Determination of the Free Radical Concentration Ratio in the Copolymerization of Methyl Acrylate and Styrene. Application of Radical Trapping and ^{15}N NMR Spectroscopy

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ABSTRACT: ^{15}N-labeled nitroxides are employed to trap propagating radicals in the copolymerization of styrene and methyl acrylate. The resulting polymeric alkoxyamines are analyzed by ^{15}N NMR. The assignment of the observed bands to the two possible end groups of the propagating copolymer chain is achieved by comparison of the spectra with the homopolymer alkoxyamines. Copolymers in the suitable molar mass range for the current investigation are obtained by the formation of initiating radicals and nitroxyl radical traps in situ, from a low molar mass ^{15}N-labeled alkoxyamine.

Introduction

The elucidation of the mechanism of free radical copolymerization remains an open problem. Comparison of experimental data (average propagation rate constant $\langle k_p \rangle$ and copolymer composition (F)) with model predictions reveals that different models describe the data equally well.[1] It is not possible to discriminate among the models that are based on qualitatively different mechanistic assumptions. The problem of the discrimination among the models originates from the fact that two types of reactants play a role in the process, i.e., radicals and monomers.

$$P^{\bullet}_{A} + M_{A(S)} \rightarrow P^{\bullet}_{A(S)}$$

$$P^{\bullet}_{S} + M_{A(S)} \rightarrow P^{\bullet}_{A(S)}$$

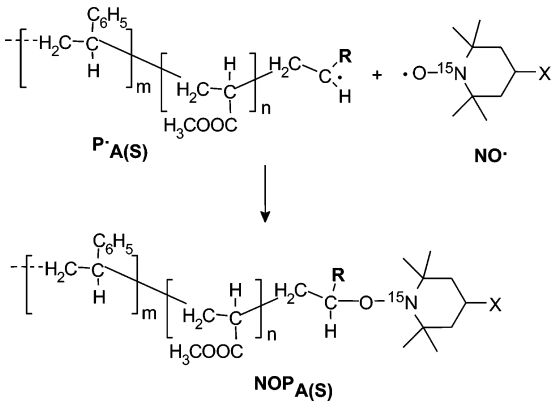
It should be noted that the subscripts A and S refer to acrylate and styrene, respectively. The applicability of the presented technique will not be limited to this comonomer combination. However, readability is enhanced by using A and S instead of indexes like 1 and 2.

The concentrations of comonomers in the copolymerization reaction are determined experimentally and are related to the experimental data of F and $\langle k_p \rangle$. However, there are no experimental data characterizing the concentrations of radicals [$P^{\bullet}_{A}$] or [$P^{\bullet}_{S}$]. They are commonly calculated from the model equations. The validity of the particular model is implicitly assumed in such an approach, and model discrimination becomes inefficient.

Measurement of experimental assumption-free concentrations of the free radicals participating in the copolymerization is the objective of our work. It is focused on the measurement of the concentration ratio of the macroradicals possessing different terminal groups.

$$A = \frac{[P^{\bullet}_{A}]}{[P^{\bullet}_{S}]}$$

Scheme 1. Formation of the Stable Product—Macromolecular Alkoxyamine—by Trapping Reaction of the (Statistical) Copolymer Macroradical with 2,2,6,6-Tetramethylpiperidine-^{15}N-1-oxyl[a]



[a] Trapping is applied in the copolymerization of methyl acrylate and styrene. −R = −$COOCH_3$ (P_A, NOP_A) or −C_6H_5 (P_S, NOP_S).

Knowledge of this quantity for the particular free radical copolymerization should provide additional information for the critical evaluation of copolymerization models.

The main problem in the determination of the ratio A consists of the short lifetime of free radicals and in their low equilibrium concentrations. Our concept of the problem solution is based on the reaction of the propagating macroradicals $P^{\bullet}_{A}$ and $P^{\bullet}_{S}$ with a nitroxide stable free radical [NO•]. They are converted into stable macromolecular trapping products NOP_A and NOP_S and subsequently analyzed (Scheme 1). The trapping of the propagating macroradicals in copolymerization and analysis of the macromolecular trapping products are reported here for the first time. The method of radical trapping has been used in the study of complex radical reactions during the initiation of copolymerization,[2−6] but only low molecular weight radicals were involved in that work.

Experimental Section

Materials. The monomers styrene (Aldrich, 99%) and methyl acrylate (Merck, 99+%) were passed through a column containing inhibitor remover and subsequently distilled at reduced pressure under argon. They were stored under an

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argon blanket at −20 °C and used within 24 h after distillation. The initiator azobis(isobutyronitrile) (AIBN, Merck, >98%) was recrystallized from methanol (Biosolve, p.a.). Alkoxyamine NOR_c (toluene-4-sulfonic acid 2,2,6,6-tetramethyl-1-(1-methyl-1-phenylethoxy)piperidin-^{15}N-4-yl ester) was prepared as described in our previous publication.[7] It was recrystallized from pentane (Biosolve, p.a.) and stored in a closed Schlenk flask under an argon atmosphere. The compound was used within 24 h after recrystallization. Benzene (Biosolve) is purified by distillation. Other solvents of p.a. purity were purchased from Biosolve and used as supplied.

