Decomposition of Model Alkoxyamines in Simple and Polymerizing Systems. I. 2,2,6,6-Tetramethylpiperidinyl-*N*-oxyl-Based Compounds

GENNADY S. ANANCHENKO, HANNS FISCHER

Physikalisch-Chemisches Institut, Universitaet Zuerich, Winterthurerstrasse 190, CH 8057 Zuerich, Switzerland

Received 22 May 2001; accepted 18 July 2001

ABSTRACT: The thermal decomposition of five alkoxyamines labeled TEMPO–R, where TEMPO was 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl and R was cumyl (Cum), 2-*tert*-butoxy-carbonyl-2-propyl (PEst), phenylethyl (PhEt), 1-*tert*-butoxy-carbonylethyl (EEst), or 1-methoxycarbonyl-3-methyl-3-phenylbutyl (Acrylate-Cum), was studied with ^{1}H NMR in the absence and presence of styrene and methyl methacrylate. The major products were alkenes and the hydroxylamine 1-hydroxy-2,2,6,6-tetramethyl-piperidine (TEMPOH), and in monomer-containing solutions, unimeric and polymeric alkoxyamines and alkenes were also found. Furthermore, the reactions between TEMPO and the radicals EEst and PEst were studied with chemically induced dynamic nuclear polarization. In comparison with coupling, TEMPO reacted with the radicals Cum, PEst, PhEt, and EEst and their unimeric styrene adducts by disproportionation to alkenes and TEMPOH only to a minor extent (0.6–3%) but with the radical adducts to methyl methacrylate to a considerable degree (≥20%). Parallel to the radical cleavage, TEMPO–EEst (but not the other alkoxyamines or TEMPO–Acrylate-Cum) underwent substantial nonradical decay. The consequences for TEMPO-mediated living radical polymerizations are discussed. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 3604–3621, 2001

Keywords: living polymerization; radical polymerization; initiators; kinetics (polym.)

INTRODUCTION

Living and controlled free-radical polymerizations mediated by nitroxides[1–3] yield polymers with low polydispersities, controlled molecular weights, and reactive nitroxide end groups that allow chain extensions and the formation of block copolymers. They are based on reactions 1–4, that is, the cleavage (reaction 1) of the nitroxide-capped dormant polymer chains R_n–Y into transient carbon-centered radicals $R_n^\bullet$ with n monomer units and persistent nitroxide radicals $Y^\bullet$, recoupling (reaction 2) and propagation (reaction 3), and termination (reaction 4), and they are often initiated by low molecular weight alkoxyamines, R_0–Y:[3]

$$R_n{-}Y \rightarrow R_n^\bullet + Y^\bullet \quad (1)$$

$$R_n^\bullet + Y^\bullet \rightarrow R_n{-}Y \quad (2)$$

$$R_n^\bullet + M \rightarrow R_{n+1}^\bullet \quad (3)$$

$$R_n^\bullet + R_m^\bullet \rightarrow P_n + P_m \quad (4)$$

For polymer systems, Solomon et al.,[4(a)] Wayland et al.,[4(b)] Fukuda et al.,[4(c)] and Greszta and Matyjaszewski[4(d)] first noticed that self-termination (reaction 4) leads to an excess of persistent radicals and to a quasiequilibrium of reactions 1

Correspondence to: H. Fischer (E-mail: hfischer@pci.unizh.ch)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 39, 3604–3621 (2001)

and 2. Theoretically, this was proven for specific kinetic conditions.[5] The excess nitroxide accelerates the cross-coupling (reaction 2) and retards the self-termination, although the latter never stops completely. If the monomer is consumed before appreciable self-termination has occurred, the self-termination products are only minor fractions. In other fields of chemistry, the dominance of the cross-coupling in reactions involving transient and persistent radicals has been known for some time, and it is called the persistent radical effect.[6] The principle operates also in living polymerizations mediated by other persistent radicals and in atom transfer radical polymerizations.[3]

Reactions that interfere with 1–4 may strongly alter the polymerization kinetics and properties of the products. One of the most detrimental processes is the formal β-hydrogen atom transfer from the transient propagating to the persistent radical. It leads to polymer chains with a terminal double bond (a macromonomer) and a hydroxylamine and can occur by a radical cross-disproportionation (reaction 5) that accompanies the cross-coupling (reaction 2)

$$R_n^{\bullet} + Y^{\bullet} \rightarrow R_n(-H) + YH \qquad (5)$$

by a radical cage disproportionation or a nonradical alkene elimination (reaction 6) that parallels the cleavage (reaction 1):

