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^{15}N NMR Spectroscopy of Labeled Alkoxyamines. ^{15}N-Labeled Model Compounds for Nitroxide-Trapping Studies in Free-Radical (Co)polymerization

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Eight ^{15}N-labeled derivatives of 1-ethoxy-2,2,6,6-tetramethylpiperidine were synthesized in order to investigate the effects of their structural units on ^{15}N NMR spectra. A single peak is found for each alkoxyamine. The chemical shift depends extensively on the nature of the α carbon atom of the alkoxy group. The remote functional group attached to position 4 of the piperidine ring has a smaller but still significant effect. The results of the ^{15}N NMR measurements are supported by the detection of the N−H and N−C spin−spin coupling from the ^{1}H and ^{13}C NMR. The investigated alkoxyamines are model compounds for the radical-trapping products of styryl, methyl methacryloyl, α-methylstyryl, and methyl acryloyl radicals by ^{15}N-labeled nitroxides. The potential of ^{15}N NMR spectroscopy to analyze such products is discussed. In addition, it is shown that the ^{13}C chemical shifts of the α carbon atom of the alkoxy group fall in an empty part of the ^{13}C NMR spectrum, which allows the identification of trapped (macro)radicals via natural abundance ^{13}C NMR.

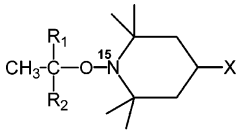
Introduction

The present work describes the preparation and NMR spectroscopy of substituted hydroxylamines (alkoxyamines) having the general formula depicted in Scheme 1.

The investigated compounds participate in many important free-radical reactions. They are known as initiators in the nitroxide-mediated controlled radical polymerization[1] and as products of radical trapping.[2] Radical trapping is used in the investigation of complex radical reactions. It is based on the conversion of a reactive carbon-centered (macro)radical into an alkoxyamine stable at ambient conditions (Scheme 2).

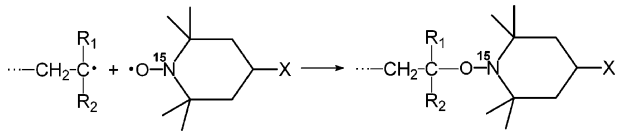
Radical trapping is followed by the analysis of the trapping products. Determination of the substituents R_1 and R_2 is of particular importance. These substituents characterize the structure of the reactive center of the original (macro)radical. Since they are located in the vicinity of the nitrogen atom of the trapping product, they may also affect the chemical shifts of the ^{15}N nuclei of the alkoxyamine. ^{15}N NMR spectroscopy can therefore be utilized for analysis of the trapping products. However, the ^{15}N NMR of substituted hydroxylamines has not been studied to date.[3] ^{15}N-labeled alkoxyamines of the general structure shown in Scheme 1 are synthesized for the first time in our work and their characterization by NMR produced original results. The compounds studied were chosen as low molecular weight models resembling the terminal unit structure of the macromolecular trapping products. The alkoxyamines resemble trapping products of terminal units formed by methyl methacrylate (**I** and **II**), methyl acrylate (**III** and **IV**), α-methyl styrene (**V** and **VI**), and styrene (**VII** and **VIII**). The effects of the various

SCHEME 1. Substituted Alkoxyamines Studied by ^{15}N NMR Spectroscopy in This Work



		X = -OH	X = -OSO$_2$-C$_6$H$_4$-CH$_3$
R_1 = -COOCH$_3$	R_2 = -CH$_3$	**I**	**II**
	R_2 = -H	**III**	**IV**
R_1 = -C$_6$H$_5$	R_2 = -CH$_3$	**V**	**VI**
	R_2 = -H	**VII**	**VIII**

SCHEME 2. Formation of a Macromolecular Alkoxyamine by Trapping of a Macroradical with 2,2,6,6-Tetramethylpiperidin-1-oxyl Derivatives



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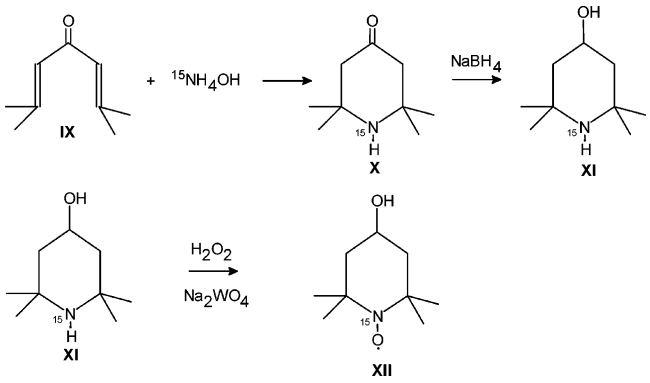
SCHEME 3. Preparation Scheme of 4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl- ^{15}N



substituents on the ^{15}N NMR shifts are subsequently compared, and the ability of ^{15}N NMR spectroscopy to identify the structure of trapping products is tested in this way.

