and polymerization rate was observed — for ${}^\bullet C_4{}^\bullet$, unexpectedly, a comparatively high rate of polymerization was observed.

The effects that could contribute to the high rate of polymerization in the presence of the ${}^\bullet C_4{}^\bullet$ biradical are not yet known. The only difference between this biradical and the others could be found in the results of recent ESR spectroscopy studies. The series of di-TEMPO biradicals under investigation showed the through space spin—spin interaction between the nitroxyl groups [15]. In order to achieve a close proximity between the two TEMPO units the separating chain should be bent adequately. It was found that to reach more effective bent chain conformations the chain has to be longer. According to the ESR experiment the ${}^\bullet C_4{}^\bullet$ biradical had the highest tendency to form the loop structure. However, whether this specificity of the ${}^\bullet C_4{}^\bullet$ biradical has any impact on NMRP kinetics of styrene remains to be proven.

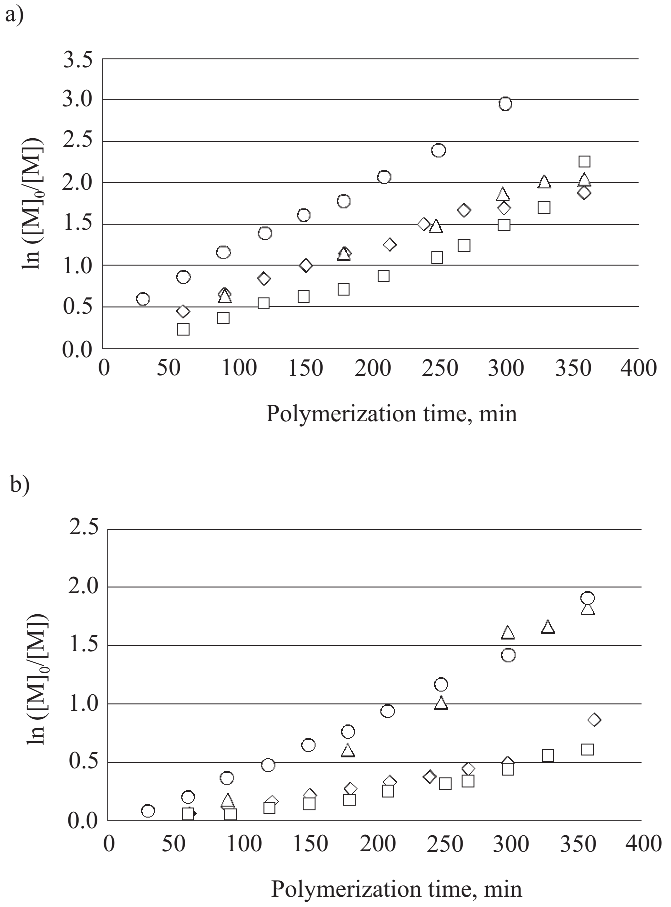

Fig. 1. Ln ($[M_0]/[M]$) versus time for polymerization of styrene at 135 °C using the synthesized binitroxides as mediators and BPO as initiator (1 wt. % of monomer): [mediator]/[initiator] = (a) 0.3 or (b) 0.5; (○ — ${}^\bullet C_0{}^\bullet$, ◇ — ${}^\bullet C_2{}^\bullet$, □ — ${}^\bullet C_3{}^\bullet$, △ — ${}^\bullet C_4{}^\bullet$)

As can be seen from Fig. 1, the reaction rate depends also on the [mediator]/[initiator] ratio. The results are in agreement with the literature [18, 19], proposing that the higher the mediator concentration, the slower the polymerization.

Products

Figure 2 shows the evolution of the experimental molecular weight (M_n) *vs.* styrene conversion. M_n values increased linearly with monomer conversion at the initial stage of polymerization for the three mediators used [mediator]/[initiator] ratio. The linear character of the plots confirms the "active" character of the polymerization.

The synthesized polymers are all paramagnetic. Exemplary ESR spectra recorded for polystyrene using ${}^\bullet C_3{}^\bullet$ as mediator is presented in Figure 3.

ESR spectra recorded for all received polystyrene samples synthesized with investigated bisnitroxide mediators revealed mononitroxide picture. Thus, it can be concluded that in the reaction mixture no or unnoticeable