$$R_n - Y \rightarrow R_n(-H) + YH \qquad (6)$$

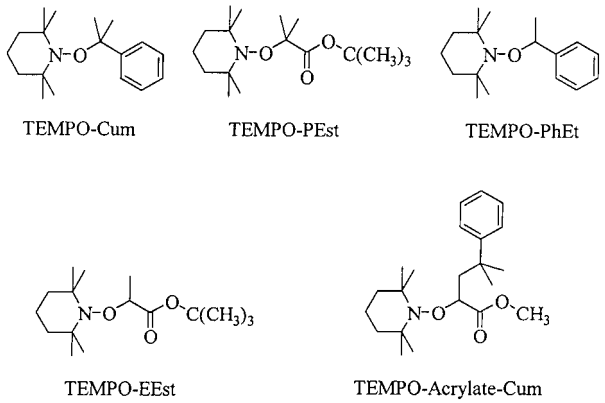
Deficiencies of experimental polymerizations have been attributed to these reactions, and the available data suggest that their extent depends strongly on the structures of the nitroxide and carbon-centered species.[4(c),5(b),7–19]

In a recent theoretical analysis,[20] we showed that the overall effects of reactions 5 and 6 are nearly undistinguishable. In the absence of other initiations, the monomer conversion ceases at an approximate time $2(k_d f_D)^{-1}$, where k_d is the rate constant for the homolytic bond cleavage (reaction 1) and f_D is the fraction of disproportionation in the radical–radical reactions 2 and 5 or the ratio of the rates of reactions 6 and 1. Even for relatively small values of f_D, the end of conversion may occur long before complete monomer conversion, and it is accompanied by a final increase in the polydispersity index.[20]

Here, we extend our experimental studies of reactions involved in nitroxide-mediated living polymerizations and related processes[21,22] and address the alkene and hydroxylamine formation in 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl) (TEMPO)-based systems. To this end, we follow with ^{1}H NMR product formation during the thermolysis of the compounds of Scheme 1 in the absence and presence of protonated and deuterated styrene and methyl methacrylate and in the solvent chlorobenzene under oxygen-free conditions. The alkoxyamines are abbreviated as TEMPO–R, and the leaving groups are R = cumyl [TEMPO–Cum; 2-phenyl-2-(2,2,6,6-tetramethylpiperidinyl-*N*-oxy)-propane], 2-*tert*-butoxy-carbonyl-2-propyl [TEMPO–PEst; 2-*tert*-butoxy-carbonyl-2-(2,2,6,6-tetramethyl-piperidinyl-*N*-oxy)-propane], phenylethyl [TEMPO–PhEt; 1-phenyl-1-(2,2,6,6-tetramethyl-piperidinyl-*N*-oxy) ethane], 1-*tert*-butoxy-carbonylethyl [TEMPO–EEst; 1-*tert*-butoxy-carbonyl-1-(2,2,6,6-tetramethylpiperidinyl-*N*-oxy)-ethane], and 1-methoxycarbonyl-3-methyl-3-phenylbutyl [TEMPO–Acrylate-Cum; 1-methoxycarbonyl-3-methyl-3-phenyl-1-(2,2,6,6-tetramethyl-piperidinyl-*N*-oxy)-butane]. The leaving radicals R · resemble the propagating radicals of α-methylstyrene (Cum), methacrylates (PEst), styrene (PhEt), and acrylates (EEst and Acrylate-Cum). Besides the mechanisms, we also deduce rate constants by kinetic simulations. In addition, we report on chemically induced dynamic nuclear polarization (CIDNP)[22] in reactions concerning TEMPO–PEst and TEMPO–EEst that support the main conclusions.

EXPERIMENTAL

TEMPO–Cum, TEMPO–PhEt, TEMPO–PEst, and TEMPO–EEst were synthesized in agreement with ref. 23, purified by recrystallization or Kugelrohr



Scheme 1

distillation (temperature ~ 50 °C at 10^{-4} mbar), and stored at −20 °C.

4-Methyl-4-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-pentanoic acid methyl ester (TEMPO–Acrylate-Cum) was synthesized as follows. A mixture of 0.4 mmol of TEMPO–Cum and 24 mmol of distilled methylacrylate in 20 mL of toluene was freed from oxygen by purging with argon for 30 min. Then, it was stirred for 1.5 h at 100 °C under an argon atmosphere. The solvent and excess methylacrylate were removed by evaporation. The residue was purified by Al_2O_3 column chromatography with 4/1 hexane/ether as an eluent, and the fraction eluting before TEMPO was collected. Solvent removal yielded a colorless solid (22%, mp = 91–92 °C).

