Di-*tert*-alkyl Nitroxyl Radicals. Synthesis, Physical Properties and Applications as Inhibitors of Vinyl Polmerization at Elevated Temperatures

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Hydrogenation of Alkenes and Alkynes, Di-*tert*-alkyl Amines, Di-*tert*-alkyl Nitroxyl (Aminoxyl) Radicals, Polymerization Inhibitors

Stable di-*tert*-alkylnitroxyl radicals, *tert*-butyl-*tert*-pentylnitroxyl (**4a**), di-*tert*-pentylnitroxyl (**4b**) and *tert*-octyl-tert-pentylnitroxyl (**4c**), the homologs of di-*tert*-butylnitroxyl (**1**), were synthesized from *tert*-alkyl amines **7a-c** via the 3-*tert*-alkylamino-3-methyl-1-butynes **8a-c**. Oxidation of **8a,b** with hydrogen peroxide lead to relatively unstable N-*tert*-alkyl-N-(1,1-dimethyl-prop-2-ynyl)nitroxyl radicals **15a,b**. The thermal stability, vapor pressure data, ultraviolet, visible and electron paramagnetic resonance spectra of **4a-c** were recorded. The radicals were explored as potential inhibitors of unwanted alkene polymerization reactions at elevated temperatures, in comparison with the aliphatic di-*tert*-butyl nitroxyl (**1**), the alicyclic nitroxyl radicals 2,2,6,6-tetramethylpiperidin-1-oxyl (**2**) and 4-hydroxy-2,2,6,6-tetramethyl-piperidin-1-oxyl (**3**), some commercial polymerization inhibitors, such as diethyl-hydroxylamine (Pennstop, **16**), ammonium salt of N-hydroxy-N-nitrosobenzenamine (Cupferron, **17**), bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin 770, **18**), and the well-known spin traps 2-methyl-2-nitrosopropane (**19**) and *tert*-butylhydroxylamine (**20**).

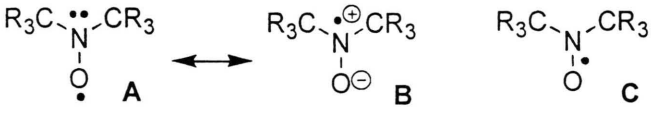
Introduction

Organic nitroxyl radicals (aminoxyls, also called by a misnomer nitroxides) have been known since the beginning of this century [1–3]. This esoteric class of compounds received little attention until the early sixties when the aliphatic di-*tert*-butylnitroxyl radical [4–7] (**1**) and the series of stable heteroalicyclic nitroxyl radicals with piperidine, pyrroline and pyrrolidine rings [1–3] became readily available. Since that time nitroxyl radicals have been extensively explored in organic chemistry, medicinal chemistry, biology and industry. Thus, in addition to several monographs, [1–3,8–16] there have been published more than 200 review articles covering almost every possible theoretical and practical aspect related to these subjects [17–26].

Nitroxyl radicals can be represented by two resonance structures **A** ↔ **B** or simply depicted by the structure **C**.

The nitrogen-oxygen bond in the nitroxyl molecules is essentially a one-and-a-half bond. According to semi-empirical calculations [27] using the SUHF INDO method, 73% of the spin density is localized on the oxygen atom. The stability of nitroxyl radicals is mainly determined by the extent they can undergo disproportionation reactions. Thus, the dialkyl nitroxyls, which have either primary or secondary alkyl groups at the adjacent positions to the nitrogen atom, are rather unstable [19] and can undergo disproportionation [19] to give hydroxylamines and nitrones (Scheme 1).

In contrast, the inherent high stability of sterically hindered nitroxyls with tertiary carbon atoms at the adjacent position to the nitrogen atom is attributable to the absence of such a mechanism for a degradation. For example, the following stable nitroxyl radicals, the aliphatic acyclic di-*tert*-butyl nitroxyl radical (DTBN, **1**) and the heterocy-



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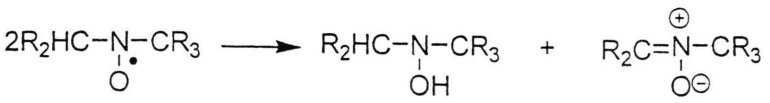
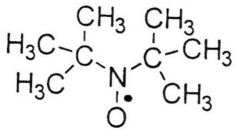


Scheme 1

clic 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, **2**) are stabilized by two adjacent *tert*-alkyl groups. An equally stable but more hydrophilic radical than **1** and **2** is the 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (**3**).



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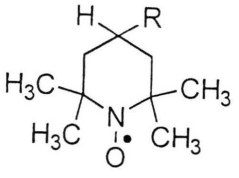


2

2 R = H
3 R = OH

These compounds are commercially available, and can be stored indefinitely at room temperature. In certain applications, such as inhibition of polymerization at elevated temperatures [28–32] and catalytic autoxidation of hydrocarbons [33–35], the thermal stability of nitroxyl radicals is critical. According to literature data [33] nitroxyls **1** and **2** should have a certain degree of stability at elevated temperatures. Thus, DTBN (**1**) can be distilled without decomposition at 74–75 °C/34 torr [4], however, the half-life time of **1** in *tert*-butylbenzene at 130 °C, both in oxygen and in an argon atmosphere, was found [33] to be only 13.4 minutes. In the case of TEMPO (**2**), no detectable decomposition was observed [33] at 130 °C for at least 200 minutes.

The di-*tert*-butyl nitroxyl radical (**1**) was first described in 1961 [4,5] and then in greater detail in 1964 [6,7]. Since that time **1** has been extensively studied in various areas, *e.g.* stabilization of chloroprene against polymerization [36,37], oxidative degradation [37], stabilization of acrylic acid [38], stabilization of anaerobic sealant compositions containing polymerizable acrylate ester monomers [39], the thermal stability [33,34], photolysis [40], catalytic inhibition of hydrocarbon autoxidation [33,34], and inhibition of vinyl polymerization [28–32,36–39], to mention only a few areas. This compound (**1**) can be prepared from 2-methyl-2-nitropropane by the reduction either with sodium metal in 1,2-dimethoxyethane [4–7] or with *tert*-butylmagnesium chloride in ether [41], or by the reaction of *tert*-butylmagnesium chloride and N-nitrosodiphenylamine [42]. These methods are unsuitable for economical large-scale preparations, including industrial production.

The preparation of the nitroxyl **2** was first reported [43] in 1962. The synthesis of the parent 2,2,6,6-tetramethylpiperidine from 2,2,6,6-tetramethyl-4-piperidone (triacetonamine) using the Wolff-Kishner reaction is also not amenable to large-scale industrial synthesis. In contrast, the synthesis of **3** can be economically accomplished from triacetonamine on an industrial scale.

While the number of literature references to **1** and **2** exceeds several hundred for each compound, the homologs of **1,** such as *tert*-butyl-*tert*-pentylnitroxyl [3,44] (**4a**) and di-*tert*-pentyl-nitroxyl (**4b**) [3] radicals have been mentioned very briefly, and subsequently forgotten for more than twenty-five years. Recently, a few di-*tert*-alkyl nitroxyl radicals enriched with deuterium and carbon-12 isotopes, such as perdeuterated DTBN, 12C-perdeuterated DTBN and higher homologs, containing 9, 10 and 11 carbons, were reported [45]. In order to better understand this mysterious lack of interest it was decided to develop a general synthetic method for these compounds, and to investigate their properties, in particular, their potential as inhibitors of vinyl polymerizations. Although over the years, the inhibition of vinyl polymerizations at ambient temperatures has been largely resolved [46–48] and the nitroxyl radicals were shown [36–39] to be effective inhibitors, prevention of polymerizations at elevated temperatures [28–32] remains a challenging task. In the present study, an attempt was made to explore the potential for applications in this particular area of five aliphatic and two heterocyclic nitroxyl radicals as compared to several industrial inhibitors.

Results and Discussion

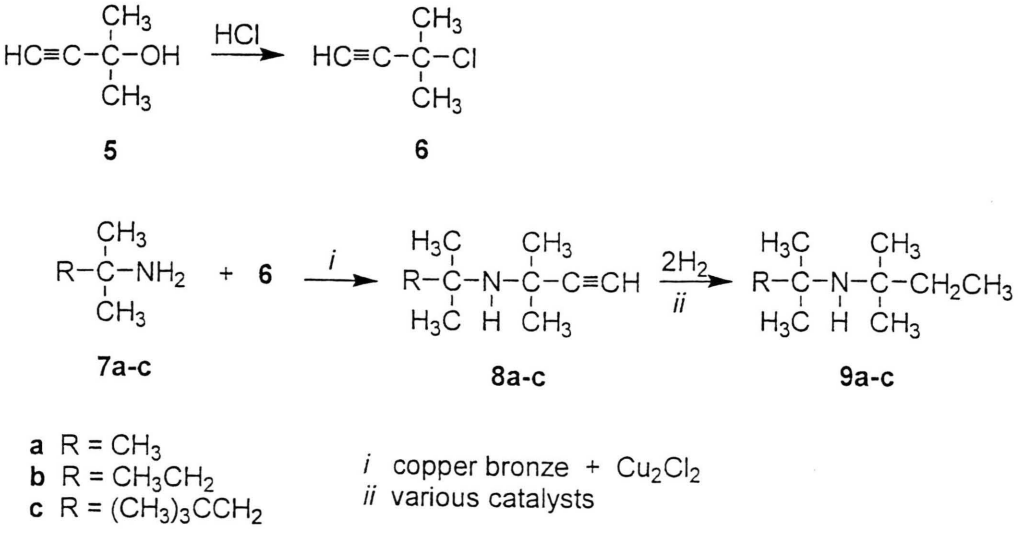
The DTBN (**1**) homologs **4a-c** can be synthesized from the corresponding amines **9a-c** which are obtained by the condensation of 2-chloro-2-methyl-1-butyne (**6**) with *tert*-alkylamines **7a-c**, followed by the catalytic hydrogenation of the intermediate acetylenic amines **8a-c** to give **9a-c** (Scheme 2).