Preparative SEC was carried out as follows. The Injector WISP 710 (Waters) has a maximum injection volume of 200 μL. Six rapid consecutive injections were performed to inject a total volume of 1.2 mL. A Waters pump model 510 operating at a flow rate of 2.0 mL min^{-1} and a Waters differential refractive index detector R401 were employed. As column, a Waters Ultra Styragel 500 Å (19 × 300 mm, bead size 7 μm) was used with THF as the eluent. The experiments were conducted at ambient temperature.

Analytical SEC. The dried polymer was dissolved in tetrahydrofuran (THF, Biosolve) to a concentration of 1 mg/mL. The solution was filtered over a 0.2 μm PTFE syringe filter. Analysis was carried out using a Waters model 510 pump, a Waters model WISP 712 autoinjector, a model 410 refractive index detector, and a model 486 UV detector (at 254 nm). The columns used were a PLgel guard (5 μm particles) 50 × 7.5 mm precolumn, followed by two PLgel mixed-C (5 μm particles) 300 × 7.5 mm columns in series (which were maintained at 40 °C for analysis). The columns used separate polymers in the molecular weight range between 500 and 2 million with high resolution. THF was used as an eluent (flow rate 1.0 mL/min). Data acquisition was performed using waters Millenium 32 (v3.05) software. Calibration was carried out using narrow molecular weight polystyrene (PSTY) standards ranging from 580 to 7 × 10^6 g/mol.

Procedure of Copolymerization and Trapping. The procedure for the copolymerization and trapping can be exemplified by the detailed description of the experiment with a fraction of methyl acrylate f_A = 0.93 in the comonomer mixture. A 10 mL volumetric flask was charged with the alkoxyamine NOR_c (toluene-4-sulfonic acid 2,2,6,6-tetramethyl-1-(1-methyl-1-phenylethoxy)piperidin-^{15}N-4-yl ester) (0.201 g, 0.451 mmol), AIBN (0.026 g, 0.158 mmol), styrene (0.402 g, 3.85 mmol), and methyl acrylate (4.403 g, 51.15 mmol). Benzene was added to a total of the reaction mixture of 10 mL at 20 °C. The solid compounds NOR_c and AIBN were dissolved, and the mixture was transferred into a clean and dry Schlenk flask equipped with magnetic stirrer bar. The Schlenk flask was connected to the vacuum line and the argon inlet. The mixture was degassed by three freeze−pump−thaw cycles. The flask was filled with argon after the last cycle. The Schlenk flask was then transferred into the thermostated bath and heated at 70.0 ± 0.1 °C for 16 min under continuous stirring. The reaction mixture was subsequently cooled to −20 °C.

Separation and Purification of Macromolecular Trapping Products. The flask was opened, and 0.1 g of a nitroxide radical (2,2,6,6-tetramethyl-4-piperidinol-1-oxyl, 0.026 mol) dissolved in 2 mL of benzene was added to the reaction mixture to prevent undesired polymerization during further processing.

The reaction mixture was transferred quantitatively to the preweighted 50 mL round-bottom flask equipped with a magnetic stirrer bar. The flask was mounted in a distillation setup. The condenser of the setup was cooled to −10 °C. This setup allows the evaporation of all volatile constituents of the reaction mixture at temperatures below 25 °C under vacuum. The solid residue was weighed after the evaporation of volatiles (0.518 g), and the mass of the formed copolymer (0.237 g) was estimated by correction for the nonvolatile constituents of the reaction mixture. The copolymer mass corresponded to a comonomer conversion of 4.9%.

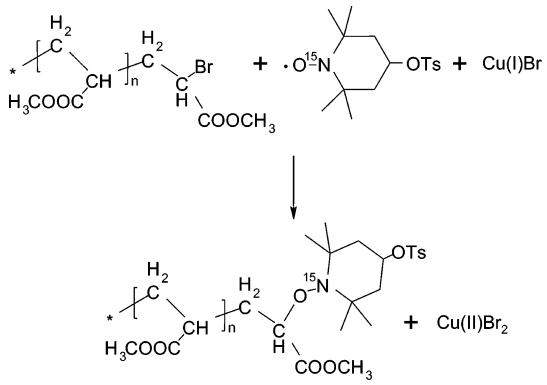
The solid residue was redissolved in 10 mL of tetrahydrofuran and purified via preparative SEC. The entire amount was purified in seven runs of 1.2 mL of crude polymer solution.

Table 1. Experimental Conditions of Radical Trapping during the Copolymerization of Methyl Acrylate and Styrene[a]

f_A	[AIBN] (mol L^{-1})	[NOR] (mol L^{-1})	reaction time (min)	conv (%)	$B_{measured}$
0.97	0.05	0.05	25	6.8	0.45
0.96	0.03	0.06	14	4.2	0.30
0.93	0.015	0.045	16	4.9	0.17
0.86	0.015	0.06	14	4.4	∼0
0.28	0.015	0.07	15	3.9	∼0

[a] Values of experimentally determined ratio of macromolecular trapping products B = [NOP_A]/[NOP_S].