^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.35–7.20 m (4 H, CH-ortho, meta), 7.12 m (1 H, CH-para), 4.01 dd ($^3J_{HH}$ = 11.3; 3.1 Hz, 1 H, CHO), 3.25 s (3 H, OCH_3), 2.37 dd ($^2J_{HH}$ = 13.6 Hz; $^3J_{HH}$ = 11.3 Hz; 1 H, H-1 in CH_2), 2.07 dd ($^2J_{HH}$ = 13.6 Hz; $^3J_{HH}$ = 3.1 Hz; 1 H, H-2 in CH_2), 1.55–1.20 br, 1.35 br s, 1.27 br s [12 H, $(CH_2)_3$ of piperidine and $2CH_3$ of Cum], 1.05 br s, 0.99 br s, 0.86 br s (12 H, 4 CH_3). ^{13}C NMR (250 MHz, $CDCl_3$, ^{13}C–^{1}H correlation, δ): 173.55 (C═O), 147.38 (C-ipso), 127.83 (C-meta), 126.10 (C-ortho), 125.73 (C-para), 82.64 (CH—O), 60.41 and 59.08 (C-2 and C-6 of piperidine), 50.95 (CH_3—O), 46.00 (CH_2), 40.26 and 40.01 (C-3 and C-5 of piperidine), 36.10 (C—Ph), 33.51, 32.66, 20.20, and 19.98 ($4CH_3$ in TEMPO), 30.33 and 28.01 (2 CH_3 in Cum), 17.01 (C-4 of piperidine). MS (70 eV) *m/z* (relative intensity): 361 $[M]^+$ (33), 346 $[M–CH_3]^+$ (28), 313 (25), 213 (40), 180 (54), 156 $[TEMPO]^+$ (100).

2,2,4,4-Tetramethyl-3-oxo-pentanedioic acid dimethylester (PEst ketone) and 2,4-dimethyl-3-oxo-pentanedioic acid dimethylester (EEst ketone) were synthesized from 3-oxo-pentanedioic acid dimethylester (Aldrich) by methylation in tetrahydrofuran with potassium hydride and methyl iodide. The NMR solvent deuterated chlorobenzene (CIL, 99% D) was distilled and stored over a molecular sieve (300 pm) to keep it free from water. Deuterated styrene (CIL, 98% D) and deuterated methyl methacrylate (CIL, 98% D, or ACROS Organics, 99% D) were distilled under vacuum at 40–60 °C and stored at 0 °C. Deuterated toluene (CIL, 99.6% D) was used as received.

For the product determinations, typically 0.7 mL of 0.019–0.020 M solutions of the alkoxyamine, pure or in the presence of the monomers in 10 (±1)-fold and 50 (±5)-fold excesses, that is, about 0.2 and 1 M, were degassed by several freeze–pump–thaw cycles to 10^{-5} mbar and sealed off under 100 mbar of He in conventional NMR tubes. This procedure proved sufficient to avoid the formation of oxidation products that were found in an earlier product study on TEMPO–PhEt.[11] Freshly prepared samples were introduced into the preheated ^{1}H probe head of a Bruker DPX 200 NMR spectrometer equipped with a Bruker BVT-1000 temperature controller. The temperature (100 or 120 °C) was calibrated to ±0.5 °C with an 80% solution of ethylene glycol in DMSO-d_6 and a standard procedure (Bruker DPX manual). The temperature drifted during the reactions by less than −1°C at 100°C and less than −2°C at 120°C. Fourier transform NMR spectra were recorded repeatedly during the reactions with a spectral width of about 7.5 ppm, 16,000 data points, single scans, $\pi/2$ pulses, digital filtering, and a line broadening factor of 0.3. We employed a minimal delay time of 4 min between the individual recordings to ensure the thermal equilibration of the magnetization before the next pulse. The NMR frequencies were internally referenced to the chemical shifts of the residual protons of the deuterated solvent, and these were referenced in nondegassed solutions at 120 °C to the internal standard tetramethylsilane as 7.14, 7.00, and 6.96 ppm for the *o*-, *m*-, and *p*-H atoms, respectively. All reactions were repeated several times, and the results were reproducible. The concentrations given later are accurate within about ±10%.