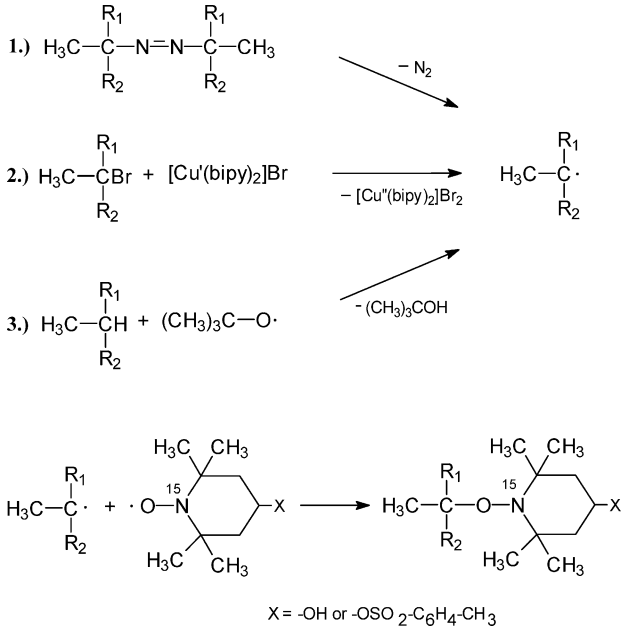
Discussion

Synthesis of the ^{15}N-Labeled Model Compounds. Stable free-radical 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl-*^{15}N* **(XII)** is used as a precursor for the synthesis of the alkoxyamines. The radical is prepared in three synthetic steps depicted in Scheme 3. The first step, synthesis of the 2,2,6,6-tetramethyl-4-piperidinone-*^{15}N* **(X),** is performed according to Yost et al.[4] Reduction of **X** by sodium borohydride according to Lutz et al.[5] is applied to obtain 2,2,6,6-tetramethyl-4-piperidinol-*^{15}N* **(XI)**. The selective oxidation of this cyclic amine using the procedure described by Rosantsev[6] provides the desired radical **XII**. The application of this scheme allowed the preparation of 12.1 mmol of **XII** from 22.1 mmol of ammonium-*^{15}N* hydroxide. The most expensive reactant (ammonium-*^{15}N* hydroxide) was utilized with efficiency higher than 50%.

Various methods for the conversion of **XII** into the desired alkoxyamines **I**−**VIII** were tested using the unlabeled analogues of **XII** and **XIII**. The preferred procedures of the alkoxyamines' syntheses are based on the coupling of the nitroxyl radical with an alkyl radical of suitable structure formed in situ. The details of the preparation are determined by the particular way of alkyl radical formation. Three alternatives are applied in this work as shown in Scheme 4: (1) the decomposition of a suitable azo compound, (2) the reaction of an alkylbromide with a Cu^{I} complex, (3) peroxide decomposition and subsequent hydrogen abstraction from a suitable hydrocarbon.

(1) Alkoxyamine **I** is prepared by heating of **XII** with dimethyl 2,2′-azobisisobutyrate. The reaction temperature and time are crucial parameters for the efficiency of the synthesis. Heating of equivalent amounts of the reactants at 85 °C for 16 h failed due to the low stability of **I** under these conditions. The reaction temperature was

SCHEME 4. Three Alternative Methods for the Generation of Carbon-Centered Radicals Employed in the Synthesis of Alkoxyamines



decreased to 65 °C, and a large excess of the azo compound was applied. The reaction is then completed in 4 h and **I** is isolated with sufficient yield. Application of this method for the preparation of other alkoxyamines is restricted by the limited availability of suitable azo compounds.