This route leading to hindered secondary amines was described in the literature [49], however, the experimental details were very sketchy.

An efficient conversion of 2-methyl-3-butyn-2-ol (**5**) to **6** was reported in the literature [50]. At temperatures below 5 °C, this procedure was used [51] to prepare **6** in kilogram quantities with a yield exceeding 90%.

The preparation of sterically hindered amines similar to **9a-c**, and the challenges encountered en route were discussed in a paper [52] dealing with highly branched secondary amines. In the present study initial attempts in condensation of **6** with an excess of aqueous **7a** were equally erratic. The addition of either sodium carbonate, potassium carbonate, or sodium hydroxide as the base resulted in low yields of 10–40%. Because of limited supplies and a high cost of *tert*-pentylamine **(7b),** the condensation with **6** was conducted in the presence of an aqueous sodium carbonate solution as hydrogen chloride scavenger. The yields of **8b** ranged between 37–39% and were not further optimized. Much better results with 50–60% yields were achieved when the reaction was carried out at 20–25 °C for several days up to two weeks using an excess of *tert*-alkylamine as hydrogen chloride scavenger, as described in a patent [53]. The highest reproducible yields of **8a** were obtained with copper bronze-cuprous chloride as the catalyst. The reaction time was shortened from two weeks to a few hours. This catalytic variant was particularly important in the case of the lipophilic *tert*-octylamine **7c**. Thus, the mixture of **6** and **7c**, kept at 23–25 °C for two months, gave 29% of **8c**. When a two-phase mixture containing **6**, **7c** and water was kept at 15–18 °C for four weeks, the conversion was lower than 20%. An addition of copper powder and copper (I) iodide to this reaction mixture instantly induced an exothermic reaction, which increased the temperature inside the flask to 75 °C, and brought the reaction to completion. The optimization of the reaction conditions resulted in a 60–80% yield for **8a-c.** This method was amenable to the preparation of kilogram batch sizes of **8a-c**.

The catalytic hydrogenation of C,C triple bonds to the corresponding alkanes is, in general, a useful transformation. However, in several cases described in the literature [54], this reaction can be accompanied by highly undesirable hydrogenolysis reactions, which destroy the expected pro-



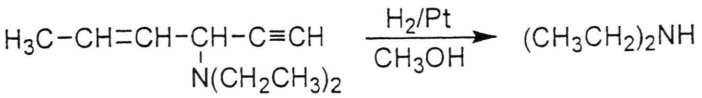
Scheme 2

ducts. Thus, the attempted hydrogenation of 1,4-acetylenic glycols at low pressure in the presence of palladium, platinum and Raney nickel catalysts resulted in extensive hydrogenolysis [55]. An addition of a small amount of either potassium or sodium hydroxide reduced the hydrogenolysis to a negligible level [55]. Hydrogenation of 4-diethylaminohex-2-en-5-yne (**10**) in methanol in the presence of an unspecified platinum catalyst resulted [56] in an almost quantitative fission of the diethylamino group attached to a carbon atom positioned between two unsaturated centers (Scheme 3). A lesser degree of fission of the carbon-nitrogen bond occurred in a cyclohexane solution.

Extensive hydrogenolysis also took place [57] during a low pressure hydrogenation of 3-diethylamino-3-methyl-1-pentyne (**11**) in methanol in the presence of Raney nickel to give a mixture of diethylamine, 3-methylpentane, and only a very small yield of 3-diethylamino-3-methylpentane (**12**) (Scheme 4).

Some saturated amines can be obtained [58] by the hydrogenation of the hydrochloride salts of acetylenic amines in the presence of platinum oxide. Although the products were isolated and positively identified [58], no yields were reported. The hydrogenation of highly branched propargyl amines and their hydrochloride salts in the presence of either of platinum or palladium catalysts in a variety of solvents gave [52] almost exclusively the hydrogenolysis products. Somewhat better results of about 20% yields were reported [52] by using low-pressure hydrogenation in the presence of W-2 grade Raney nickel. The hydrogenations in the presence of more reactive grades of Raney nickel, such as W-4 and W-6, resulted [52] in a more extensive hydrogenolysis. In this case, however, the hydrogenolysis reaction could be suppressed [52] by the addition of an excess of potassium hydroxide to the W-2 catalyst. On the basis of these examples, it is evident that the ordinary hydrogenation reactions are by no means straightforward and predictable.

The preparation of hindered amines **9a** and **9b** by the hydrogenation of appropriate acetylenic compounds **8a** and **8b** has been reported in the literature [3,49,52]. Thus, *tert*-butyl-*tert*-pentylamine (**8a**) was obtained [49] in a 42% yield by the hydrogenation of 3-*tert*-butylamino-3-methyl-1-butyne (**8a**) in the presence of a mildly active Raney nickel in ethanol, however, it was stated [49] that the amount and activity of the nickel catalyst are critical. A very rapid hydrogenation, especially with the nickel catalyst, resulted [49] in excessive hydrogenolysis which was probably caused by a rapid rise in temperature. Di-*tert*-pentylamine (**9b**) was obtained [3] in a 52% yield by the hydrogenation of 3-methyl-3-*tert*-pentylamino-1-butyne (**8b**), and in an 80% yield [52] by the hydrogenation of N-bis(1,1-dimethyl-2-propynyl)amine (**13**) in absolute ethanol using a W-2 Raney nickel catalyst which was deactivated with potassium hydroxide. The definition of mildly "active Raney nickel" [49] is quite vague since there are, at least, seven grades of Raney nickel, known as W-1 through W-7 catalysts [59–64]. These various grades of catalysts are not commercially available and must be



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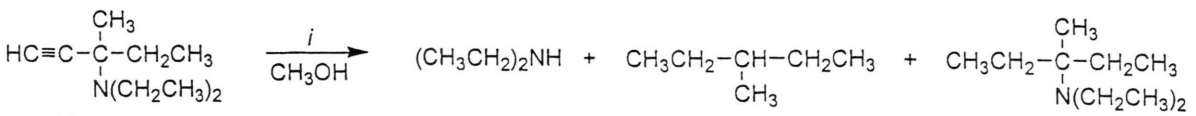
Scheme 3

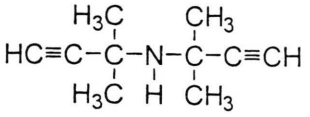


11 **12**

i = H_2/Raney nickel

Scheme 4

prepared each time under strictly controlled conditions.



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In the present study, the hydrogenation experiments with a commercial grade of Raney nickel, which was described by the supplier as analogous to either Raney 28 or W-2, failed to produce any significant amounts of the secondary amines. Thus, the hydrogenation of **8a** in methanol produced only a small quantity of **9a**. Instead, the reaction mixture contained mainly *tert*-butylamine, and other unidentified low-molecular-weight hydrogenolysis products. The hydrogenation of **8a** in hexane in the presence of a 10% Pd/C catalyst resulted in the complete hydrogenolysis. Much better results were obtained with a W-2 type Raney nickel catalyst which was prepared from a commercial aluminum-nickel alloy according to the literature procedure [62], and then partially deactivated by aging for several weeks under deionized water. In order to better understand the processes which occur during the hydrogenation reaction of **8a**, the composition of the reaction mixture was periodically analyzed by gas liquid chromatography and correlated with the volume of hydrogen gas consumption during this process (Table I).

The hydrogenolysis of **8a** to give some *tert*-butylamine (TBA) ensued at the very onset of the process. The intermediate alkene **14a** (Scheme 5) seemed to be more resistant to hydrogenolysis. After 225 minutes almost the entire alkyne **8a** was converted to a mixture of the hydrogenation products **9a** and **14a**, *tert*-butylamine and a mixture of unidentified hydrogenolysis products (Table I). About 30% of the initial alkyne **8a** underwent hydrogenolysis, as indicated by the amount of *tert*-butylamine found in the reaction mixture. The addition of the second molecule of hydrogen gas was much slower, and was accompanied by a much less pronounced hydrogenolysis. The hydrogenolysis and cleavage of the C-N bond occurred at the unsaturated side of the molecule to produce the *tert*-butylamine. The identity of the components was established by GC/MS.

The reaction with the same Raney nickel catalyst failed in *n*-pentane. Thus, the hydrogen gas uptake was extremely slow, and after 6 days, with about 25% of conversion, the experiment was terminated. The reaction in diethyl ether was somewhat faster, however, the hydrogenation ceased at the intermediate stage of the alkene **14a** with about a 60% yield.