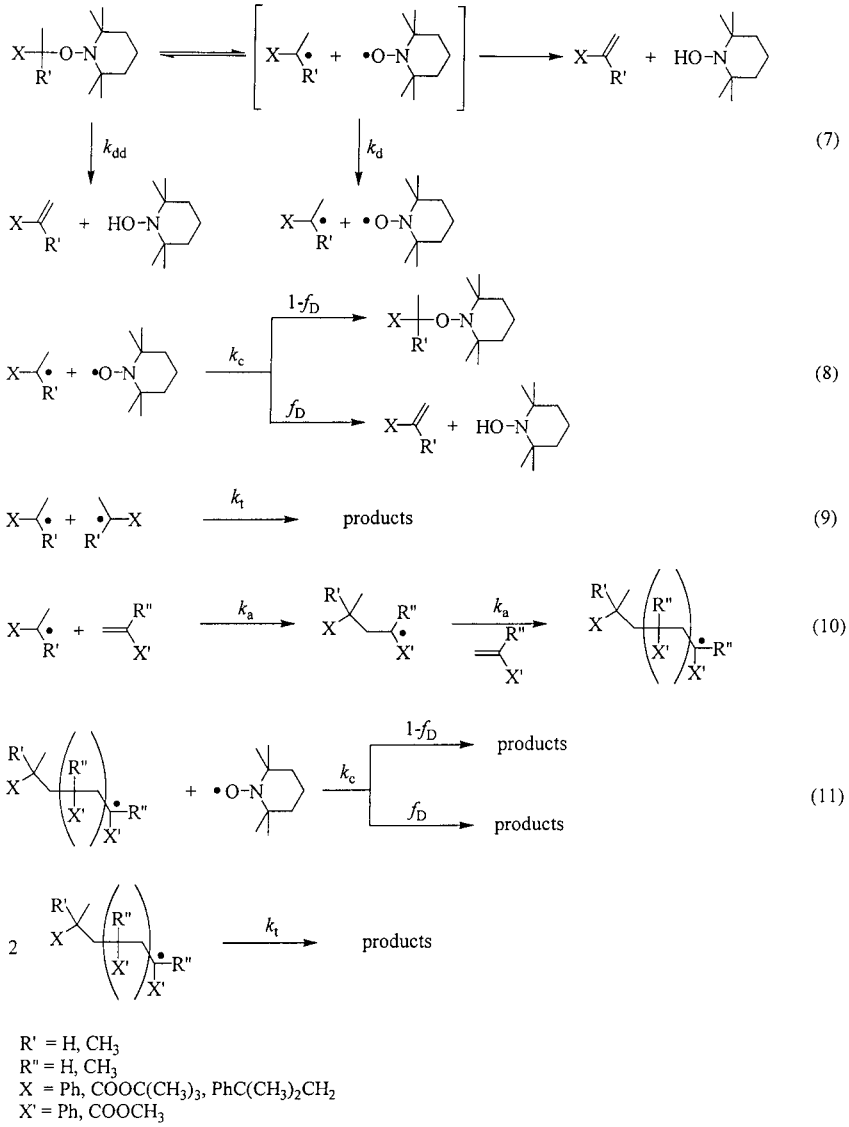
The experimental arrangement for time-resolved CIDNP has been described before.[24] Degassed ketone solutions were irradiated from the side within the CIDNP probe head (Bruker) of the NMR spectrometer with 20-ns pulses of a Lambda Physik EMG 100 excimer laser at 308 nm. After the individual light pulses, CIDNP spectra were recorded with a 1.850μs $\pi/2$ NMR pulse that detected only net polarizations.

Rate constants for the formation of TEMPO from the alkoxyamines were obtained in chlorobenzene by electron spin resonance (ESR; Bruker ER 100E), as in earlier work,[21(a,b),22] from the increase of the TEMPO concentration during thermolysis under scavenging of the alkyl radicals with oxygen (air), which prevented the regeneration of the starting compounds.

REACTION MECHANISMS

Expectation

Scheme 2 shows the expected principal reactions. The homolytic cleavage of the C—O bond of the



Scheme 2

alkoxyamines yields geminate singlet pairs of transient carbon-centered and persistent nitroxide radicals. In parallel, a concerted alkene elimination (reaction 6) may occur. Upon diffusional reencounters, the radical pairs form geminate (cage) products by coupling to the alkoxyamine and by disproportionation to an alkene and to 1-hydroxy-2,2,6,6-tetramethylpiperidine (TEMPOH). The geminate (cage) processes (reaction 7) last a few nanoseconds in low-viscosity media. It is known that carbon-centered radicals react with TEMPO with smaller than diffusion-controlled rates;[21(c),25] therefore, large cage effects are very unlikely in alkoxyamine decays.[10]

In the bulk, the radicals undergo the cross reaction (reaction 8) with the total rate constant k_c either by coupling (fraction $1 - f_D$) to the parent alkoxyamine or by disproportionation (fraction f_D) to an alkene and TEMPOH.[26] The transient radicals also self-terminate by coupling and disproportionation with the total rate constant k_t (reaction 9). Furthermore, they add (reaction 10) to the monomer (k_a), and the resulting unimeric carbon-centered radicals react with TEMPO (reaction 11) by coupling to unimeric alkoxyamines or by disproportionation to TEMPOH and unimeric alkenes and undergo further monomer addition (k_p). Decomposition of the unimeric alkoxyamines starts the repetition of all these processes and leads to propagating radicals, dormant alkoxyamines, alkenes, TEMPOH, and self-termination products with increasing monomer content.