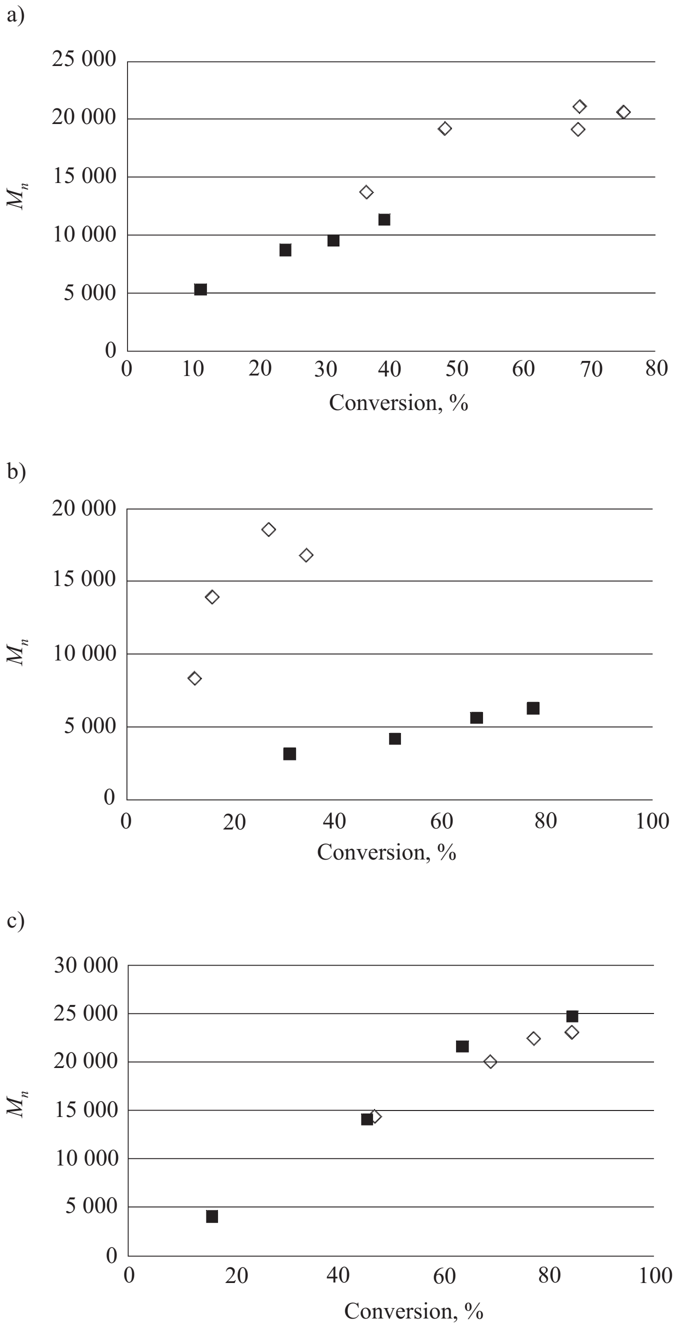

Fig. 2. M_n values versus conversion for polymerization of styrene at 135 °C using the synthesized binitroxides as mediators and BPO (1 wt. % of monomer) as initiator. Kind of mediator: a) $^{\bullet}C_2^{\bullet}$, b) $^{\bullet}C_3^{\bullet}$, c) $^{\bullet}C_4^{\bullet}$; [mediator]/[initiator]: ◇ — 0.3, ■ — 0.5

amount of a free biradical is present during the dinitroxide mediated CRP.

The polydispersity (*PD*) values presented in Table 1 for all [mediator]/[initiator] ratios are not much higher than that for bisnitroxide iniferters studied by Hill *et al.* [11] and depends also on the [mediator]/[BPO] ratio.

The experimental molecular weight distribution (*PD*) for polystyrene at 31 % conversion of monomer is presented in Figure 4. GPC chromatogram for polystyrene synthesized with $^{\bullet}C_3^{\bullet}$ mediator exhibits a high-molecular weight shoulder. This has been assigned to peak 2 with maximum *M* ~ 17 810 (~50 % of polymer sample) estimated theoretically with high coefficient of determination R^2 > 0.99 and corresponds to the undecomposed "bidirectional" polymer chain P-C_3-P or P-P molecules (reaction 3). The left peak 1 corresponds to irreversibly separated polymer chain arms P, with *M* ~ 9520 (~50 % of polymer sample) possibly as a result of reactions 2, 4 and 5. The percentage of the fractions was estimated using OriginPro 7.0 assuming the Gaussian molecular weight distribution (see parameters A_1 and A_2 in the inserts of Figure 4).

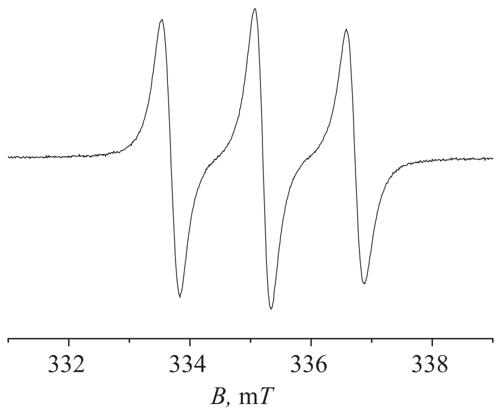

Fig. 3. ESR spectra recorded at room temperature for polystyrene synthesized at 135 °C using $^{\bullet}C_3^{\bullet}$ as mediator and BPO (1 wt. % of monomer) ([C3]/[initiator] = 0.5, polymerization time 300 min)