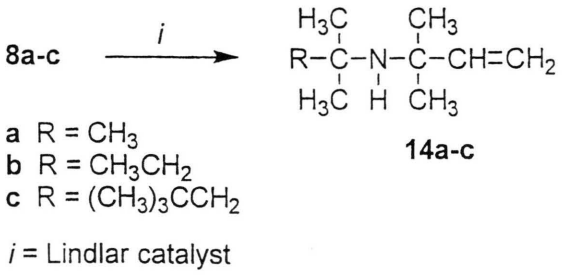
In an attempt to develop a method, which would be amenable for the use of commercially available catalysts with predictable results, various combinations of catalysts and solvents were tested. Thus, the 5% Ru/C catalyst in methanol was ineffective. The 5% Ru/alumina catalyst in methanol had a higher activity, however, the conversion after 48 hours was still incomplete, and in spite of a slow reaction, the extent of hydrogenolysis was high. The hydrogenation of **8a** in methanol in a Parr shaker in the presence of a Raney cobalt catalyst resulted in a 65% yield of **9a**. Comparable results were obtained in the temperature-controlled hydrogenation of **8a** using a 10% Pd/C catalyst in

Table I. Catalytic hydrogenation of 3-*tert*-butylamino-3-methyl-1-butyne (**8a**) in ethanol in the presence of W-2 Raney nickel.

Time [min]	Hydrogen uptake[a] [% of theory]	Composition of reaction mixture[b]							
		Alkyne **8a**		Alkene **14a**		Alkane **9a**		*tert*-Butylamine	
		weight%	molar%	weight%	molar%	weight%	molar%	weight%	molar%
40	25.0	68.0	65.6	23.0	21.8	3.3	3.1	5.2	9.5
60	33.0	59.6	56.5	29.3	27.4	4.3	4.0	6.8	12.2
150	55.0	31.3	28.6	49.6	44.7	7.6	6.7	11.5	20.1
225	86.0	0.7	0.6	51.6	43.3	26.2	21.3	21.5	34.5
720	105.0	0.0	0.0	7.5	6.2	67.0	54.0	25.6	40.0

[a] Volume of hydrogen gas consumed compared to the theoretical volume required to complete the conversion of **8a** to **9a**; [b] determined by GC.

tert-butyl methyl ether. In this case, the hydrogenolysis was suppressed to such an extent that in large-scale experiments the reproducible yields of **9a** were in the range of 60–72%. The hydrogenation in a Parr hydrogenator, especially in a larger 2 l glass vessel, generally gave lower yields which were caused by a lack of internal and external cooling. Thus, a series of hydrogenation experiments with **8c** in *tert*-butyl methyl ether in the presence of a 5% Pd/C catalyst resulted in low 10–32% yields of *tert*-octyl-*tert*-pentylamine (**9c**), and in high yields of 70–90% of the hydrogenolysis product, *i.e. tert*-octylamine (**7c**). A moderate improvement was accomplished by dividing the hydrogenation process into two stages. The first stage of the hydrogenation was carried out in *tert*-butyl methyl ether in the presence of a Lindlar catalyst, *i.e.* 5% palladium on calcium carbonate poisoned with lead. Thus, the alkynes **8a-c** were selectively converted to **14a-c** (Scheme 5), then the catalyst was filtered off and the second stage of hydrogenation was conducted in the presence of a 5% Pd/C catalyst. When the process was terminated after the first stage, relatively pure alkenes **14a-c,** contaminated with small admixtures (less than 3%) of **9a-c,** were isolated.



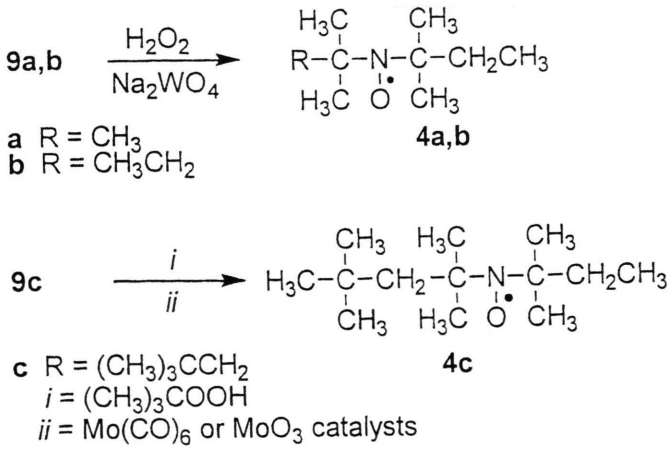
Scheme 5

Large-scale experiments in 300 ml and 4000 ml autoclaves equipped with cooling coils allowed the maintenance of the reaction temperatures below 30–35 °C, and resulted in higher yields of 65–80% of amines **9a-c.**

The routine oxidation of **9a,b** with a 30% aqueous hydrogen peroxide solution in methanol in the presence of sodium tungstate gave [3] high yields of nitroxyl radicals **4a** and **4b,** respectively, however, in the case of the lipophilic **9c**, the oxidation of the heterogenous reaction mixture failed to produce the desired radical **4c**. The oxidation of **9c** with *tert*-butyl hydroperoxide in 1,2-dichloroethane at 20–25 °C in the presence of either $Mo(CO)_6$ or MoO_3 catalyst [65] gave **4c** in a 25% yield.

The isolated **4c** had a much lower thermal stability than those of compounds **1, 4a** and **4b,** and the distillation even at a reduced pressure at 72–75 °C/0.5 torr resulted in a partial decomposition.

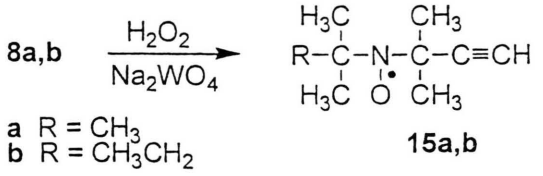
All three radicals **4a-c** are dark red-orange liquids with a strong terpene-like odor. Their color is attributable to the absorbance in the visible range at 464–465 nm. The ultraviolet and visible spectra in n-heptane have two maxima, one at 464–465 nm in the visible region (ε = 7.5–8) and the other, a much stronger one, at 247–249 nm. The electron paramagnetic resonance spectra (EPR) spectra of all di-*tert*-alkylnitroxyl radicals **1**



Scheme 6

and **4a-c** consist of three lines of equal intensity with the spin density located on a ^{14}N nitrogen atom (S=1). The hyperfine coupling constants of di-*tert*-alkylnitroxyl radicals **1** and **4a-c** ranged between 14.75 to 15.00 Gauss (Table II).

The branched acetylenic amines **8a,b** also can be oxidized [66] to the corresponding nitroxyl radicals **15 a,b** (Scheme 7, Table II).



Scheme 7

Table II. UV-Vis spectra and EPR hyperfine coupling constants of di-*tert*-alkylnitroxyl radicals.

Radical	λ_{max} (UV) nm	λ_{max} (Vis) nm	ε^a	EPR^b a_N (Gauss)
1	249	466	8.5	15.00
2		471	10.6	
4a	247	464	8.0	15.00
4b	249	464	8.0	14.75
4c	247	465	7.5	15.25
15a	240	437	25.45	15.00

[a] In n-heptane; [b] in cyclohexane 10^{-3} M; 3 lines of equal intensity.

The stability of these compounds under normal conditions is limited to several weeks for **15a** and a few days for **15b**. Compound **15a** can be stored for a prolonged period of time in a freezer at – 30 °C, otherwise, the decomposition occurs slowly even at 3–5 °C.

The temperature dependence of vapor pressure for **1** and **4a** was measured with an isoteniscope, and compared with that of **2** and **3.** The available quantities of **4b** and **4c** were too small for the isoteniscope measurements. The numerical results from the Table III were plotted as shown in Figure 1.

The thermal stability of di-*tert*-butyl nitroxyl (**1**) was found to be somewhat limited. The reported [33] half-life at 130 °C was only 13.4 minutes. Heating of **1** in *tert*-butylbenzene for 50 minutes at 130 °C, both in oxygen and in an argon atmosphere resulted in a 82% yield of 2-methyl-2-nitrosopropane [33–35] as one of the decomposition products. The thermal decomposition of the nitroxyl containing an acetylenic function, *i.e.* **15a**

Table III. Vapor pressure of nitroxyl radicals at various temperatures.