Scheme 2. Reaction Scheme of Preparation of the Macromolecular Model Compound Ib



The effluent was divided in 2 mL fractions. Fractions containing copolymer were eluted in time interval corresponding to the elution time of the polymer signal of the RI detector. Fractions containing mainly unreacted NOR_c, AIBN, and further low molecular weight impurities elute later. Fractions of polymer that immediately preceded the first impurity fraction were discarded to ensure the absence of any impurity in the sample. The polymer was isolated by evaporation of tetrahydrofuran in a vacuum at ambient temperature. Seven purification runs were performed to obtain 0.18 g of purified polymer. The polymer was dissolved in 1 mL of the $CDCl_3$, and this solution was used for the ^{15}N NMR measurement.

^{15}N NMR spectra were measured on Unity Inova 500 MHz spectrometer. Conditions of FID acquisition were as follows: transmitter frequency, 50.6 MHz; pulse width, 10.0 ms; spectral width, 8 kHz; filter bandwidth, 4 kHz; acquisition time, 2 s; number of data points, 32 000; delay in pulse sequence, 10 s. Proton decoupling in asynchronous mode was applied using the WALTZ 16 modulation. Nitromethane was used as a chemical shift standard. The signals of 5000 pulses were accumulated for further processing.

Signal Processing. The FID signals were weighted using an exponential window function $\exp(-t\pi l)$ with line broadening parameter l = 1 Hz. Subsequent Fourier transformation provided the NMR spectrum. Phase and baseline of the spectra were corrected. The signal intensities in the regions corresponding to different structures of the terminal segments were integrated. The results obtained for various f_A are given in Table 1.

Preparation of Model Compounds. The preparation of low molecular weight model compounds **Ia**, **IIa**, and **IIIa** was described in our previous publication.[7] Macromolecular model compounds were prepared as follows:

*Poly(methyl acrylate) Capped with ^{15}N-Labeled Alkoxyamine Group **Ib***. The preparation scheme is depicted in Scheme 2. The preparation is based on the procedure of Matyjaszewski et al.[8]

The ethyl 2-bromoisobutyrate (0.9753 g, 5.03 mmol), ethyl acrylate (9.35 g, 109 mmol), and xylene (16.35 g, 18.9 mL) were mixed in a three-necked flask equipped with condenser, magnetic stirrer bar, and argon inlet. The mixture was flushed with argon for 60 min, and then CuBr (0.29 g, 2.0 mmol), $CuBr_2$ (0.11 g, 0.5 mmol), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldieth-

ylenetriamine (0.43 g, 2.5 mmol) were added. The reaction proceeded at 65 °C for 6 h. The mixture was then diluted with tetrahydrofuran and passed through a layer of basic alumina to remove the copper complex. The solvents were subsequently evaporated. The resulting polymer was analyzed by SEC and found to possess an M_n = 1850 g/mol and PDI = 1.06.

The polymer prepared in the previous step was used as a precursor in the preparation of the model compound **Ib**. The polymer (1 g, 0.54 mmol) was dissolved in benzene (10 mL). Toluene-4-sulfonyl-(2,2,6,6-tetramethylpiperidin-^{15}N-1-oxyl)-4-1-yl (213 mg, 0.65 mmol), copper triflate (72 mg, 0.2 mmol), copper (700 mg, 11 mmol), and 2,2′-di-*tert*-butylbipyridyl (109 mg, 0.4 mmol) were added. The reaction mixture was degassed by three freeze−vacuum−thaw cycles and stirred at 75 °C for 16 h. Benzene was evaporated in vacuum. The polymer was redissolved in tetrahydofuran and passed through a layer of basic alumina. The polymer was separated from low molecular weight impurities using preparative SEC under the conditions described in the section Purification and Isolation of Trapping Compounds.

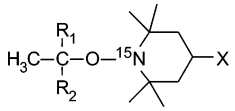
The yield of the substitution was estimated from the comparison of the theoretical number of alkoxyamine end groups calculated from the M_n determined by SEC and the total number of end groups determined from the ^{1}H NMR spectrum of the prepared polymer. Four aromatic protons of the 4-methylphenylsulfonyl group present two doublets in the region of 7.26−7.32 and 7.68−7.74 ppm. They do not overlap with other peaks of the polymer spectrum. The relative contents of the end groups can be calculated from the ratio of their integral and the integral of the peak corresponding with the protons of the methoxy carbonyl side groups in the poly(methyl acrylate) polymer (3.50−3.64 ppm). The measured ratio of these integrals (4.82×10^{-2}) corresponds with a ratio of 36.2 alkoxyamine end groups per 1000 monomer units. The theoretical ratio calculated from the M_n measured by SEC is 46.5 per 1000 units. Their comparison provides a yield of substitution of 78%.

*Polystyrene Capped with ^{15}N-Labeled Alkoxyamine Groups **IIb** and **IIIb***. Model compound **IIb** (polystyrene capped with the alkoxyamine end group, substituent = −OH) was prepared by nitroxide-mediated living radical polymerization of styrene initiated with 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidin-^{15}N-4-ol.