Besides these reactions, TEMPO may add slowly to the monomers.[27] This process is not included in Scheme 2 because we did not find the corresponding reaction products, and this is presumably due to the rather small concentrations of liberated TEMPO and the monomers under our experimental conditions.

For several alkoxyamines, the formation of alkenes and hydroxylamines has been addressed earlier. During the decomposition of TEMPO–PhEt, Priddy et al.[9] observed the formation of styrene, phenylethane, and 1,2-diphenylethane with styrene in a large excess. Because the self-reactions of the 1-phenyl-1-ethyl (PhEt, styryl) radical alone would lead to equal yields of styrene and phenylethane, the excess of styrene was attributed to the disproportionation between PhEt and TEMPO, and this was visualized as a cage process. Fukuda et al.[12] attributed the decay of TEMPO–polystyrene and benzoyloxy–styrene–TEMPO to a direct decomposition and bulk disproportionation. Their rate constants reveal a small fraction of these processes for styryl-type radicals and TEMPO of about 0.4% at 100 °C. In a product study on TEMPO–PhEt, Georges et al.[11] observed the formation of TEMPOH and styrene in about equal amounts and attributed this to bulk disproportionation (reaction 8). Evidence for the formation of alkenes in TEMPO-mediated polymerizations of styrene was also given by Vairon et al.[28]

For the reaction between the Cum radical and TEMPO in the bulk at 70 °C, we previously determined a fraction of bulk disproportionation of about 0.5%.[22] More recently, Scaiano et al.[10] reported fractions of 3% for TEMPO–PhEt and about 5% for TEMPO–Cum at 125°C. These values are considerably larger than those found by Fukuda et al.[12] and in our earlier work.[22] Scaiano et al. ruled out cage disproportionation (reaction 7) and cited findings that seem to discard bulk disproportionation (reaction 8). Hence, they attributed the formation of alkene and hydroxylamine entirely to a nonradical decay of the alkoxylamine. The latter mechanism also suggests itself by the large alkene fractions found in Studer's work on other TEMPO-based alkoxyamines.[13]

In nitroxide-mediated polymerizations of methyl methacrylate, the formation of alkenes (macromonomers) and hydroxylamine is very important.[7,18] Only limited conversions are possible, and the products are mainly hydroxylamine and alkenes (macromonomer) with relatively high polydispersities. In simulations, Moad et al.[7] assumed bulk disproportionation only and deduced a disproportionation/combination ratio of 0.06 % for the reaction of the propagating methyl methacrylate radical with 1,1,3,3-tetraethylisoindoline-*N*-oxyl at 90 °C. This ratio is much smaller than the ratios for the styrene- and TEMPO-based systems given previously, and it contrasts with the experience from polymerizations. However, in the simulations, a rather large dissociation constant ($k_d = 1\ s^{-1}$) of the dormant alkoxyamine-capped methyl methacrylate chains was assumed. On the basis of TEMPO–PEst, a more reasonable value would be $k_d = 1 \times 10^{-3}\ s^{-1}$.[21(a)] The effects of disproportionation scale with the product $k_d f_D$.[20] Hence, the actual fraction of disproportionation for methyl methacrylate may be much larger than stated.[7] In systems involving acrylates and TEMPO, the extent of alkene and hydroxylamine formation has not yet been studied.

As pointed out previously, there are three pathways for the formation of alkene and TEMPOH, namely, the concerted nonradical route (k_{dd}), bulk disproportionation, and the small reaction of the geminate radical pair, although this is less probable.[10] With these means, the concerted decay and geminate radical disproportionation cannot be separated because both occur on nanosecond or subnanosecond timescales.[10] However, bulk disproportionation can be distinguished from these fast processes because it is suppressed by a scavenging of the transient radicals, for instance, by their addition to the monomer. For the geminate and bulk disproportionations, f_D values should be approximately equal. Hence, if f_D is small for the bulk, large alkene and TEMPOH fractions from the fast processes are likely due to the direct nonradical decay. Moreover, reaction systems in which the transient radicals are generated separately and react with the nitroxide thereafter allow us to study the extent of bulk disproportionation separately. These methods are applied in the following studies.

TEMPO–Cum and TEMPO–PEst

Figure 1 shows an NMR spectrum taken during the thermolysis of 0.020 M TEMPO–Cum in the absence of monomer at 100°C and at about a 60% alkoxyamine conversion. Apart from the residual alkoxyamine (I), one observes the products α-methylstyrene (II; olefinic protons, 5.27 and 4.98 ppm; methyl group, 2.01 ppm) and TEMPOH (III, OH; broad singlet ~ 4 ppm; ring methylene protons, 1.4 ppm; four methyl groups, 1.12 ppm).