(2) The method utilizing alkyl bromides in the alkoxyamine preparation has been developed by Matyjaszewski and co-workers. The availability of a large variety of bromo-substituted compounds enhances its versatility, which has been demonstrated by the synthesis of various alkoxyamines from 2,2,6,6-tetramethylpiperidin-1-oxyl.[7] This method is applied in the syntheses of the alkoxyamines **I**−**IV.** The experiments with unlabeled analogues of nitroxyl radicals **XII** and **XIII** have shown that it is advantageous to decrease reaction times to periods of 2−3 h instead of 4−12 h reported by the authors of this method. It is known that −OH-containing solvents accelerate the Cu^{I}-catalyzed cleavage of the C−Br bond located on the α carbon of 2-bromoesters.[8,9] This fact is utilized in the preparation of the thermally unstable product **I**. Substitution of benzene by 2-ethoxyethanol as solvent allowed the reaction temperature to be decreased to 20 °C.

(3) Peroxide decomposition has been applied in the preparation of **V** and **VII.** 1-(2,2,6,6,-Tetramethyl-4-hydroxypiperidin-1-oxy)-1-phenylethane **(V)** has been prepared according to the procedure applied by Hawker.[10] The 1-phenylethyl radicals have been generated by the thermal decomposition of di-*tert*-butyl peroxide and subsequent reaction of the *tert*-butoxy radicals with the

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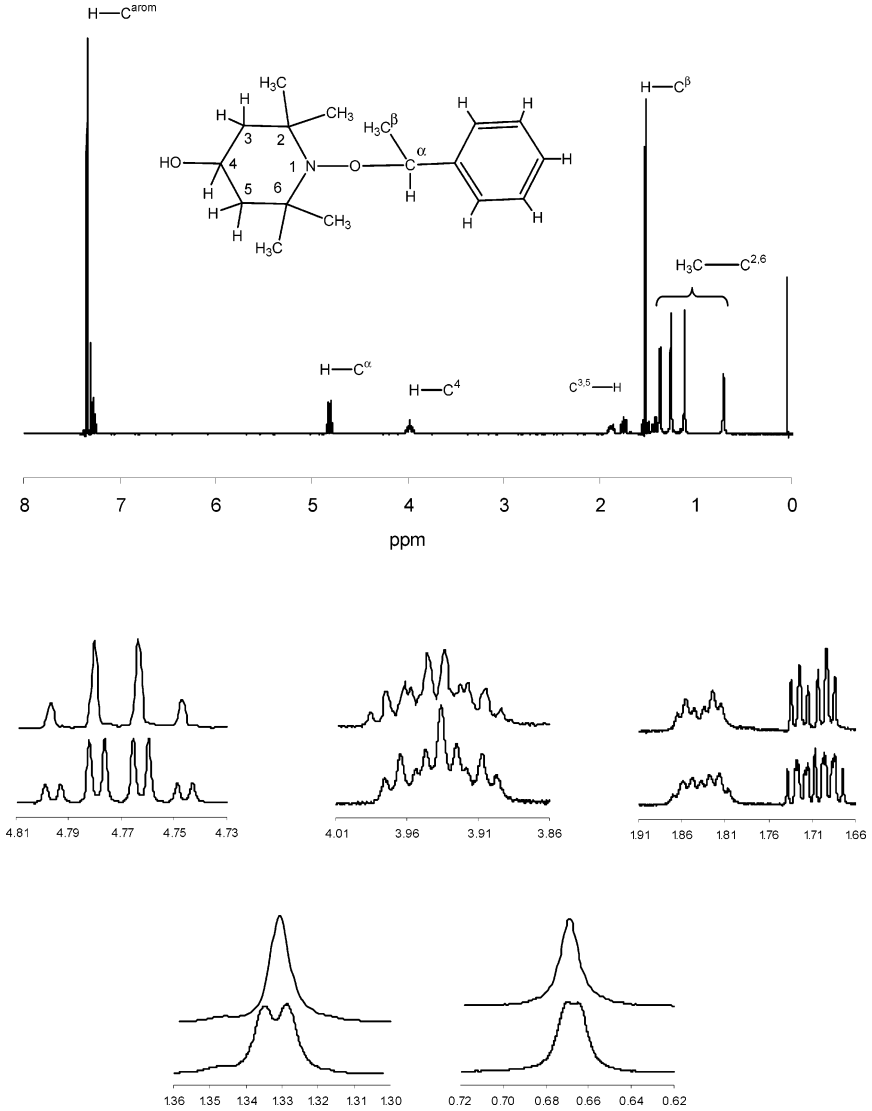