Initiator (80 mg, 0.29 mmol), styrene (1.50 g, 14.4 mmol), and toluene (1.1 g) were mixed in a three-necked flask equipped with condenser, magnetic stirrer bar, and argon inlet to obtain a solution of reactants of total volume 2.9 mL. The solution was flushed with argon for 45 min and stirred at 105 °C for 26 h. After the reaction time was over, the reaction mixture was poured into methanol (150 mL). The precipitate was filtered, washed with another 100 mL of methanol, dried, and weighed to determine the yield of 260 mg of the polymer. The monomer conversion of 17.3% corresponds with a theoretical $M_{n,th}$ = 900 g/mol. The M_n found by SEC was substantially higher ($M_{n,exp}$ = 2300 g/mol, PDI = 1.04). The difference can be explained from the method employed for the polymer isolation. Because of the relatively low molar mass of the polymer, there will be a fraction that does not precipitate upon pouring the reaction mixture into methanol. This results in an underestimated conversion and $M_{n,th}$ calculated from the conversion. In addition, the predominant loss of the lower molecular weight fraction increases the apparent $M_{n,exp}$ as measured from the precipitate. The kinetic measurements of the nitroxide-mediated free radical polymerization were not the goal of our work, and the obtained amount of the sample was sufficient for ^{15}N NMR measurement. However, all other samples were isolated by preparative SEC instead of by precipitation.

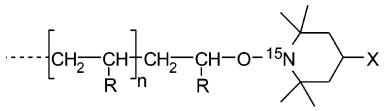
Model compound **IIIb** (polystyrene capped with the alkoxyamine end group, substituent −OTs) was prepared by the radical trapping technique as described in the section Procedure of Copolymerization and Trapping. A solution of styrene (5.73 g, 55.0 mmol), AIBN (49.3 mg, 0.3 mmol), and toluene-4-sulfonic acid 2,2,6,6-tetramethyl-1-(1-methyl-1-phenylethoxy)piperidin-^{15}N-4-yl ester (0.134 mg, 0.3 mmol) in benzene possessing a total volume of 10 mL was degassed by three freeze−vacuum−thaw cycles and heated at 70 °C. Monomer conversion was 3.9% after 22 min. The polymer was analyzed by SEC and found to have an M_n = 3350 g/mol and PDI = 1.8.

Scheme 3. Structure of the Low Molecular Weight Model Compound of the Trapping Products NOP[a]



[a] $-R_1 = -C_6H_5$ or $-COOCH_3$; $-R_2 = -Ch_3$ or $-H$; $-X =$ $-OH$ or $-O-SO_2-C_6H_4-CH_3$.

Scheme 4. General Structure of the Macromolecular Model Compound



Results and Discussion

Use of ^{15}N NMR in the Analysis of Macromolecular Trapping Products. The macromolecular nature of the trapping products complicates their analysis. They differ only in the structure of their terminal unit. Other properties (average composition, molecular weight, etc.) are practically the same and do not allow an analysis based on physical separation.

The described method of analysis of the macromolecular trapping products is based on ^{15}N NMR spectroscopy of the obtained alkoxyamines. We have measured the ^{15}N NMR spectra of low molecular weight alkoxyamines in previous work.[7] Their general structure (Scheme 3) shows that they are low molecular weight models of the macromolecular trapping products NOP.

The ^{15}N NMR spectrum of any low molecular weight model alkoxyamine consists of a single sharp peak.[7] The chemical shift of the peak is affected by structural details of the alkoxyamine. The most significant effect has been observed with the functional groups $-R_1$ and $-R_2$. The simplicity of the ^{15}N NMR spectra and the differences in the chemical shifts provide a possibility to analyze the mixture of the low molecular weight alkoxyamines without their previous separation.

The expected trapping products NOP_A and NOP_S are of macromolecular nature. It was therefore necessary to investigate also macromolecular model compounds (Scheme 4). Higher complexity of their ^{15}N NMR spectra is revealed when compared with the spectra of the low molecular weight alkoxyamines (Figure 1). The spectra consist of multiple broad bands instead of single peaks. The spectral bands of each macromolecular alkoxyamine are located in the region of chemical shifts that corresponds well with the chemical shift of the single peak in the spectrum of its low molecular weight analogue.

The chemical shifts of the low molecular alkoxyamine having the functional group $-R = -C_6H_5$ are 9.7 ppm lower than that of the alkoxyamine having $-R = -COOCH_3$. Spectra of the macromolecular alkoxyamines are compared in a similar manner. Lower and upper limits of the ranges where the spectral bands occur are taken into account. The values of the lower and upper limit of the macromolecular alkoxyamine with $-R = -C_6H_5$ are 11.4 and 10.7 ppm lower, respectively, than the limits found in the spectrum of the alkoxyamine with $-R = -COOCH_3$.