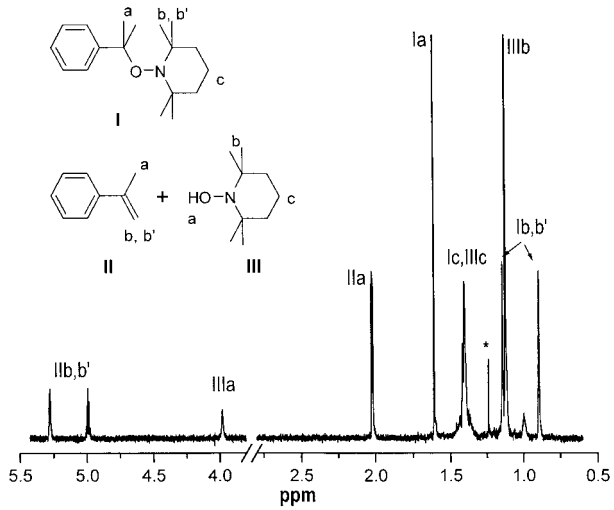


Figure 1. NMR spectrum taken after 2 h of the thermolysis of TEMPO–Cum at 100 °C.

The assignments for α-methylstyrene were made by comparison with the authentic compound, and the chemical shift of the TEMPOH methyl groups is close to that known for *o*-xylene solutions.[11] Furthermore, there is a weak signal of dicumyl (asterisk; four methyl groups, 1.24 ppm) and a small broad signal at about 1 ppm that belongs to traces of water. Throughout the reaction, α-methylstyrene and TEMPOH appear in equal concentrations, and this indicates that they are formed in a common process. To a very good approximation, their buildup balances the loss of TEMPO–Cum. At about 80% alkoxyamine conversion, dicumyl accounts only for about 3% of the alkoxyamine conversion; that is, self-termination is a very minor process, indeed. Figure 2(a,b) displays the time dependencies of the concentrations of the alkoxyamine, α-methylstyrene, and TEMPOH in solid symbols.

The findings support the expected mechanism (Scheme 2), the homolysis of the alkoxyamine, the (unobservable) back reaction between the carbon-centered Cum radical and TEMPO by coupling, the formation of alkene and TEMPOH in the early and/or bulk stages, and the self-termination of Cum (reaction 9) by coupling to dicumyl.[29] Our previous work[22] with independently generated radicals provided an upper limit $f_D = 1\%$ for bulk disproportionation between TEMPO and Cum. Obviously, the coupling between these radicals dominates strongly.

By stoichiometry, the concentration of liberated TEMPO is twice the concentration of dicumyl. Hence, at large conversions, the TEMPO concentration approaches 10^{-3} M. This specifies the excess of the persistent species in the reaction course. It is large enough to explain the minor yield of the self-termination product dicumyl but is also small enough to be compatible with the absence of NMR line broadening.[30]

Figure 3 shows an NMR spectrum taken during the decomposition of 0.02 M TEMPO–Cum at 100 °C in the presence of about a sevenfold excess of styrene at approximately an 80% conversion of the alkoxyamine. Apart from residual alkoxyamine (I), α-methylstyrene (II), TEMPOH (III), and dicumyl that were already discussed, one observes resonances that are assigned to 1,3-diphenyl-1-(2,2,6,6-tetramethyl-piperidinyloxy)-3-methylbutane.[31] This is the expected unimer (IV) formed by the coupling of TEMPO with the unimeric adduct radical of Cum to styrene. In the presence of deuterated styrene, only the methyl

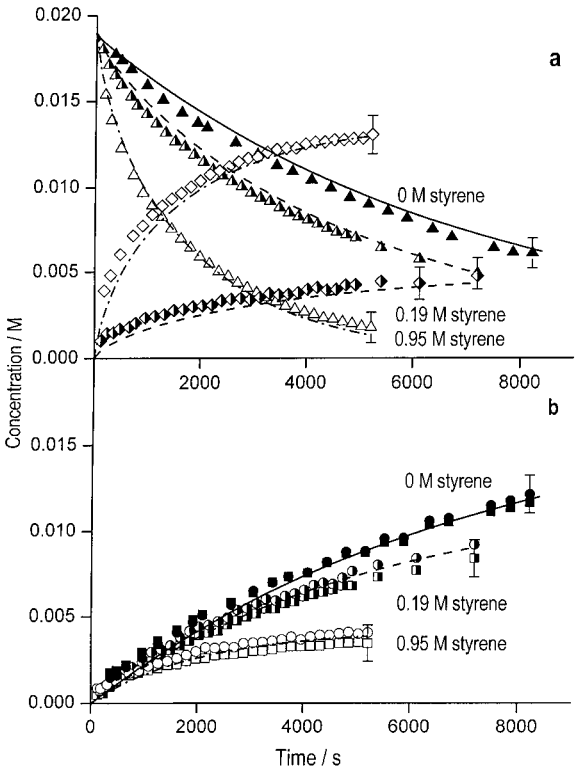


Figure 2. Time dependence of concentrations during the thermolysis of TEMPO–Cum at 100 °C in the absence and presence of styrene-d_8. Solid, half-filled, and open symbols denote concentrations in the absence of monomer, the presence of a 10-fold monomer excess, and the presence of a 50-fold excess, respectively. Triangles, squares, circles, and diamonds represent initial alkoxyamine, TEMPOH, alkene, and unimeric alkoxyamine, respectively.