FIGURE 1. ^{1}H NMR spectrum of the alkoxyamine (**VII**). Insets: lower line, spectrum of ^{15}N-labeled compound; upper line, spectrum of the unlabeled analogue.

ethylbenzene. The authors of this procedure recommend the preparation at the temperature of ethylbenzene reflux (ca. 136 °C). A mixture of alkoxyamines is obtained at this temperature. The ^{1}H NMR spectrum contains peaks, which can be ascribed to the unlabeled analogue of **V**[11] and another group of peaks corresponding to 1-methoxy-4-hydroxy-2,2,6,6-tetramethylpiperidine.[12] The latter compound is formed by coupling of **XII** with a methyl radical generated by β scission of the *tert*-butoxy radical at 136 °C. Decrease of the reaction temperature to 115 °C suppresses this side reaction. The preparation of the thermally less stable 2-(2,2,6,6,-tetramethyl-4-hydroxypiperidin-1-oxy)-2-phenylpropane **(VII)** is performed according to Connoly et al.[13] using photolytic decomposition of *tert*-butyl peroxide at ambient temperature in the presence of 2-phenylpropane and **XII**.

The compounds **II** and **VI** are prepared by esterification of the 4-hydroxy functional group of the corresponding alkoxyamine.

The presence of the hydroxyl or *p*-methylphenylsulfonyl functional group in the position 4 of the piperidine ring affects advantageously the melting points of the prepared alkoxyamines. They are in the range of 73−135 °C. This feature enables to purify the studied compounds efficiently by a combination of flush chromatography and recrystallization.

Effect of the ^{15}N Labeling on ^{1}H and ^{13}C NMR Spectra of the Alkoxyamines. The synthesized alkoxyamines were characterized by routine ^{1}H and ^{13}C NMR at first. The effect of the labeling with the ^{15}N isotope on the spectra can be revealed by the comparison of labeled and unlabeled compounds. The spectra are measured under conditions that enable the detection of spin−spin coupling of the ^{15}N nucleus with the nuclei of hydrogen or carbon. The ^{1}H and ^{13}C NMR spectra of the 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidin-*^{15}N*-4-ol (**VII**) are compared with its unlabeled analogue in Figures 1 and

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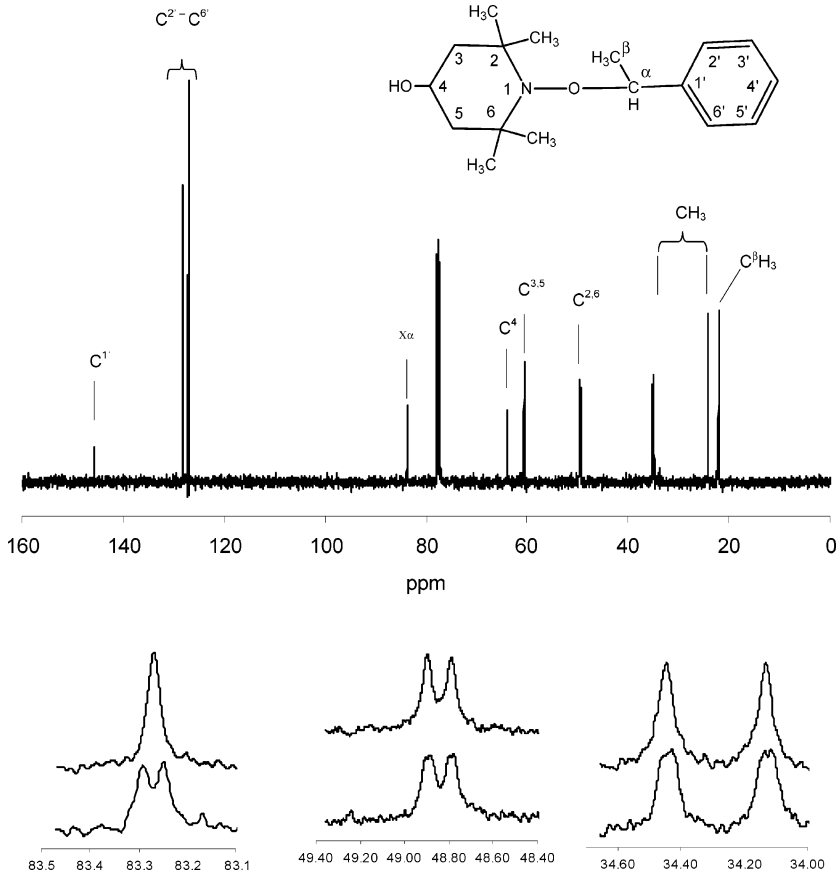

FIGURE 2. ^{13}C NMR spectrum of the alkoxyamine (**VII**). Insets: lower line, spectrum of ^{15}N-labeled compound; upper line, spectrum of the unlabeled analogue.