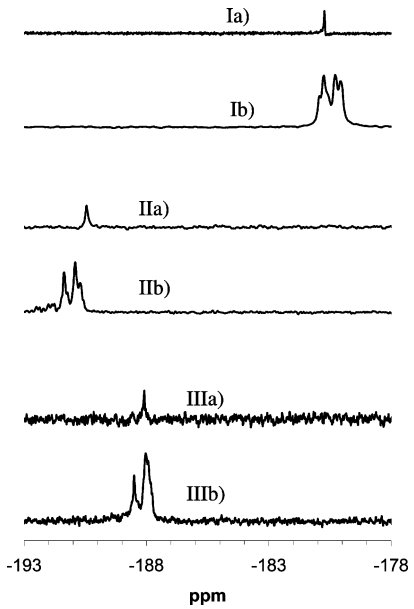


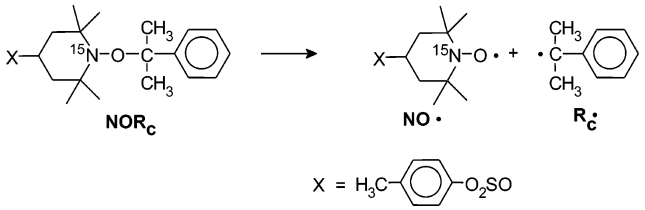
Figure 1. ^{15}N NMR spectra of macromolecular model compounds compared with the spectra of low molecular weight model compounds. **Ia**: low molecular weight, $-R_1 = -H$, $-R_2 = -COOCH_3$, $-X = -OTs$. **Ib**: macromolecular, $-R = -COOCH_3$, $-X = -OTs$. **IIa**: low molecular weight, $-R_1 = -H$, $-R_2 = -C_6H_5$, $X = -OTs$. **IIb**: macromolecular, $-R = -C_6H_5$, $-X = -OTs$. **IIIa**: low molecular weight, $-R_1 = -H$, $-R_2 = -C_6H_5$, $-X = -OH$. **IIIb**: macromolecular, $-R = -C_6H_5$, $-X = -OH$.

The functional group $-X = -OTs$ is present in the alkoxyamines compared above. It is also possible to compare the spectra of macromolecular alkoxyamines with $-R = -C_6H_5$ and differing in their functional group $-X$. The values of the lower and upper limits of the macromolecular alkoxyamine with $-X = -OTs$ are 3.4 and 2.9 ppm lower, respectively, than those in the spectrum of the macromolecular alkoxyamine with $-X = -OH$. A similar comparison between low molecular weight model compounds resulted in a chemical shift difference of 2.3 ppm.[7]

This comparison shows that the differences in the structure of the functional groups $-R$ and $-X$ affect the chemical shifts of the ^{15}N NMR spectra of macromolecular alkoxyamines in the same manner as in the spectra of their low molecular weight analogues. Their complicated nature can be explained by the effect of functional groups located at larger distance from the ^{15}N nucleus. It is well-known from ^{13}C and ^{1}H NMR spectroscopy that the chemical shifts of particular nuclei are affected by the steric configuration of adjacent units. The chemical shift of the macromolecular alkoxyamine in the ^{15}N NMR spectrum is similarly affected by the configuration of groups on the α carbon (terminal unit) and also on more distant atoms (penultimate and antepenultimate units). The macromolecular alkoxyamines are formed by a radical process which is not stereospecific, and they represent a complicated mixture of many stereoisomers. This complexity in the stereochemistry is consequently reflected in the complexity of the ^{15}N NMR spectrum.

The structure of the functional group $-R$ controls the chemical shifts substantially, and spectral bands of alkoxyamines differing in this group are well separated from each other despite their multiplicity and broadening. This result is of high practical importance for our work because it confirms that ^{15}N NMR spectroscopy can be applied in the analysis of macromolecular trapping products.

Scheme 5. Structure of the Thermally Unstable Alkoxyamine NOR_c and Its Decomposition into Trapping Radical NO• and Initiating Radical $R_c^•$



Trapping of Macroradicals by Nitroxyl Radicals Formed "in Situ". The experiments with macromolecular model compounds of the trapping products have shown that the amount of the sample necessary for one measurement is about 10^{-4} mol (sample volume is 1 mL) to achieve sufficient signal-to-noise ratio (SNR) in a reasonable measurement time (12−15 h). The method of radical trapping should allow obtaining this required minimum amount under realistic experimental conditions. The low concentration of macroradicals ($c \approx 10^{-7}$ mol/L) under the conditions of free radical copolymerization sets the necessity to apply a procedure, which enables to accumulate trapping products in the course of the copolymerization.

We have designed a trapping method which is based on the formation of the nitroxide radical in situ from a thermally labile alkoxyamine (Scheme 5)

The process of copolymerization and simultaneous formation of the macromolecular trapping products can be described as follows.

A thermally labile alkoxyamine NOR_c decomposes and forms trapping agent NO• and initiating radical $R_c^•$.

$$NOR_c \xrightarrow{k_{dN}} NO^• + R_c^•$$

The initiating radical $R_c^•$ reacts quickly with monomer A or S to form propagating radical $P_A^•$ or $P_S^•$.

$$R_c^• + M_{A(S)} \rightarrow P_{A(S)}^•$$

The degree of polymerization of the propagating radicals $P_A^•$ and $P_S^•$ increases as they add more monomer molecules. The equilibrium concentration ratio

$$A = \frac{[P_A^•]_e}{[P_S^•]_e}$$

is established due to the cross-propagation reactions

$$P_A^• + M_S \xrightarrow{\bar{k}_{AS}} P_S^•$$

$$P_S^• + M_A \xrightarrow{\bar{k}_{SA}} P_A^•$$

A certain fraction of radicals $P_A^•$ and $P_S^•$ undergoes bimolecular termination to form dead polymer:

$$P_{A(S)}^• + P_{A(S)}^• \xrightarrow{\langle k_t \rangle} D$$

Additional initiator I is present to compensate the loss of the propagating radicals $P_A^•$ and $P_S^•$ by bimolecular

termination. New propagating radicals are formed by fast reaction of the initiating radicals $R_I^\bullet$ with monomers A and S:

$$I \xrightarrow{k_{dI}} 2R_I^\bullet + M_{A(S)} \xrightarrow{2fk_{dI}} P_{A(S)}^\bullet$$