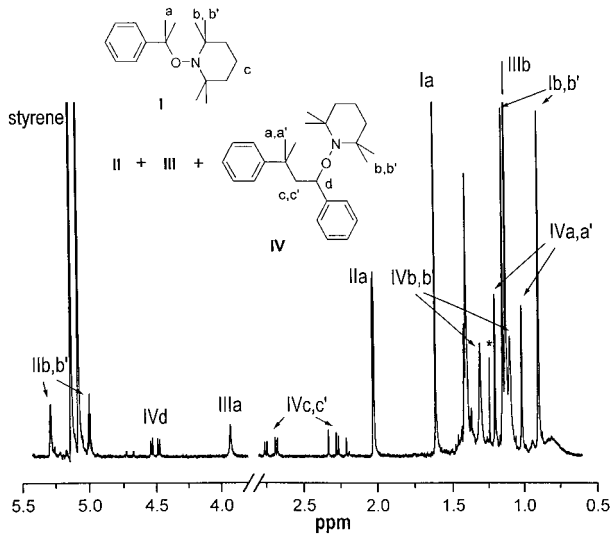


Figure 3. NMR spectrum taken after 1.5 h of the thermolysis of TEMPO–Cum at 100 °C for a sevenfold excess of styrene-h_8.

groups of the unimer IV are observed. Alkenes from disproportionation between the unimeric radical and TEMPO are absent, and this confirms the small disproportionation/combination ratio for styryl-type radicals and TEMPO.[12]

Figure 2(a,b) also displays the kinetics of the decay of the alkoxyamine and the formation of the unimer, α-methylstyrene, and TEMPOH for 0.19 M styrene-d_8 (half-filled symbols) and 0.95 M styrene-d_8 (open symbols). With increasing styrene concentration, the alkoxyamine decays faster and the unimer formation increases. As expected from Scheme 1, the regeneration of TEMPO–Cum is now suppressed by the addition of Cum to styrene. The scavenging of Cum also reduces the yields of α-methylstyrene and TEMPOH, and so these products cannot be formed extensively by a direct decay of TEMPO–Cum. At large alkoxyamine conversions and for the higher styrene concentration, there are also small broad signals of methyl groups of unidentified polymeric products.

The thermolysis of TEMPO–PEst at 100 °C shows the same product pattern as that of TEMPO–Cum. The major products are *tert*-butylmethacrylate (olefinic protons, 5.99 and 5.28 ppm; methyl group, 1.84 ppm; *tert*-butoxy group, 1.43 ppm) and TEMPOH in nearly 1:1 ratios. The self-termination products of PEst are hardly observable. No additional signals appear up to at least 80% alkoxyamine conversion. In the presence of styrene-d_8, the alkoxyamine decay is again markedly accelerated, and the formations of alkene and TEMPOH are reduced. Furthermore, there is the expected unimer[32] formed by the coupling of the adduct of PEst to styrene with TEMPO. As for TEMPO–Cum, the corresponding disproportionation product is not detected.

Figure 4 displays the time evolution of the major species. The unimer is not included because severe line overlap prevented accurate measurements of the concentration. However, the similarity of Figures 2 and 4 confirms that the major reactions for TEMPO–Cum and TEMPO–PEst are the same in the absence and presence of styrene. There is no detectable concerted alkene elimination from the alkoxyamine, and f_D is small for the bulk disproportionation. Furthermore, the adduct of PEst to styrene prefers to couple with TEMPO, as does the adduct of Cum. For both TEMPO–Cum and TEMPO–PEst, the buildup of the unimeric alkoxyamines means that these cleave more slowly to radicals than the parent compounds.