2. The spectral peaks of both compounds have the same chemical shifts corresponding with the structural units of the molecule. Magnetic properties of ^{15}N and ^{14}N nuclei result in different spin−spin coupling and the multiplicity of some peaks in the same position differs for labeled and unlabeled compounds. The proton located on the α carbon of the alkoxy group resonates at 4.77 ppm. The coupling with the vicinal protons of the neighboring methyl group produces a quartet. This pattern is observed in the spectrum of the unlabeled compound. Labeling with the ^{15}N isotope causes additional splitting of the signal, and eight lines (quartet of doublets) are observed. The absolute value of 2.3 Hz can be estimated for the interaction constant of the heteronuclear N−H spin−spin coupling in this position of the molecule. The bands at 0.67, 1.07, 1.22, and 1.33 ppm are assigned to protons of the methyl groups attached to the piperidin-4-ol ring in the positions 2 and 6. They form broad singlets in the spectrum of the unlabeled **VII**. However, bimodal bands are observed in the spectrum of the labeled compound at 1.33 and 0.67 ppm. The protons in the positions 3, 4, and 5 of the ring form a spin system characterized by multiplets in the ranges 3.89−3.98 ppm (C^4-H) and 1.37−1.51 ppm (C^3-H and C^5-H). The patterns of these multiplets differ for the labeled **VII** and its unlabeled analogue. The differences indicate that the spin of the ^{15}N nucleus affects the NMR resonance of the protons in the entire piperidin-4-ol ring. On the other hand, no effect of the labeling is observed on the signals of the protons attached to the aromatic ring and to the β carbon of the alkoxy group. The strongest effect is observed on the proton present at the α carbon of the alkoxy group. The absolute values of the coupling constants found for the measured alkoxyamines are summarized in Table 1.

The effect of the ^{15}N labeling on the ^{13}C spectra is clearly found on the resonance signal of the α carbon at 83.27 ppm. The splitting in two lines is clearly observed for the ^{15}N-labeled **VII** and corresponds to an absolute value of the interaction constant equal to 4.00 Hz. The unlabeled compound produces only a single line. The resonance signals at 48.80, 48.90, 34.13, and 34.45 ppm are also affected by the nucleus ^{15}N. These lines are not split, but broadened forming peaks with flat tops. The analogous signals of the unlabeled compound are sharp narrow lines resembling Lorenz curves.

^{15}N NMR Spectra of the Alkoxyamines. The ^{15}N nucleus interacts with numerous atoms in the molecule of the alkoxyamine, as the previous comparison has shown. The spin−spin coupling should produce a complicated multiplet on the ^{15}N NMR spectrum. A broad band is found as a result of the overlap of single lines and the limited resolution of the instrument. Application of proton decoupling eliminates the complications caused by N−H heteronuclear interactions. A narrow single peak is obtained under these conditions. The effect of the proton decoupling on the ^{15}N NMR spectrum of alkoxyamines is exemplified in Figure 3.

The previous results show that the ^{15}N nucleus affects the NMR resonance of the proton and ^{13}C isotope at the α position of the alkoxy group. The effect of the substit-

TABLE 1. Chemical Shifts and Absolute Values of Spin−Spin Coupling Constants with ^{15}N Isotope[a]

alkoxyamine	R_1	R_2	X	δ *H*-C$^{\alpha}$ (ppm)	$\|J_{H-N}\|$ (Hz)	δ C$^{\alpha}$ (ppm)	$\|J_{C-N}\|$ (Hz)
I	$-COOCH_3$	$-CH_3$	−OH	n.a.	n.a.	81.47	3.05
II	$-COOCH_3$	$-CH_3$	−OTs	n.a.	n.a.	81.47	3.06
III	$-COOCH_3$	−H	−OH	4.36	2.6	81.69	4.20
IV	$-COOCH_3$	−H	−OTs	4.28	2.6	81.70	4.20
V	$-C_6H_5$	$-CH_3$	−OH	n.a.	n.a.	80.00	3.05
VI	$-C_6H_5$	$-CH_3$	−OTs	n.a.	n.a.	80.24	3.43
VII	$-C_6H_5$	−H	−OH	4.77	2.3	83.27	4.00
VIII	$-C_6H_5$	−H	−OTs	n.a.[b]	n.a.[b]	83.48	3.80