The formation of trapping products proceeds in the reaction of propagating radicals $P_A^\bullet$ and $P_S^\bullet$ with nitroxide radicals $NO^\bullet$ formed in situ:

$$P_{A(S)}^\bullet + NO^\bullet \xrightarrow{k_{cNA(S)}} NOP_{A(S)}$$

The radical trapping must be performed under thermal conditions, where the decomposition of the precursor NOR_c produces a sufficiently large concentration of the trapping agent $NO^\bullet$, and the trapping products NOP_A and NOP_S are still stable enough, so that their eventual decomposition will not interfere with the measured quantity of the radical concentration ratio. Both requirements are fulfilled at a temperature of 70 °C. The estimation of the kinetic data of the decomposition of the alkoxyamines NOR_c, NOP_A, and NOP_S is given in the Supporting Information for the system methyl acrylate−styrene. It proves the fast decomposition of NOR_c as well as the good thermal stability of NOP_A and NOP_S at 70 °C.

The applied trapping with nitroxide radicals formed in situ differs significantly from nitroxide-mediated controlled radical polymerization. In the latter process, the alkoxyamine decomposition, addition of monomers, and nitroxide coupling is repeated many times during the growth of one macromolecule. In contrast, one macromolecular trapping product is formed by one sequence of the elemental reactions mentioned above; i.e., radical trapping is irreversible.

The "in situ" formation of the trapping agent $NO^\bullet$ proceeds homogeneously in the entire reaction volume without any local variation. Its concentration can be simply adjusted by the concentration of precursor NOR_c. Good control over the process of the radical trapping enables to perform it under the conditions, where the macroradicals are predominantly trapped.

It enables to extend the application of the radical trapping to the investigation of the copolymerization process. This is the main advantage of our method in comparison with the trapping performed by direct addition of the trapping agent into the reaction mixture.[2−6] Only low molecular weight trapping products can be prepared by the latter way. The maximum value of their degree of polymerization is eight, and it was achieved by a very cautious tuning of the trapping agent addition.[9]

The details of the importance of the polymerization degree for the determination of the radical concentration ratio A are given in the Supporting Information. The analysis shows, that the ratio A in the presence of the trapping agent $NO^\bullet$ is given by the relation

$$A = \frac{[P_A^\bullet]_e}{[P_S^\bullet]_e} = \frac{\frac{\bar{k}_{SS}}{\bar{r}_S}[M_A] + pk_{cNS}[NO^\bullet]}{\frac{\bar{k}_{AA}}{\bar{r}_A}[M_S] + (1-p)k_{cNA}[NO^\bullet]}$$

where p is the probability that a primary radical adds to monomer A.

When the average degree of polymerization of the trapping products exceeds a lower limit, the ratio A will be independent of the concentration of trapping agent. The ratio A will be then approximated with the equation

$$A = \frac{\bar{k}_{SS}[A]\bar{r}_A}{\bar{k}_{AA}[S]\bar{r}_S}$$

The minimum value of the average polymerization degree depends on particular composition of the monomer feed. It varies from 24 to 50 in the composition range $f_A = 0.15-0.97$ when the system of methyl acrylate−styrene is investigated.

The upper limit of the average polymerization degree is determined by the conditions of the analysis of the trapping products by ^{15}N NMR spectroscopy. The analysis is focused on the alkoxyamine end groups in the sample. The concentration of the end groups decreases with increasing degree of polymerization, and the upper limit of the degree of polymerization is determined by the minimum concentration of the end groups in the sample required for the analysis. Calculations given in the Supporting Information show that the upper limit of the polymerization degree depends on the monomer feed and varies from 51 to 58.

When the trapping proceeds under the conditions of quasi-equilibrium, then the rate of accumulation of the trapping products is determined by the rate of trapping reactions of the two different chain end radicals ($P_A^\bullet$ and $P_S^\bullet$):

$$\frac{\partial[NOP_A]}{\partial t} = k_{cNA}[P_A^\bullet][NO^\bullet]$$

$$\frac{\partial[NOP_S]}{\partial t} = k_{cNS}[P_S^\bullet][NO^\bullet]$$

The ratio of trapping products accumulated during the experiment is then

$$B = \frac{[NOP_A]}{[NOP_S]} = \frac{k_{cNA}[P_A^\bullet]}{k_{cNS}[P_S^\bullet]} = \frac{k_{cNA}}{k_{cNS}}A$$

^{15}N NMR Spectra of Trapping Products. Trapping of macroradicals formed during the copolymerization of methyl acrylate and styrene is performed at various fractions of methyl acrylate (f_A) in the monomer feed. The ^{15}N NMR spectra of the trapping products obtained in these experiments are shown in Figure 2. The appearance of the spectrum depends on the composition of the monomer feed f_A.