1		**2**		**4a**		**3**	
t [°C]	p [torr]	t [°C]	p [torr]	t [°C]	p [torr]	t [°C]	p [torr]
0	0.13	0	0.1	20	0.18	20	0.10
10	0.30	38	1.2	38	0.64	38	0.18
20	0.63	66	19	66	4.0	66	0.76
30	1.3	93	58	93	18	93	2.4
40	2.5	121	150	121	65	121	6.5
50	4.7	149	365	149	210	149	15.5
60	8.1	177	780	163	650	177	34
70	14	204				204	85
80	23					232	290
90	39						
100	60						
110	93						
120	145						
130	210						
140	305						
150	440						

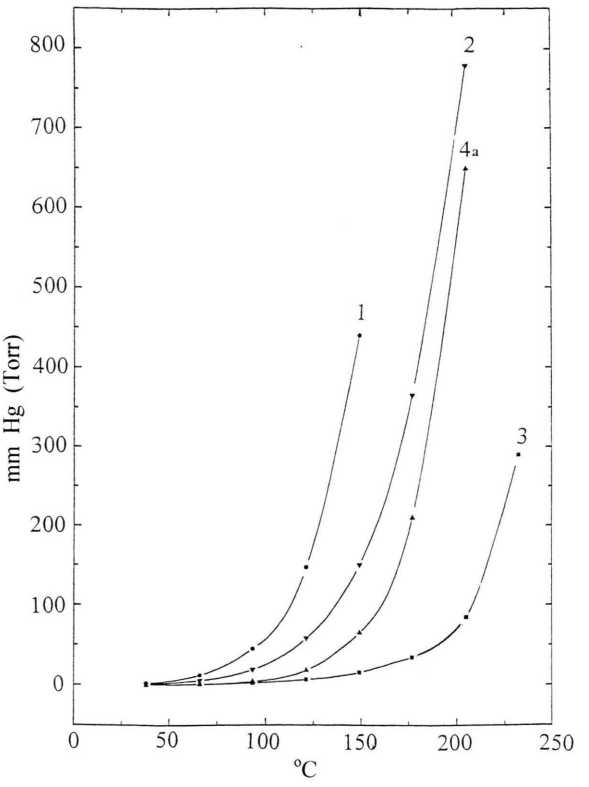


Fig. 1. The temperature dependence of vapor pressures of nitroxyl radicals DTBN (**1**), 2,2,6,6-tetramethylpiperidin-1-oxyl (**2**), 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-nitroxyl (**3**) and *tert*-butyl-*tert*-pentylnitroxyl (**4a**).

gave at 80 °C in 5 minutes a mixture of products [67], while the decomposition of the alkene analog, *i.e.* N-*tert*-butyl-N-(1,1-dimethylprop-2-enyl)-nitroxyl occurred readily at 25 °C [68]. The thermal stability of **1** and **4a-c** was investigated at 98 °C and 128 °C, in boiling *n*-heptane and *n*-octane, respectively. The decomposition was monitored by measuring the decrease in absorbance of the nitroxyl moiety at 464–465 nm (Table II). The characteristic orange-red color of the nitroxyl compounds gradually faded and changed first into a green, and then into a blue color. In all cases, a new maximum at 680–684 nm developed, which is indicative of the presence of aliphatic nitroso compounds (Table IV).

On the basis of the results presented in Table IV, it is evident that the thermal stability decreases with the increasing molecular weight. Such a tendency is also characteristic [69–73] of some other classes of compounds, such as branched azoalkanes, peroxides, highly branched hydrocarbons, and free radicals obtained by thermolysis thereof.

Table IV. Thermal decomposition of nitroxyl radicals.

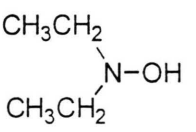
Radical	Time	λ [d] [nm]	Absorbance [A]	λ [e] [nm]	Absorbance [A]
1[a]	0	466	0.50		
	5 h 45 min	465	0.50		
	12 h 35 min	464	0.46		
	22 h 45 min	462	0.29		
	26 h	449	0.19		
	30 h	–	0.00		
4a[a]	0	464	0.27		
	1 h	468	0.29		
	4 h	473	0.28		
	12 h	474	0.23		0.23
	16 h	464	0.00	680	0.44
4b[a]	0	464	0.36		
	1 h	464	0.36		
	3 h	464	0.34		
	6 h	464	0.31		
	14 h 30 min	464	0.07	684	0.29
4c[a]	0	465	0.60		
	5 min	–	0.00		
1[b]	0	465	0.27		
	1 h	465	0.13		
	2 h	464	0.02		
4a[b]	0	464	0.21		
	30 min	476	0.15		
	1 h	514	0.08		
		480	0.08		
		464	0.07		
	1 h 10 min	–	0.00		
4b[b]	0	464	0.42		
	30 min	463	0.22	683	0.21
	1 h	463	0.06	683	0.37
	1 h 15 min	464	0.03	684	0.40
2[b]	0	468	0.90		
	44 h	468	0.92		
3[b]	0	478	0.85		
	48 h	478	0.88		
2[c]	0	471	0.83		
30 min	464	0.55			
	60 min	464	0.41		
3[c]	0	–	0.72		
	30 min	–	0.38		
	60 min	–	0.11		

[a] In boiling n-hexane at 98±2 °C; [b] in boiling n-octane at 128±2 °C; [c] in boiling 1,2,4-trimethylbenzene at 167±3 °C; [d] nitroxyl moiety; [e] nitroso moiety.

The cyclic nitroxyl radicals **2** and **3**, which were used for comparison, were stable in boiling *n*-octane for two days. After 44 and 48 hours the absorbance at 465 nm remained unchanged, then the experiments were terminated. A considerable decomposition was observed only at a higher temperature when *n*-octane was replaced with 1,2,4-trimethylbenzene. Thus, the half-life of TEMPO (**2**) at 167 °C was only one hour.

Nitroxyl radicals have been recognized [28–32,36–39] as effective polymerization inhibitors and mentioned in a comprehensive review article [74], in several publications [28,29,75,76], and in recent [30–32] and relatively old patents [36–39]. The substantial vapor pressure, volatility and satisfactory stability up to 100 °C, and in some cases much higher, are the prerequisites for radicals which could be employed as inhibitors of undesired polymerization at elevated temperatures. Polymerization inhibitors are needed in industry to prevent unwanted polymerizations, which are started by random free radical initiators. Such random initiators can be spontaneously produced either by autoxidative processes or by thermal fragmentation of molecules. Undesired and unexpected polymerization that may occur either during the synthesis or purification of various vinyl monomers, results in great economical losses. It was intriguing to evaluate the efficacy of aliphatic di-*tert*-alkyl nitroxyl radicals **1, 4a-c,** and **15a** as potential inhibitors of such unwanted vinyl polymerization in comparison with two heterocyclic nitroxyls with different lipophilicity, namely **2** and **3**, and commercial inhibitors, such as diethylhydroxylamine (**16**, commercial Pennstop PF2697), ammonium salt of N-hydroxy-N-nitrosoaniline (**17**, Cupferron), and bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (**18,** Tinuvin770). In addition, 2-methyl-2-nitrosopropane (**19**) and *tert*-butylhydroxylamine (**20**) were tested (Tables V–VIII).

Several vinyl monomers, *i.e.* styrene, acrylonitryle, butyl acrylate, methyl acrylate, and vinyl acetate were subjected to polymerization at 70–75 °C, initiated either with benzoyl peroxide or azoisobutyronitrile (AIBN). These upper temperature limits were imposed by the boiling points of the chosen monomers used in the study, *e.g.* acrylonitryle boiling at 77 °C, and methyl acrylate boiling at 80 °C. For those monomers, which undergo polymerizations at a moderate rate, the reaction progress could be monitored by measuring changes in the refractive indices. Thus, for example, styrene at 75 °C in the absence of an initiator failed to polymerize during several hours, whereas, in the presence of either benzoyl peroxide or AIBN, the polymerization commenced immediately, and in 75 minutes the sample attained a viscosity level that prevented further measurements of the refractive index. In contrast, an addition of the inhibitor appreciably delayed the beginning of the polymerization reaction. After the cessation of the inhibition period, during which time the refractive index remained constant, the polymerization of styrene commenced and proceeded at about the same rate as that without inhibitor, and reached the same level of completion in 75 minutes. The polymerization of the reference samples of the vinyl monomers without inhibitors proceeded much faster, *i.e.* within 2 to 10 minutes. The refractive indices of mixtures containing the inhibitor remained constant during the entire inhibition period, then a vigorous polymerization commenced, causing a sudden formation of the respective polymer. In some cases, when the polymerization failed to begin within several hours of heating, the experiments were terminated. The results pre-



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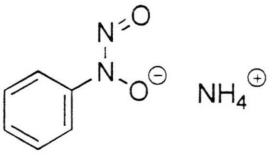

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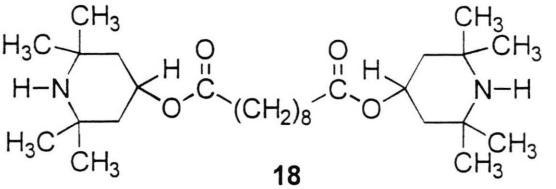

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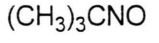

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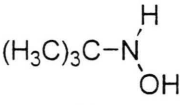

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Table V. Retardation of polymerization of styrene at 75 °C using 10 ml of the monomer and 0.35 g of benzoyl peroxide.

a			b			c			d			e			f			g		
time, [min]	n_D^{20}	Δn	time, [min]	n_D^{20}	Δn	time, [min]	n_D^{20}	Δn	time, [min]	n_D^{20}	Δn	time, [min]	n_D^{20}	Δn	time, [min]	n_D^{20}	Δn	time, [min]	n_D^{20}	Δn
0	1.5456	–	0	1.5450	–	0	1.5453	–	0	1.5430	–	0	1.5420	–	0	1.5439	–	0	1.5430	–
7	1.5508	0.0052	10	1.5446	–	12	1.5448	–	20	1.5422	–	10	1.5420	–	35	1.5439	–	60	1.5422	–
15	1.5562	0.0106	27	1.5466	–	29	1.5442	–	40	1.5422	–	25	1.5412	–	70	1.5418	–	80	1.5424	–
47	1.5578	0.0162	50	1.5438	–	52	1.5450	–	60	1.5445	0.0015	45	1.5397	–	100	1.5420	–	105	1.5420	–
63	1.5678	0.0222	78	1.5438	–	81	1.5450	–	80	1.5458	0.0028	70	1.5405	–	150	1.5433	–	160	1.5443	0.00
74	1.5718	0.0262	97	1.5440	–	95	1.5483	0.0030	100	1.5463	0.0033	90	1.5397	–	210	1.5465	0.0036	210	1.5503	0.00
thick polymer			115	1.5440	–	112	1.5522	0.0069	120	1.5478	0.0048	115	1.5400	–	240	1.5482	0.0043	240	1.5520	0.00
			129	1.5440	–	127	1.5556	0.0103	140	1.5510	0.0080	140	1.5415	–	260	1.5500	0.0061	265	1.5538	0.01
			144	1.5462	0.0012	140	1.5586	0.0133	170	1.5538	0.0108	200	1.5415	–	300	1.5558	0.0119	300	1.5565	0.01
			160	1.5504	0.0054	158	1.5623	0.0170	200	1.5556	0.0126	247	1.5422	–						

[a] No inhibitor; [b] 0.1 ml **1**; [c] 0.1 ml of **4a**; [d] 0.1 ml of **4b**; [e] 0.1 ml of **4c;** [f] 100 mg of TEMPO **(2)**; [g] 100 mg of 4-OH-TEMPO **(3)**.