[a] The quantities are measured for carbons in the α position of the alkoxy group and the adjacent hydrogen if present. [b] Determination not possible due to the peak overlap.

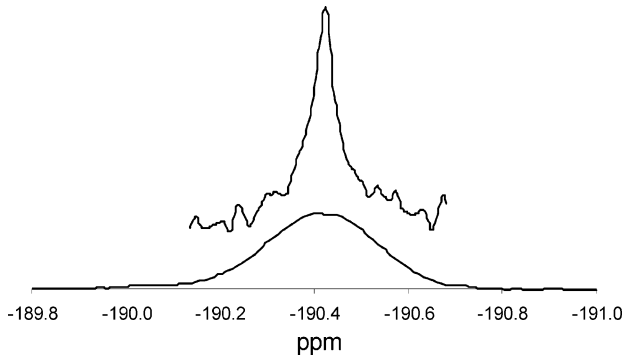

FIGURE 3. Normalized ^{15}N NMR spectrum of the alkoxyamine **(VIII)**. Effect of the proton decoupling on the signal: lower line, without decoupling, 8000 scans; upper line, decoupled, 500 scans.

TABLE 2. ^{15}N NMR Chemical Shifts of the Alkoxyamines I−VIII

alkoxyamine	R_1	R_2	X	chemical shift (ppm)
I	$-COOCH_3$	$-CH_3$	−OH	−198.5
II	$-COOCH_3$	$-CH_3$	−OTs	−200.7
III	$-COOCH_3$	−H	−OH	−177.8
IV	$-COOCH_3$	−H	−OTs	−180.7
V	$-C_6H_5$	$-CH_3$	−OH	−200.9
VI	$-C_6H_5$	$-CH_3$	−OTs	−203.0
VII	$-C_6H_5$	−H	−OH	−188.1
VIII	$-C_6H_5$	−H	−OTs	−190.4

uents present on this atom on the NMR resonance of the ^{15}N isotope can also be anticipated. It is investigated by measurement of the ^{15}N NMR chemical shifts of alkoxyamines having various structural units $-R_1$ and $-R_2$. Since the ^{15}N nucleus affected the ^{1}H NMR resonance of the remote protons located on the piperidin-4-ol ring, it is also expected that remote nuclei will affect the ^{15}N NMR resonance. The effect of the remote group is tested by ^{15}N NMR measurements of alkoxyamines possessing a functional group −X in the 4-position of the piperidine ring.

The set of studied compounds is designed by variation of the structural units R_1, R_2, and X. Two alternatives are chosen for each substituent resulting in eight different compounds. The chemical shifts of the single peak ^{15}N NMR spectra are shown in Table 2. The effect of each substituent on the ^{15}N NMR spectrum can be evaluated by comparison of the pairs of alkoxyamines differing in one substituent of interest and having identical other structural units.

Effect of Substituent −X. The model alkoxyamines having the same substituents R_1 and R_2 are grouped in pairs and the differences in their chemical shifts are related to the difference in the nature of substituent X (Table 3). It is seen, that the substitution of the hydrogen by *p*-toluenesulfonyl in the hydroxyl functional group always results in a decrease of the chemical shift values by 2.1−2.9 ppm. The nature of the substituents R_1 and R_2 has a minor effect on this difference.