Two separate groups of bands can be distinguished in the spectrum of trapping products formed when $f_A = 0.93$ or higher. They are compared with the spectra of trapping products obtained in the homopolymerization of methyl acrylate and styrene (spectra I and VII of Figure 2, respectively). The first group of peaks corresponds with products obtained by trapping of macroradicals possessing a terminal methyl acrylate unit (product NOP_A). They can be found in the region of −179.6 to −181.1 ppm. The relative intensity of these spectral bands decreases significantly with decreasing f_A and cannot be distinguished from the noise line when $f_A \leq 0.86$. The second group can be ascribed to the trapping products derived from macroradical having

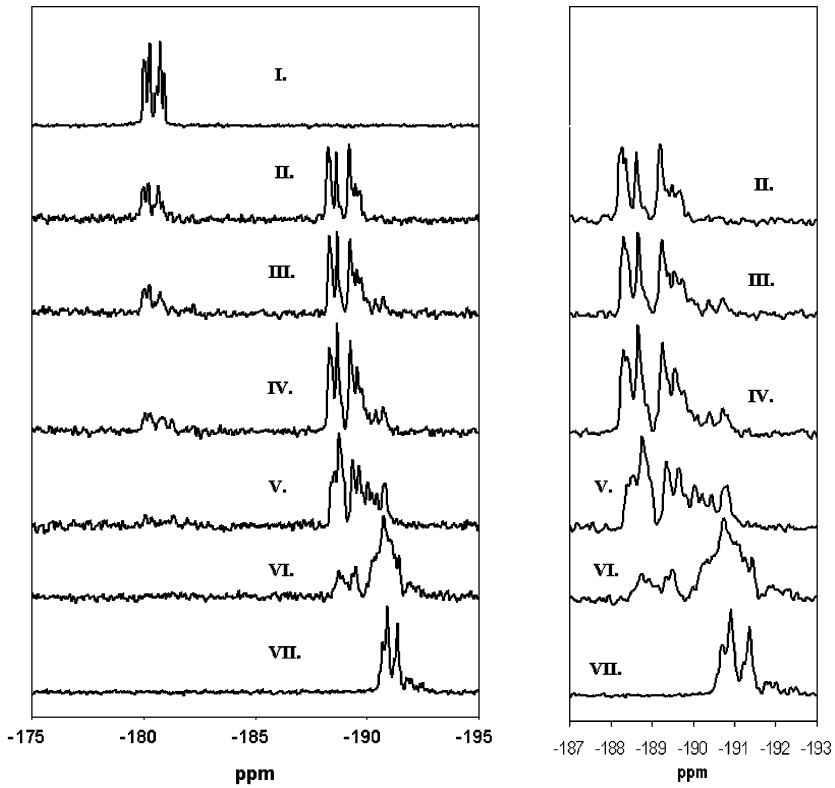


Figure 2. ^{15}N NMR spectra of the trapping products obtained during the copolymerization at various compositions of the monomer feed f_A. I: $f_A = 1.00$; II: $f_A = 0.97$; III: $f_A = 0.96$; IV: $f_A = 0.93$; V: $f_A = 0.86$; VI: $f_A = 0.28$; VII: $f_A = 0.00$. The right-hand side depicts the expanded parts of the spectra in the region −187 to −193 ppm.

styryl terminal unit (product NOP_S). It is located in the region of −192.7 to −188.1 ppm.

The spectral bands ascribed to the products NOP_S are well distinguished from the noise level. Their shape changes with changing f_A. The bands are located in the range from −192.7 to −190.5 ppm when $f_A = 0$. New bands in the range from −190.5 to −188.2 ppm are observed in the spectra when methyl acrylate is present in the monomer feed during the trapping. Their relative intensity increases with increasing f_A, and the intensity of bands in the former region decreases. The spectrum of trapping products obtained at $f_A = 0.97$ has spectral bands related to product NOP_S solely in the region from −190.0 to −188.0 ppm.

This change is explained when the effect of the distant units is taken into account. The spectrum VII is measured for the trapping product having all units (terminal, penultimate, and antepenultimate) derived from styrene. Conversely, trapping products NOP_S formed in the presence of methyl acrylate will possess part of penultimate and antepenultimate units derived from this monomer. These units will affect the ^{15}N NMR spectra of the NOP_S products in a way different from the units derived from styrene. This difference is reflected by change in the location and intensity of the bands in the region from −192.7 to −188.2 ppm.

Radicals $P^{\bullet}_S$ having the penultimate unit derived from styrene ($P^{\bullet}_{SS}$) or from methyl acrylate ($P^{\bullet}_{AS}$) can therefore be identified from the ^{15}N NMR spectra of their trapping products. The mutual concentration ratio of these radicals is given by the equation

$$C = \frac{[P^{\bullet}_{SS}]}{[P^{\bullet}_{AS}]} = r_{SS}s_S\frac{[S]}{[A]}$$

Table 2. Fraction of Radicals $P^{\bullet}_{AS}$ Present in the Reaction Mixture When $f_A = 0.97$ Calculated for Various Values of s_S[a]

s_S	$[P^{\bullet}_{SS}]/[P^{\bullet}_{AS}]$	fraction of $P^{\bullet}_{AS}$ (mol %)
0.94[10]	0.021	97.9
1.10[11]	0.024	97.6
0.59[11]	0.013	98.7
0.41[8]	0.009	99.1

[a] Value of parameter $r_{SS} = 0.73$.