Note: Cupferron (**17**, 100 mg) and diethylhydroxylamine (PennstopPF2697, **16**, 0.1 ml) inhibited polymerization of styrene for 8 h. In the samples containing 0.1 ml of **9a** or 0.1 ml of **9b** the polymerization started immediately and proceeded at the same rate as in sample a. The refractive index of the sample without initiator and inhibitor remained constant for 240 min, $n_D^{20} = 1.5442$.

Table VI. Retardation of polymerization of *n*-butyl acrylate at 70 °C using 10 ml of the monomer and 0.35 g of benzoyl peroxide.

a		b		c		d		e		f		g	
time [min]	n_D^{20}	time [min]	n_D^{20}	time [min]	n_D^{20}	time [min]	n_D^{20}	time [min]	n_D^{20}	time [min]	n_D^{20}	time [min]	n_D^{20}
0	1.4145	10	1.4178	10	1.4178	12	1.4185	10	1.4200	7	1.4188	10	1.4200
40	1.4148	30	1.4182	40	1.4182	22	1.4180	20	1.4203	35	1.4175	35	1.4205
60	1.4141	60	1.4185	50	1.4187	30 polymerization		35	1.4205	60	1.4185	45 polymerization	
120	1.4140	130	1.4188	70 polymerization				45 polymerization		110	1.4190		
190	1.4145	200	1.4213							140	1.4190		
250	1.4135	210 polymerization								180	1.4190		
340	1.4137									240	1.4194		
385	1.4137									300	1.4178		
420	1.4141									No polymerization			
505	1.4143												

[a] No initiator; [b] 0.1 ml of **1**; [c] 0.1 ml of **4a**; [d] 0.1 ml of **4b**; [e] 0.1 ml of **4c**; [f] 0.1 ml of Pennstop PF2697 (**16**); [g] 0.35 g of Tinuvin 770 (**18**). A reference sample containing 0.35 g of benzoyl peroxide and no inhibitor polymerized at 70 °C instantenously. A sample containing 0.35 g of benzoyl peroxide and 100 mg of TEMPO (**2**) failed to polymerize during 450 min of heating at 75 °C.

Table VII. Retardation of polymerization of vinyl monomers in the presence of benzoyl peroxide initiator and various inhibitors.

Inhibitor	Quantity	Vinyl acetate at 70 °C time [min]	Acrylonitrile at 70 °C time [min]	Methyl acrylate at 75 °C time [min]
1	0.1 ml	130	180	320
2	0.1 g	385	60	180
3	0.1 g			150
4a	0.1 ml	395	400	450
4b	0.1 ml	510	330	360
4c	0.1 ml	345		240
15a	0.1 g	180		300
16	0.1 ml	>570	55	>480
19	0.1 g	360	260	360
20	0.1 g	480	90	>510

Table VIII. Retardation of polymerization of vinyl monomers in the presence of AIBN initiator and various inhibitors at 75 °C.

Inhibitor	Acrylonitrile time [min]	Methyl methacrylate time [min]	Vinyl acetate time [min]
1	145	>360	>540
2	180	190	240
4a	150	>900	>540
15a	50	60	50
17	16	120	220
19	>240	>900	>540
20	16	80	300

sented in Tables V-VIII were obtained with the practical, arbitrarily chosen, nonstoichiometric quantities of various inhibitors, *i.e.* 0.1 g for the solids and 0.1 ml for the liquids. Nevertheless, on the basis of results obtained in the present study, it can be concluded that all of the investigated radicals can be employed in practical applications.

On the basis of the results of experiments shown in Tables V, VII, VIII, the following conclusions can be made:

1) There is no general correlation between the decrease in the inhibition time and the decrease in the concentration of the nitroxyl molecule.
2) There is no general correlation between the decrease in the inhibition time and the decrease in the thermal stability.

In fact, in the series of **1** and **4a-c,** the least stable radical **4c** at the lowest molar concentration was found to be in all cases superior to the more stable DTBN (**1**). These observations can be explained by an assumption that the thermal degradations of nitroxyls during the experiment lead to formation of the hindered nitroso compounds which have been known as efficient spin traps [77–80] and polymerization inhibitors [80–83]. To support this assumption, a few experiments were conducted using 2-methyl-2-nitroso-propane (**19**) instead of the nitroxyl radicals (Tables VII and VIII). It was confirmed that the admixture of **19** to vinyl monomers offers a remarkable protection against unwanted polymerization of vinyl monomers with inhibition times comparable to those obtained with nitroxyls. Nevertheless, even in the extreme case of **15a**, which undergoes decomposition below 70 °C, the inhibition times were satisfactory (Tables VII and VIII).

Experimental Part

Materials. The following reagent-grade starting materials of 97–99% purity were purchased from commercial sources and used without further purification: *tert*-Butylamine (**7a**), *tert*-pentylamine (**7b**), *tert*-octylamine (**7c**), 2-methyl-3-butyn-2-ol (**5**), 2-methyl-2-nitrosopropane dimer (**19**), *tert*-butylhydroxylamine (**20**), styrene, methyl methacrylate, 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO, **2**), 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-hydroxy-TEMPO, **3**), molybdenum (IV) oxide, molybdenum hexacarbonyl, copper bronze, cuprous chloride, Raney nickel active catalyst (analogous to Raney 28 or W-2, 50% slurry in water), palladium on calcium carbonate poisoned with lead (Lindlar catalyst), ammonium salt of N-hydroxy-N-nitrosoaniline (Cupferron, **17**), *n*-heptane, *n*-octane, cyclohexane, hydrochloric acid, *tert*-butyl methyl ether, *tert*-butyl hydroxyperoxide, and benzoyl peroxide were purchased from Aldrich Chemical Co., Milwaukee, WI. Nickel-aluminum Raney nickel was obtained from Fluka AG, Buchs, Switzerland. Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin 770, **18**) was purchased from Ciba-Geigy, Additives Division, Hawthorne, New York. Palladium on powdered charcoal (10%) was obtained from E. H. Sargent & Co. Palladium 5% on carbon, type 37 – from Johnson Matthey, West Depford, NJ, Ruthenium on carbon (5%) – from Engelhard Corporation, Newark, NJ. Raney cobalt 2700 Catalyst in water – from Grace Davidson, Chattanooga, TN. Acrylonitrile, methyl methacrylate and butyl acrylate were obtained from Janssen Chimica, Geel, Belgium. Vinyl acetate was purchased from Matheson Coleman and Bell, Norwood, Cincinnati, Ohio. Diethylhydroxylamine (Pennstop PF 2697, **16**) was donated by ATO Chem North America, Woodbury, New Jersey. Sodium tungstate was purchased from Fisher Scientific Co., Fair Lawn, New Jersey, and azoisobutyronitrile, (AIBN, 2,2'-azobis-2-methylpropionitrile) was purchased from Kodak, Rochester, NY. The di-*tert*-butyl nitroxyl radical (DTBN) was prepared according to the published procedure [4,6] from 2-methyl-2-nitropropane, Nova Molecular Technology, Janesville, 3-chloro-3-methyl-1-butyne (**6**) was prepared from 2-methyl-3-butyn-2-ol (**5**) [50–51]. The N-*tert*-butyl- and N-*tert*-pentyl-N-(1,1-dimethylprop-2-ynyl)nitroxyl radicals, **15a** and **15b**, respectively, were obtained by the oxidation of **8a** and **8b**, in accordance with the literature procedure [66].

Analytical procedures. Melting points were determined on a Thomas-Hoover capillary melting point apparatus, Model 6406-K, using a calibrated thermometer. Mass spectra were recorded on a Hewlett-Packard mass spectrometer, Model 5985 GS either in the electron impact (EI) or chemical ionization (CI) modes. In the latter case methane was used as the reactant gas. ^{1}H NMR spectra were recorded on a 250 MHz Bruker NMR spectrometer, Model WM-250, using $CDCl_3$ as a solvent and TMS as the reference. Microanalyses were performed on a Perkin-Elmer elemental analyzer, Model 240C. Capillary gas chromatography was carried out on a Hewlett-Packard gas chromatograph, Model 5890, using a 15 m DB-1 column. UV-Vis spectra were recorded on a Nicolet spectrophotometer, in quartz cuvettes either in n-heptane or n-octane. EPR spectra were recorded using 10^{-3} M cyclohexane solutions on a Varian E115 spectrometer with a E102 microwave bridge in 5 mm glass tubes. The vapor pressures of nitroxyl radicals were obtained at Phoenix Chemical Laboratory, Inc., Chicago, IL by the static determinations of vapor pressure using an Isoteniscope ASTM D2879.