TABLE 3. Effect of the Structure of Substituent X on the Position of the Resonance Peak in the ^{15}N NMR Spectrum Measured as the Difference in the Chemical Shifts in Pairs of Model Alkoxyamines

pair of alkoxyamines	−X	$-R_1$	$-R_2$	difference in chemical shift (ppm)
I	−OH	-$COOCH_3$	$-CH_3$	2.2
II	−O-Ts			
III	−OH	$-COOCH_3$	−H	2.9
IV	−OTs			
V	−OH	$-C_6H_5$	$-CH_3$	2.1
VI	−OTs			
VII	−OH	$-C_6H_5$	−H	2.3
VIII	−OTs			

TABLE 4. Effect of the Substituents of the α Carbon on the ^{15}N NMR Chemical Shift

pair of alkoxyamines	$-R_2$	$-R_1$	−X	difference in chemical shift (ppm)
I	−H	$-COOCH_3$	−OH	20.7
III	$-CH_3$			
II	−H	$-COOCH_3$	−OTs	20.0
IV	$-CH_3$			
V	−H	$-C_6H_5$	−OH	12.8
VII	$-CH_3$			
VI	−H	$-C_6H_5$	−OTs	12.6
VIII	$-CH_3$			

Effect of the Substituents R_1 and R_2. The effects of these two functional groups cannot be evaluated separately, in contrast to the substituent X. The largest differences in the ^{15}N NMR chemical shifts are found in pairs of the alkoxyamines differing in structural unit $-R_2$. The extensive effect of the α methyl group is revealed in Table 4. This substitution also affects the quality of the carbon atom localized in the α position with respect to the oxygen atom of the alkyloxy functional group. The observed effect of substituent $-R_2$ can be interpreted as the difference in chemical shift values between the alkoxyamines having a secondary ($-R_2 = -H$) and a tertiary α carbon ($-R_2 = -CH_3$).

The presence or absence of an α methyl group also determines the effect of the substituent $-R_1$ on the ^{15}N NMR chemical shift. Table 5 shows that the effect of $-R_1$ in alkoxyamines with a secondary α carbon is much stronger than in the analogous compounds having a

TABLE 5. Effect of the Substituent $-R_1$ on the ^{15}N NMR Chemical Shifts[a]

pair of alkoxyamines	$-R_1$	$-R_2$	$-X$	difference in chemical shift (ppm)
I	$-COOCH_3$	$-CH_3$	$-OH$	2.4
V	$-C_6H_5$			
II	$-COOCH_3$	$-CH_3$	$-OTs$	2.3
VI	$-C_6H_5$			
III	$-COOCH_3$	$-H$	$-OH$	10.3
VII	$-C_6H_5$			
IV	$-COOCH_3$	$-H$	$-OTs$	9.7
VIII	$-C_6H_5$			

[a] Chemical shift differences found in pairs of alkoxyamines having $-R_1$ methoxycarbonyl or phenyl.

tertiary α carbon. The presence of a phenyl group on the secondary α carbon results in chemical shift values ca. 10 ppm lower compared to compounds having a methoxycarbonyl group in the same position. However, the same structural difference between the compounds with a tertiary α carbon is reflected in a decrease of the chemical shift value by only 2.3−2.4 ppm.

The comparison of chemical shifts described above reveals a high sensitivity of the ^{15}N isotope of the piperidine ring to the structural details of substituents attached in the various positions of the molecule. This result is in accordance with the detection of spin−spin coupling on ^1H and ^{13}C NMR spectra. The strongest effect is observed on the α carbon atom of the alkoxy group. The ^{15}N NMR measurements confirmed that the steric and electronic effects of units $-R_1$ and $-R_2$ impose a combined influence on the ^{15}N NMR chemical shift. The influence of the remote $-X$ functional group is weaker but significant and is in accordance with the remote interactions of the ^{15}N nucleus detected by the observation of N−H spin−spin coupling.