The outcome of the calculation will generally depend on parameters r_{SS} and s_S. The value of parameter s_S is not unambiguously determined, and there are four different values published in the literature. However, in any case this calculation predicts that 97.6−99% of all radicals $P^{\bullet}_S$ will possess a penultimate unit derived from methyl acrylate when f_A is equal to 0.97 (Table 2).

It follows from the above calculation that within the accuracy of the measurement all trapping products NOP_S obtained at $f_A = 0.97$ will possess penultimate units derived from methyl acrylate. They are characterized with ^{15}N NMR spectral bands recorded in the region from −190.0 to −188.0 ppm. On the other hand, spectrum of NOP_S products collected at $f_A = 0$ identifies trapped radicals $P^{\bullet}_S$ having all the penultimate and antepenultimate units derived from styrene. They are located in a separate region from −192.7 to −190.5 ppm. Spectra of trapping products NOP_S obtained at $0.27 \le f_A \le 0.96$ are spread over the entire range −192.7 to −188.2 ppm. Their complexity does not allow an exact assignment to the particular products obtained from radicals $P^{\bullet}_{AS}$ or $P^{\bullet}_{SS}$.

The terminal units in the products NOP_A and NOP_S can be clearly detected from the ^{15}N NMR spectrum because the corresponding spectral bands are located

Table 3. Experimentally Determined Estimates of the Radical Concentration Ratio *A* in the Copolymerization of A and St at 70 °C and Their Comparison with Values Predicted by the Implicit Penultimate Model Using Two Different Sets of Parameters

f_A	$A_{measured}$	A_{calcd} (set 1)	A_{calcd} (set 2)
0.97	≤0.45	2.70	0.106
0.96	≤0.30	2.31	0.083
0.93	≤0.17	1.72	0.051
0.86	∼0	1.14	0.003

in separate regions for any value of f_A. The concentration ratio $B = [NOP_A]/[NOP_S]$ is obtained by integration of the spectral bands. The results are collected in Table 1. As indicated above, the radical ratio A could be estimated if the values of the constants k_{cNA} and k_{cNS} are known. Accurate values of the constants are not measured yet, but they can be estimated from the rate constants measured for the low molecular weight analogues of macroradicals $P^{\bullet}_{MA}$ and $P^{\bullet}_{S}$.[12] The coupling of the methoxycarbonylethyl radical (analogue of $P^{\bullet}_{MA}$) with nitroxide proceeds faster than coupling of the phenyl ethyl radical (analogue of $P^{\bullet}_{S}$). This comparison leads us to the conclusion that

$$\frac{k_{cNA}}{k_{cNS}} \geq 1 \quad \text{and} \quad B \geq A$$

Values of B determined experimentally represent an estimation of the upper limit of the radical concentration ratio A.

The information about the value of A provides a useful tool for the critical evaluation of copolymerization models. A brief illustration of its discriminating power can be exemplified, when two sets of parameters are tested and their ability to predict correct values of A is compared. Both sets predict the copolymer composition and average propagation rate constants equally well in the copolymerization of methyl acrylate and styrene at 50 °C. The first set of parameters is determined by Davis et al.[10] The implicit penultimate model is applied for the description of the copolymerization:

set 1:

$$r_{AA} = r_{SA} = 0.19;\ r_{SS} = r_{AS} = 0.73;\ s_A = 0.11;$$
$$s_S = 0.94;\ k_{AAA} = 1500\ \text{L/(mol s)};$$
$$k_{SSS} = 218\ \text{L/(mol s)}$$

The same process is described by Schoonbrood[11] using another set of parameters:

set 2:

$$r_{AA} = r_{SA} = 0.19;\ r_{SS} = r_{AS} = 0.73;$$
$$s_A = s_S = 0.41;\ k_{AAA} = 10700\ \text{L/(mol s)};$$
$$k_{SSS} = 258\ \text{L/(mol s)}$$

The authors have used different methods for the determination of the homopropagation rate constant of methyl acrylate (k_{AAA}).

Values of A calculated using both sets are compared with the experimentally determined upper limit for various f_A.

It is seen from Table 3 that the first set of parameters overestimates the A value. The second one provides A values lower than the upper limit and is therefore closer to reality.

Application of the experimentally determined upper limit of A in a more detailed analysis of several copolymerization models will be the subject of a separate publication.

Conclusion

Trapping of macroradicals in the process of free radical copolymerization is possible when the trapping agent—a stable nitroxyl radical—is formed in situ from a thermally labile precursor, i.e., an alkoxyamine. This method is applied in the trapping of macroradicals formed during the copolymerization of styrene and methyl acrylate.

The macromolecular trapping products are accessible for analysis via ^{15}N NMR spectroscopy. This method enables to distinguish the structure of the terminal segments of trapped macroradicals. Peaks corresponding to the styrene and methyl acrylate terminal segments are well separated. Their correct assignment is performed by comparison with the ^{15}N NMR peaks of model compounds prepared by independent methods. Integration of the spectrum enables to estimate the upper limit of the concentration ratio of propagating radicals having different terminal units.

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Supporting Information Available: Calculations that support the experimental study and indicate the boundary conditions on a kinetic basis. This material is available free of charge via the Internet at http://pubs.acs.org.

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