3-tert-Butylamino-3-methyl-1-butyne (**8a**). *Procedure A.* 3-Chloro-3-methyl-1-butyne (**6**, 225 g, 2.2 mol), *tert*-butylamine (**7a,** 392 g, 536 ml, 5.36 mol) and water (200 ml) were mixed in a 2 l Erlenmeyer flask to form a homogeneous solution, whereby the temperature spontaneously rose to about 35 °C. The resulting reaction mixture was kept for two weeks at 20–25 °C. During this time the mixture separated into two layers. The mixture was diluted with water (200 ml), the organic top layer was separated, and the aqueous layer was extracted with *tert*-butyl methyl ether (2 × 50 ml). The combined organic layers were dried with anhydrous sodium carbonate, and then with potassium hydroxide pellets. The solvent and other volatile components were removed by distillation between 55 and 135 °C at 743±3 torr and the remaining liquid was distilled at 50–70 °C/70–80 torr in order to remove the product from the unsaturated by-product. It is important to perform this distillation at this point at a reduced pressure, otherwise a vigorous decomposition of the brown residue in the final stages of the distillation can occur, resulting in a contamination of the distillate. The final distillation at 135–136 °C/743±3 torr (lit. [49] 135–136 °C), gave 185 g (60%) of **8a** as a colorless product of 99% purity by GC, d_{20} = 0.787, n_D^{20} = 1.4322. ^{1}H NMR ($CDCl_3$, TMS): δ = 1.27 (s, 9H, *t*-Bu), 1.43 (s, 6H, 2Me), 2.28 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS): δ = 31.75, 33.34, 47.77, 52.12, 69.91, 92.03. MS (CI): *m/z* = 140 [M^+ + 1].

A solution of **8a** (0.5 g) in diethyl ether (7 ml) was slowly added into a 1.0 M solution of hydrogen chloride in diethyl ether (10 ml) to precipitate the corresponding hydrochloride salt, m.p. 220–223 °C (dec.) (lit. [49] m.p. 221–223 °C).

$C_9H_{18}ClN$ (175.70)

Calcd	C 61.52	H 10.33	N 7.97%,
Found	C 61.60	H 10.48	N 8.16%.

Procedure B. tert-Butylamine (**7a**, 106.6 g, 153 ml, 1.46 mol) and water (55 ml) were combined in a 1000 ml 3-neck flask equipped with a stirrer, pressure equalizing funnel and thermometer. Since the temperature of the mixture spontaneously rose to about 55 °C, it was lowered to about 30 °C by external cooling with cold water. Catalytic quantities of cuprous chloride (0.1 g) and copper bronze (0.05 g) were added to the stirred mixture, followed by a dropwise addition of 3-chloro-3-methyl-1-butyne-1 (**6,** 60 g, 0.58 mol) for 10 min. In spite of the external cooling with cold water the temperature in the flask rose to about 55 °C. The reaction mixture was stirred for an additional 15 min, then transferred to a separatory funnel. The dark top layer (about 100 ml) was separated, dried with anhydrous sodium carbonate, filtered, and flash-distilled at 50–70 °C/70–80 torr to give 50 g (0.36 mol, 62%) of **8a** with a 95% purity. The product was redistilled at 135–136 °C/743±3 torr to the 98.5% purity by GC.

Procedure C. A 6-fold scale-up was carried out in a 3 l flask, placed in a cooling bath, with the following quantities of the starting materials: **7a** (534 g, 767 ml, 7.3 mol), water (300 ml), copper (I) chloride (0.7 g), copper bronze (0.2 g), and **6** (90%, technical grade, 362 g , equivalent to 3.2 mol of pure **6**). Compound **6** was added to the reaction mixture over a period of 40 min. The temperature of the reaction mixture was maintained at 30–35 °C, but never to exceed 45 °C. The isolation and purification procedures of the reaction mixture, as described in B, gave 380 g (86%) of **8a**. The initial purification of crude product can also be accomplished by steam distillation. In this case, an efficient cooling must be provided to trap the *tert*-butylamine. The distillate separates into two phases. The aqueous phase contains an excess of *tert*-butylamine, which can be recovered by adding sodium hydroxide. The organic phase of the distillate can be dried with potassium hydroxide and distilled. This procedure can be conveniently em-

ployed for the recovery of most of the tertiary amine, which was used as HCl scavenger.

3-Methyl-3-tert-pentylamino-1-butyne (**8b**). *Procedure A.* The compound was prepared by an analogous procedure as described for **8a**. Reaction of *tert*-pentylamine (**7b**, 50 g, 0.574 mol) and 3-chloro-3-methyl-1-butyne (**6**, 45 g, 50 ml, 0.44 mol) for 4 weeks gave 27 g (39%) of **8b** of 97% purity by GC, b.p. 155–158 °C (lit. [3,66] 52–53 °C/15 torr), n_D^{20} = 1,4432 (lit. [3] n_D^{20} = 1.4430). MS (EI): *m/z* = 153 [M^+, 1.4], 138 [M^+ - CH_3, 3], 124 (18), 83 (9), 72 (29), 71 (14), 68 (26), 67 (12), 58 (100). ^{1}H NMR ($CDCl_3$, TMS): d = 0.87 (t, 3H), 1.22 (s, 6H, 2Me), 1.43 (s, 6H), 1.53 (s, 2H), 2.26 (s, 1H). In a similar experiment, with the identical quantities of the starting materials, the recovery of the product and the yield were improved to 50% by repeated distillation of the extracts under reduced pressure at 76–80 °C/20 torr (lit. [3,66] b.p. 52–53 °C/15 torr).

Procedure B. tert-Pentylamine (**7b**, 1271 g, 14.58 mol), water (580 ml), cuprous chloride (2 g), and copper bronze (1 g) were combined with stirring in a 3 l flask. The temperature of the mixture rose immediately to 41 °C. The flask was cooled until the temperature reached 25 °C. 3-Chloro-3-methyl-1-butyne (**6**, 684 g, 6.67 mol) was added dropwise over a period of one h. The exothermic reaction was controlled by the rate of addition and external cooling, maintaining the reaction mixture below 30–35 °C. After the addition the reaction mixture was stirred for an additional 2 h at 25–35 °C. The reaction mixture was transferred to a separatory funnel and the bottom aqueous layer containing the hydrochloride salts was removed, neutralized with a 50% aqueous sodium hydroxide solution and extracted with *tert*-butyl methyl ether (3 × 500 ml). The combined organic layers were dried with solid sodium hydroxide (100 g), then the solvent and the excess of *tert*-pentylamine were removed at the prevailing barometric pressure. The distillation of the remaining liquid at 52–54 °C/15 torr gave 700 g (68%) of **8b** with a 99% purity by GC.

3-Methyl-3-tert-octylamino-1-butyne (**8c**). *Procedure A.* A heterogenous mixture of *tert*-octylamine (**7c**, 129 g, 1 mol), 3-chloro-3-methyl-1-butyne (**6**, 51 g, 0.5 mol) and water (100 ml) was left in a closed flask at 23–25 °C for three weeks. Then, the mixture was diluted with water (100 ml), and the organic layer was separated. The aqueous layer was extracted with *tert*-butyl methyl ether (3 × 25 ml), and the solvent was removed at 20–30 torr to give 12 g of **7c**. A 50% solution of sodium hydroxide was added to the aqueous layer to give an additional quantity of **7c** (64 g). The organic layer was dried with potassium hydroxide pellets (5 g), decanted and distilled. The first fraction (3.5 g) collected at 35–45 °C/90 torr contained mostly **7c**, the second fraction (26 g), collected at 80–85 °C/85 torr contained a 3:2 mixture of **7c** and **8c**, and the third fraction (36 g), collected at 95–97 °C/25 torr, was the expected product (**8c**). The second fraction was redistilled and the product was collected at 206–209 °C/749 torr to give an additional quantity (8.1 g) of **8c.** The combined product (44.3 g, 0.23 mol) was obtained in a 46% yield. MS (EI): *m/z* = 180 ([M^+ -CH_3] 2.4), 124 (54), 108 (11), 68 (18), 67 (23), 65 (14), 58 (100). ^{1}H NMR ($CDCl_3$, TMS): δ = 1.02 (s, 9H, *t*-Bu), 1.34 (s, 6H, 2Me), 1.41 (s, 6H, 2Me), 1.53 (s, 2H), 2.27 (s, 1H). ^{13}C NMR ($CDCl_3$, TMS): δ = 30.66, 31.80, 31.98, 33.79, 47.42, 56.26, 56.95, 70.14, 91.99.