Table 1. Polydispersity (*PD*) of polystyrene obtained in mediated polymerization initiated with BPO (1 wt. % of monomer); polymerization time 180 min

Mediator	*PD*	
	[mediator]/[BPO]	
	0.3	0.5
$^{\bullet}C_0^{\bullet}$	1.75	1.51
$^{\bullet}C_2^{\bullet}$	1.63	1.42
$^{\bullet}C_3^{\bullet}$	1.49	1.23
$^{\bullet}C_4^{\bullet}$	1.49	1.59

The molecular weight distribution for polystyrene at 77.4 % conversion of styrene (R^2 = 0.99) are presented in Figure 5. The corresponding peak 1 on the left in this case reveals *M* ~ 15 640 (~50 %) while the right peak 2, corresponding to irreversibly separated polymer chain arms P is *M* ~ 30 330 (~50 %). It can be seen that *M* of polystyrene rises with polymerization time, although the contribution of the P-C_3-P + P-P polymer chains remains approximately constant. The correlation between polydispersity and polymerization time (conversion) as well as [mediator]/[initiator] ratio is under further investigation.

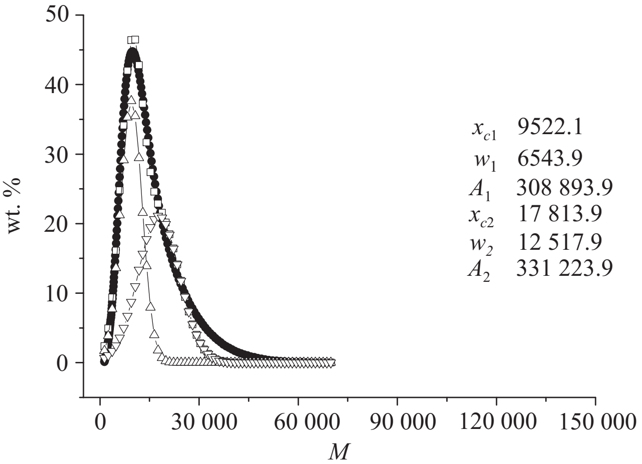

Fig. 4. GPC profiles for polystyrene synthesized at 135 °C ([BPO] = 1 wt. % of monomer, [•C_3•]/[BPO] = 0.3, conversion 31 %): (•) — measured profile, (Δ) and (∇) — theoretical bimodal molecular weight distribution, ☐ — sum of the theoretical molecular weight distributions. Parameters in the insert have following meaning: xc_n — center of the peak n, w_n — full width of the peak n at half height, A_n — the total area under the curve n (n = 1 or 2)

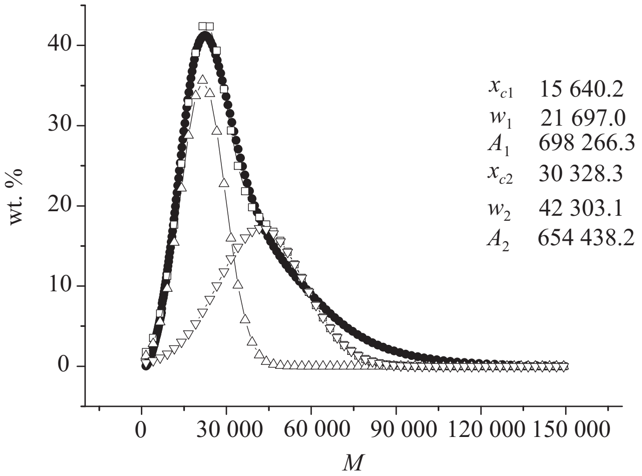

Fig. 5. GPC profiles for polystyrene synthesized at 135 °C ([BPO] = 1 wt. % of monomer, [•C_3•]/[BPO] = 0.3, conversion 77.4 %): (●) — measured profile, (Δ) and (∇) — theoretical bimodal molecular weight distribution, ☐ — sum of theoretical molecular weight distributions. For parameters in the insert see Fig. 4

CONCLUSIONS

The length of the spacer linking two TEMPO moieties most probably influences the activity of the mediator in controlling radical polymerization. However, no simple correlation between the number of methylene groups in the spacer and polymerization rate of styrene was observed. GPC studies of polystyrene revealed a bimodal distribution of the molecular weight corresponding roughly to chain length 2P and P. For increasing conversion, for example from 31 % to 77.4 %, the contribution of these polymer chains does not change irrespective of the length. The *PD* value for synthesized polystyrenes depends on the [mediator]/[initiator] ratio.

It was shown that the activity of a single nitroxide group in the investigated biradicals differs in controlling radical polymerization of styrene when compared to TEMPO. However, to explain in more detail the correlation between the seize of mediator and its controlling properties in radical polymerization further studies have to be done.

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