^{15}N NMR spectra of the measured alkoxyamines present narrow single peaks. Differences in chemical shifts are large enough to prevent an overlap of peaks of different alkoxyamines. This feature can be practically exploited in the detection and analysis of various alkoxyamines in a mixture possessing different structural units. The strong effect of the substituents located on the α carbon atom is of special importance. They represent the structure of the reactive site of the original (macro) radical converted into the alkoxyamine in the process of radical trapping (Scheme 2). The efficiency of trapping in the investigation of complex radical reactions is already proven by Rizzardo et al.[14] and by Busfield et al.[15−18] Identification of 8 different radicals formed in the system of ethyl vinyl ether and methyl methacrylate during the initiation is a good example. However, application of liquid chromatography for the analysis restricts their method to low molecular weight trapping products. Our results open the possibility to use ^{15}N NMR as an alternative analytical tool. This method enables to also analyze alkoxyamines that cannot be separated physically. It is expected that this situation will occur after the trapping of macroradicals, because different terminal units of the macromolecular alkoxyamines formed are attached to chains having the same average size and composition. The results obtained by ^{15}N NMR measurements may enable to discriminate among various possible alkoxyamines by extrapolation of the information about the chemical shifts of low molecular weight model compounds to their macromolecular analogues. Low molecular weight model compounds have been applied for the assignment of the characteristic ^1H and ^{13}C NMR chemical shifts to different functional groups of polymers in the work of Kolbert et al.[19,20] The authors have used these assignments to discriminate among vinyl, vinylidene, and vinylene end groups formed during extrusion of ethylene−propylene copolymer. Due to the specific chemical shifts of the end groups, Kolbert and co-workers were able to quantify the occurrence of the various end groups using natural abundance ^{13}C NMR. The polymers in their study had molar masses in the range of $10^4 < M_n < 10^5$. In our work, it is clear that the trapping of the radicals leads to a very specific chemical shift of the α carbon atom of the alkoxy group into an empty part of the (polymer) ^{13}C NMR spectrum. The presence of the electron-withdrawing nitroxide leads to chemical shifts in the range of 80−84 ppm, where the exact peak position is controlled by the nature of the other substituents (see Table 1). This could be used as an additional method to quantify the radical chain ends in a free radical copolymerization. Similarly, the discrimination among five membered and six membered cycles in the structure of the polymer chain formed by the cyclopolymerization of diallyldimethylammonium chloride is performed by assignment of ^{15}N NMR chemical shifts using low molecular weight model compounds. The exclusive formation of five-membered rings has been proven.[21] Bevington[22] has applied an analogous method in the investigation of fragments of AIBN attached to macromolecules during the process of polymerization. He proved that during initiation $(CH_3)_2(CN)C-$ is the only initiator fragment incorporated in the polymer. Our results enable to extend the application of ^{15}N NMR spectroscopy to the investigation of products formed during the trapping of macromolecular radicals.

Conclusions

Synthetic methods developed by various research groups in the past have been optimized for the preparation of ^{15}N labeled derivatives of 1-ethoxy-2,2,6,6-tetramethylpiperidine. These methods enabled to prepare a set of 8 compounds by variation of three structural units. The effects of the units on the ^{15}N NMR spectra are systematically evaluated as relation of the chemical shift differences to the structural differences in pairs of the particular compounds.

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The most extensive change of the ^{15}N NMR chemical shift is found with the structural variations altering the nature of the α carbon atom of the alkoxy group. Substitution of hydrogen for methyl transforms the secondary carbon into a tertiary one and causes the largest change in the chemical shift in the ^{15}N NMR spectrum. The nature of the functional group (methoxycarbonyl or phenyl) attached to the α carbon has also a significant, but somewhat smaller effect. The ^{15}N isotope is separated from the α carbon only by the oxygen atom in the alkoxyamine and mutual effects of their nuclei on the NMR resonances are not surprising. It is also confirmed by the detection of the N−C and N−H spin−spin coupling between the ^{15}N and α carbon or proton attached to the α carbon, respectively.

The effect of the substituents attached to the α carbon will enable the product analysis after radical trapping. The carbon in the α position represents the reactive center of the trapped radical. The chemical shifts of the trapping products may provide information about the structure of the radical. This sensitivity in ^{15}N NMR is combined with the simplicity of the single peak spectra. It provides possibilities to analyze complex mixtures of trapping products without preliminary separation. The features mentioned above open possibilities to use ^{15}N NMR spectroscopy in the investigation of complex radical reactions.

The ^{15}N isotope also interacts with the remote nuclei in the alkoxyamine molecule as proven by the detection of N−H spin−spin coupling in ^{1}H NMR spectra. The remote functional group attached to the piperidine ring in the 4-position has a relatively small but significant effect on the ^{15}N NMR chemical shift. The difference between the chemical shifts caused by the variation of the remote functional unit is still large enough to avoid overlap of the peaks and can also be utilized for the analysis.

Finally, due to the presence of the nitroxide-substituent in the alkoxyamine, the chemical shifts of the α carbon atom of the alkoxy groups in ^{13}C NMR are in a part of the spectrum (80−84 ppm) that is quite empty. This may provide an additional tool for the identification and quantification of trapped (macro)radical chain ends using natural abundance ^{13}C NMR.

Experimental Section

All experimental details can be found in the Supporting Information.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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