Procedure B. A three-neck 5 l flask equipped with a stirrer, 1 liter addition funnel and thermometer was placed in an ice/water bath. The flask was filled with *tert*-octylamine (**7c**, 1450 g, 11.2 mol), water (450 ml), copper bronze (0.3 g) and cuprous chloride (1 g) and the addition funnel with 3-chloro-3-methyl-1-butyne (**6**, 500 g, 4.9 mol). The first 250 ml portion of **6** was added rapidly for 7 minutes. The initial reaction temperature (22 °C) rose during 15 min to 38 °C and then subsided. The remaining **6** was added during 40 min period while maintaining the temperature in the flask between 25–38 °C, then the reaction mixture was stirred for 30 min. The total reaction time was 90 min. The reaction mixture was transferred to a separatory funnel. The top organic layer (450 g) contained mainly 81% **8c** by GC, 13% of **7c** and several minor products. The aqueous layer treated with a 50% sodium hydroxide solution formed an organic layer containing 61% of **7c** and 31% of **8c**. The combined organic layers were dried overnight with sodium hydroxide pellets (50 g), and then distilled to give **7c** (970 g, 7.5 mol), collected at 40–45 °C/15 torr, an interim fraction (63 g) and the product **8c** (576 g, 2.95 mol, 60%), collected at 100–102 °C/25 torr, then at 55–57 °C/0.25 torr. The flask residue (120 g) contained some amount of **8c** and other unsaturated products, which tended to polymerize when overheated. The product was redistilled at 103–107 °C/30–35 torr to give 561 g (59%) of **8c** with a 97% purity, n_D^{20} = 1.4500, d_{20} = 0.8153.

3-tert-Butylamino-3-methyl-1-butene (**14a**). A solution of 3-*tert*-butylamino-3-methyl-1-butyne (**8a,** 309 g, 2.22 mol) in *tert*-butyl methyl ether (500 ml) was placed in a 2 l glass Parr hydrogenation bottle and cooled to -20 °C. To the solution was added the Lindlar catalyst, *i.e.* 5% palladium

on calcium carbonate, poisoned with lead (3 g). The flask was connected to the Parr shaker, evacuated to 30 torr, purged twice with nitrogen gas, then twice with hydrogen gas. The flask was pressurized to 50 psi (3.4 atm) and the agitation started. Every 10 to 15 min, the reaction was interrupted, and the solution was cooled to -10 °C. Each time, the reaction mixture was analyzed by GC. After 30 min the hydrogen gas uptake ceased, although the reaction was incomplete. A new portion of a fresh catalyst (2 g) was added, and the procedure was repeated until the absorption of hydrogen gas stopped and the compound **8a** was exhausted. The reaction mixture contained a substantial amount (17%) of *tert*-butylamine, produced by the hydrogenolysis, and a small amount (2.7%) of *tert*-butyl-*tert*-pentylamine. The catalyst was removed by filtration through a Celite filter aid on high-density filter paper, using a weak suction, and the solvent was removed at about 20–25 °C/100 -200 torr. A distillation at 82–83 °C/40 torr gave 200 g (64%) of colorless **14a** with a 97% purity by GC. An analytical sample was obtained by a distillation at 141–143 °C/760 torr, d_{20} = 0.7743, n_D^{20} = 1.4316. ^{1}H NMR ($CDCl_3$, TMS): δ = 1.14 (s, 9H, *t*-Bu), 1.24 (s, 6H, 2Me), 4.87–5.01, (m, J = 10.8, 17.6, 0.04 Hz, 2H), and 5.95–6.04 (d of d, J = 10.8, 17.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS): δ = 30.55, 32.68, 52.05, 54.87, 109.74, 150.34.

3-Methyl-3-tert-pentylamino-1-butene (**14b**). A solution of 3-methyl-3-pentylamino-1-butyne (**8b**, 200 g, 1.3 mol) in *tert*-butyl methyl ether (300 ml) was hydrogenated in the presence of the Lindlar catalyst (1 g), as described for **14a**. The catalyst was removed by filtration, and the filtrate was saved. The hydrogenation was repeated using 100 g and 200 g of **8b**, and the filtrates from all three experiments were combined. The solvent was removed and the residual liquid was distilled at 53–56 °C/15 torr to give of 415 g (83%) of **14b** with a 100% purity by GC. d_{20} = 0.793, n_D^{20} = 1.4395. ^{1}H NMR ($CDCl_3$, TMS): δ = 0.85 (t, 3H, Me), 1.07 (s, 6H, 2Me), 1.12 (s, 1H, NH), 1.24 (s, 6H, 2Me), 1.40 (q, 2H, CH_2), 4.92–5.0 (m, 2H, CH_2), 5.97–6.03 (m, 1H, CH).

3-Methyl-3-tert-octylamino-1-butene (**14c**). The reaction was carried out in the same fashion as in the case of **14a**. A solution of 3-methyl-3-*tert*-octylamino-1-butyne (**8c**, 420 g, 2.14 mol) in *tert*-butyl methyl ether (600 ml) was hydrogenated in a 2 l glass vessel in the presence of the Lindlar catalyst (6 g), added in two portions. The reaction mixture was distilled at 48–52 °C/0.2 torr to give 332 g (79%) of **14c** with a 97% purity by GC. The analytical sample was distilled at 215–216 °C/760 torr; d_{20} = 0.8225, n_D^{20} = 1.4493. ^{1}H NMR ($CDCl_3$, TMS): δ = 1.01 (s, 9H, *t*-Bu), 1.18 and 1.23 (s, 6H, 2Me), 1.44 (s, CH_2), 4.84–4.98, (m, J = 10.8, 17.6, 0.04 Hz, 2H), 5.96–6.06 (d of d, J = 10.8, 17.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS): δ = 30.85, 31.62, 31.90, 32.08, 54.75, 56.37, 58.41, 109.36, 150.76.

tert-Butyl-tert-pentylamine (**9a**). *Procedure A. Hydrogenation using a 5% palladium on carbon catalyst in tert-butyl methyl ether.* A solution of 3-*tert*-butylamino-3-methyl-1-butyne (**8a**, 60 g, 0.43 mol) in *tert*-butyl methyl ether (150 ml) was placed in a 300 ml stainless steel autoclave equipped with a sampling outlet, cooling coil and mechanical agitator. To the solution sparged with a stream of nitrogen gas, was added the Johnson-Matthey 87L 5% Pd/C catalyst (0.5 g). The autoclave was closed, and first purged with nitrogen gas, then with hydrogen gas, and pressurized to 200 psig. The temperature of the agitated mixture was maintained between 17 and 25 °C by internal cooling with cold water. The hydrogenation process was monitored by GC, and was completed in 6 h. The catalyst was removed by filtration through a Celite filter aid on high-density filter paper, aided with mild suction, and the reaction mixture was distilled under atmospheric pressure. The first fraction contained the solvent and the hydrogenolysis products. Further distillation of the remaining liquid at 143–145 °C/743±3 torr gave 45 g (73%) of **9a** with a 98% purity by GC, n_D^{20} = 1.4218 (lit [49] n_D^{25} = 1,4179).

Procedure B. – The above procedure was scaled up 16.7 times and carried out in a 3.8 l autoclave. In this case, the hydrogenation of **8a** (1000 g, 7.2 mol) yielded 700 g (4.9 mol, 68%) of **9a**.

Procedure C. Hydrogenation using a Raney nickel catalyst. a) Preparation of the catalyst. Nickel-aluminum alloy (30 g, 50–50) was digested in a 20% aqueous sodium hydroxide solution (250 ml). The initial exothermic reaction required external cooling. Subsequently, the mixture was heated on a steam bath to 80 °C and kept at this temperature for 6 h. The resulting slurry was diluted with deionized water (500 ml) and the aqueous layer was carefully decanted. The nickel was washed with deionized water (30 × 100–150 ml), each time the decanted water was discarded. Then, the slurry was washed several times with ethanol (5 × 50 ml) and the catalyst was stored under ethanol in a closed flask. The flask was shaken vigorously before each hydrogenation experiment, and an aliquot of the resulting suspension (1–2 ml) was transferred with a wide plastic pipet to the hydrogenation flask.

b) Hydrogenation. The hydrogenation experiments were carried out in a 3-neck 100 ml flask placed in a water cooling bath. The central neck was closed with a glass three-way stopcock adapter. One arm of the stopcock was connected to a cylinder with hydrogen gas. The second arm was connected with a tygon tubing to a glass tube going through a rubber stopper to the top of an inverted 2 l calibrated glass cylinder filled with water. This cylinder was also connected through a second shorter glass tube, inserted in the same rubber stopper, to a pressure equalizing burette filled with water. The flask, equipped with a small magnetic stirring bar, was filled with methanol (25 ml), compound **9a** (5 g) and the Ra/Ni catalyst (2 ml). The remaining two necks of the reaction flask were closed with rubber septa allowing a withdrawal of small aliquots of the reaction mixture for gas chromatography. The flask was purged several times with hydrogen gas, the burette was filled with hydrogen gas and the magnetic stirrer was started. Hydrogen uptake began immediately as measured by the rising water level. The results are presented in Table I. The aliquots corresponding to the 55% and 86% of the theoretical hydrogen uptake were analyzed by GC/MS analysis carried out in the electron impact (EI) mode. The MS scans were taken every 2 seconds. The initial temperature was 50 °C and the program rate 20 °C/min. The identity of the major peaks was confirmed by comparison of the retention times (RT) of standards injected independently and the fragmentation patterns. Thus, the RT of 36 sec corresponded to **7a**, however, the parent peak (MW= 73) was missing. The most prominent peak 59 was recorded for [$M^+ - CH_3 + H$]. The RT of 146–150 sec concurred with **8a**; the weak parent peak at 139, and the fragmentation peaks at 124 [$M^+ - CH_3$], 68, and 58 were observed. The RT of 168 sec was assigned to 3-*tert*-butylamino-3-methyl-1-butene (MW=141) on the basis of a weak peak at 141, and the fragmentation peaks at 126, 70 and 58. The RT of 184 sec corresponded to **9a**, however, the parent peak at 143 was absent. Other fragmentation peaks were observed at 128 [$M^+ - CH_3$], 114 [$M^+ - C_2H_5$], 99, 84, 72, and 58.

Di-tert-pentylamine (**9b**). *Procedure A.* The catalytic hydrogenation of **8b** (15.7 g, 0.11 mol) was carried out in a Parr shaker in methanol (100 ml) in the presence of Raney cobalt (2 g) for 10 h. The initial hydrogen pressure decreased from 57 to 41 psi (2.8–4 atm). The catalyst was removed by filtration, and the filtrate was distilled through a short path (25 cm) column. The product 4 g (25%) was collected at 155–160 °C (lit. [8] 93–95 °C/62 torr or 92–95 °C/60 torr); n_D^{20} 1.4301 (lit. [3] n_D^{25} 1.4281). MS(EI): *m/z* (70 eV) = 157 [M^+, weak], 128 [$M^+ - C_2H_5$, 6], 72 [isopentane, 31], 71 [t-pentyl, 11], 58 (100). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.87 (t, 6H), 1.07 (s, 1H), 1.11 (s, 12H), 1.42 (q, 4H).

Procedure B. 3-Methyl-3-*tert*-pentylamino-1-butene (**14b**,170 g, 1.08 mol) in *tert*-butyl methyl ether (300 ml) was hydrogenated in a 2 l Parr shaker in the presence of a 5% Pd/C catalyst (2.1 g) to give 127 g (71%) of **9b** with a 98% purity by GC.

tert-Octyl-tert-pentylamine (**9c**). A solution of 3-methyl-3-*tert*-octylamino-1-butyne (**8c**, 113 g, 0.55 mol) in *tert*-butyl methyl ether (150 ml) was hydrogenated in a 300 ml glass flask overnight in a Parr shaker (Parr Instrument Co. Moline, Illinois) in the presence of a 5% Pd/C catalyst (1 g) at 57 psi (-3.9 atm). The catalyst was removed by filtration and the filtrate (223 g) was distilled. The first fraction (130 ml), collected at 43–55 °C, contained, in addition to *tert*-butyl methyl ether, the low-boiling unidentified neutral hydrogenolysis products. The second fraction, collected at 48–53 °C/28–32 torr, contained 56 g (0.43 mol, 79%) of **7c**. The third fraction, collected at 111–112 °C/30 torr, contained 26 g (0.11 mol, 20%) of **9c**.

The recovered catalyst was used several times in consecutive experiments in which the concentration of **8c** was gradually decreased. Deactivation of the catalyst and lower concentrations of **8c** resulted in increased yields of **9c** . Thus, a reduced quantity of **8c** (82 g, 0.42 mol) in the same amount of *tert*-butyl methyl ether (150 ml) was converted to **9c** (20 g, 0.1 mol, 24%) and **7c** (39 g, 0.3 mol, 72%). Further dilution (*e.g.* 60 g, 0,31 mol of **8c**) with t*ert*-butyl methyl ether (200 ml) caused some additional improvement, *i.e.* 19.5 g (32%) of **9c**. In another experiment, using 81 g (100 ml, 0.42 mol) of **8c** in *tert*-butyl methyl ether (200 ml) **9c** and **7c** were obtained in 35% and 60% yield, respectively. d_{25} = 0.808, n_D^{20} = 1.4426, MS (EI) (15 eV): *m/z* = 184 [M^+-Me, 1], 129 (13), 114 (6), 72 (13), 71 (4), 59 (4), 58 (100), 57 (12); MS(CI): *m/z* = 198 (6.5), 184 (29), 170 (8), 129 (9), 128 (100), 89 (7), 88 (89), 86 (10), 72 (8) 71 (12), 61 (10), 58 (18), 57 (52), 56 (8), 55 (28). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.87 (t, 3H, Me0, 1.02 (s, 9H, *t*-Bu), 1.12 (s, 6H, 2Me), 1.23 (s, 6H, 2Me), 1.39 (q, 2H CH_2), 1.42 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, TMS): δ = 9.72 (Me), 30.02, 31.99, 32.17 (t, 3Me in *t*-Bu), 38.26 (t, CH_2, 52.88, 55.95, 59.25 (t, CH_2).

Large-scale hydrogenation experiments carried out in 300 ml and 3.8 l autoclaves, in a fashion similar to that described for **9a**, gave **9c** in 65–80% yields.

tert-Butyl-tert-pentylnitroxyl (**4a**). To a stirred solution of *tert*-butyl-*tert*-pentylamine (**9a**, 85 g, 0.59 mol) in methanol (400 ml) was added sodium tungstate dihydrate (2 g) followed by one portion of a 30% aqueous solution of hydrogen peroxide (160 ml). The temperature of the reaction mixture rose to 31 °C as a result of exothermic reaction, however, no external cooling was necessary. The color of the solution changed gradually from a faint yellow to dark orange. The reaction mixture was stirred for 48 h without external cooling. The solution was transferred to a separatory funnel, and diluted with water (500 ml). The top brown layer was separated, and the bottom aqueous layer was extracted with *tert*-butyl methyl ether (3 × 50 ml). The combined organic layers were dried with anhydrous magnesium sulfate and distilled at 60–63 °C/2 torr to give 82 g (87%) of **4a** as a red liquid with a strong terpene-like odor (lit. [3] b.p. 56–57 °C/5 torr). EPR (in cyclohexane): a_N = 15 Gauss. UV-Vis (*n*-octane): λ_{max} = 247 (ε = 8.0), 464 nm.

Di-tert-pentylnitroxyl (**4b**). To a solution of di-*tert*-amylamine (**9b**, 3 g, 0.002 mol) in methanol (16 ml) was added sodium tungstate dihydrate (0.1 g) and a 30% aqueous hydrogen peroxide solution (8 ml). Reaction for 3 days and work-up as described for **4a** gave **4b** (2.5 g, 76%), b.p. 52–54 °C/0.35 torr (lit. [3] 76–77 °C/5 torr). MS(EI) (70 eV): *m/z* = 172 [M^+, 1.2], 102 (5), 88 (4), 83 (4), 74(15), 71 (100), 74 (15), 58 (9), 55 (15).

tert-Octyl-tert-pentylnitroxyl (**4c**). A solution of *tert*-butyl hydroperoxide (4 ml, 40 mmol) in 1,2-dichloroethane (50 ml) was added to a stirred solution of *tert*-octyl-*tert*-pentylamine (**9c**, 4.0 g, 20 mmol) in 1,2-dichloroethane (50 ml) containing a mixture of molybdenum (IV) oxide (100 mg) and molybdenum hexacarbonyl (100 mg), in a 3-neck 200 ml reaction flask equipped with a stirrer and reflux condenser. The reaction mixture was brought to a gentle boiling. After 30 min the reaction mixture became light yellow in color. The reaction mixture was left at 23–25 °C for 3 weeks during which time it turned brown in color. The reaction mixture was diluted with *tert*-butyl methyl ether (200 ml) to precipitate the inorganic products. The solution was filtered through a Celite filter aid, and the solvent was removed *in vacuo*. The residue was distilled at 72–75 °C/0.5 torr using a short path distillation apparatus to give 1.7 g (40%) of **4c**. MS (EI, 15 eV): *m/z* = 214 [M^+, 6], 170 (8), 152 (10), 144 (11), 129 (11), 128 (12), 114 (22), 113 (100), 103 (10), 102 (13).

Thermal stability measurements

The thermal decomposition studies were carried out by heating solutions of selected nitroxyl radicals in either *n*-heptane, *n*-octane, or in 1,2,4-trimethylbenzene in a 3-neck 250-ml flask equipped with a magnetic stirring bar, thermometer, and reflux condenser. One of the necks was closed with a rubber septum. The flask was placed in a heating mantle on top of a magnetic stirring plate, and filled with a nitroxyl solution (100 ml). The agitated solutions were heated to boiling until complete decomposition occurred which was indicated by the disappearance of the brown-red color and a change into a bluish solution. Small samples were removed periodically with a glass syringe and used for measuring the UV-Vis spectra. After each analysis the samples were returned to the flask.

Polymerization experiments

Polymerization experiments were carried out in 25 ml glass tubes which were open to the air, and filled with portions of vinyl monomers (10 ml). To each sample was added an initiator and inhibitor as shown in Tables V-VIII. The samples were placed in test tube racks and heated in a water bath, which was equipped with a thermostat. Because of the toxic, hazardous character of many vinyl monomers, the experiments were conducted in an exhaust hood. In those cases, when applicable, small samples of the solutions were removed with glass pipets and used for refractive index measurements. After each measurement the prisms in the refractometer were carefully cleaned with toluene and acetone. In other cases, the samples were heated until the action of the inhibitors ceased and the samples polymerized.

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