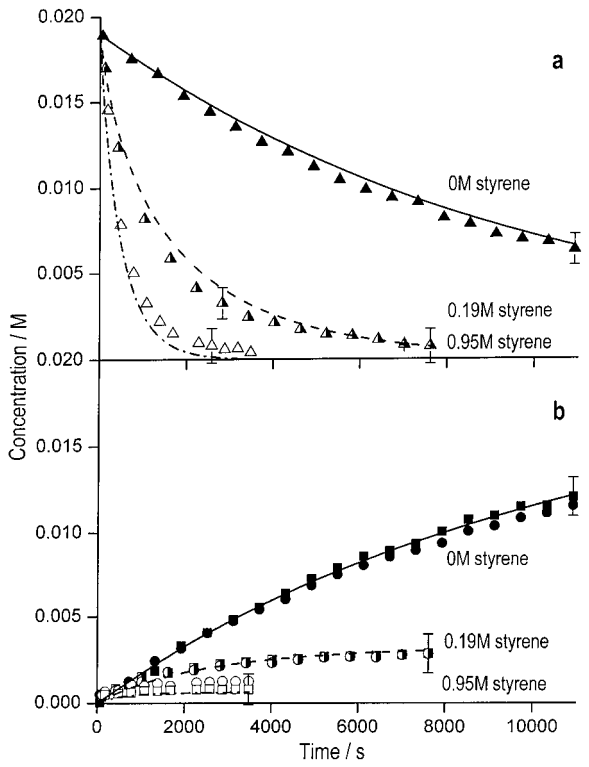


Figure 4. Time dependence of concentrations during the thermolysis of TEMPO–PEst at 100 °C in the absence and presence of styrene-d_8. Solid, half-filled, and open symbols denote concentrations in the absence of monomer, the presence of a 10-fold monomer excess, and the presence of a 50-fold excess, respectively. Triangles, squares, and circles represent initial alkoxyamine, TEMPOH, and alkene, respectively.

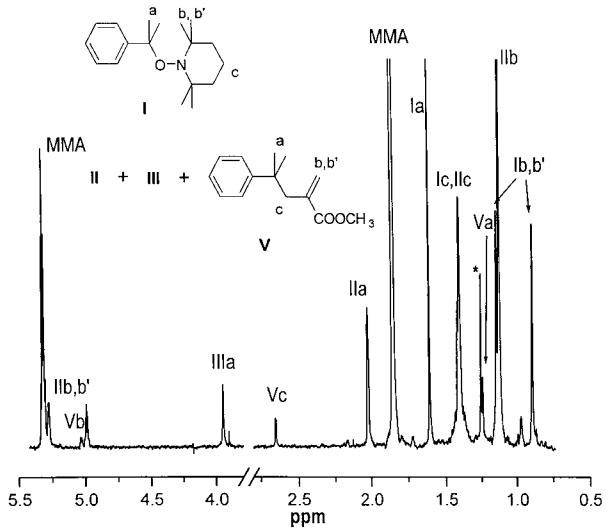


Figure 5. NMR spectrum taken after 1.5 h of the thermolysis of TEMPO–Cum at 100 °C for a fivefold excess of methyl methacrylate-h_8.

Figure 5 shows an NMR spectrum taken at 100 °C during the decomposition of TEMPO–Cum in the presence of a fivefold excess of methyl methacrylate at approximately a 70% alkoxyamine conversion. Apart from the familiar products α-methylstyrene (II), TEMPOH (III), and dicumyl (asterisk), one also observes an unimer. However, this is not the coupling product found for styrene but is instead, by comparison with literature data,[33] 4-methyl-2-methylene-4-phenylpentanoic acid methyl ester (V). This alkene arises from the disproportionation between the Cum adduct to methyl methacrylate and TEMPO and/or a direct alkene elimination from the unimeric coupling product. However, the latter compound is not observed, and this renders the direct process unlikely.

In agreement with earlier findings,[7] the β-hydrogen atoms are transferred from the methyl group of the methacrylate-derived radical and not from the methylene group. Obviously, for the radical adducts to methyl methacrylate, the cross reaction with TEMPO leads mainly to alkene and TEMPOH, whereas for styrene, it leads mainly to the coupling product. The dominant disproportionation of methacrylate-derived radicals is further confirmed by the observation of the corresponding alkene during the decomposition of TEMPO–PEst at 100 °C in the presence of excess methyl methacrylate. The chemical shifts of the alkene 4-carbomethoxy-2,2-dimethyl-4-pentenoic acid t-butyl ester[34] are close to literature data for a similar compound.[35]

Figure 6 shows the time dependence of the concentrations of TEMPO–Cum, α-methylstyrene, and TEMPOH for different methyl methacrylate concentrations. As seen in Figures 2 and 4 for the monomer styrene, the lifetime of TEMPO–Cum is shortened by the presence of the monomer, and the formation of α-methylstyrene is suppressed. However, the yield of TEMPOH now increases with increasing monomer concentration, and this is due to its formation of TEMPOH from the unimeric radicals and TEMPO. This reaction prevents further propagation;[7] therefore, in contrast to the styrene-containing solutions, no signals of polymeric products were observed. The decay of TEMPO–PEst in methyl methacrylate-containing solutions led to very similar results.

TEMPO–PhEt and TEMPO–EEst

The thermolysis of TEMPO–PhEt at 120 °C provides the products styrene and TEMPOH in about

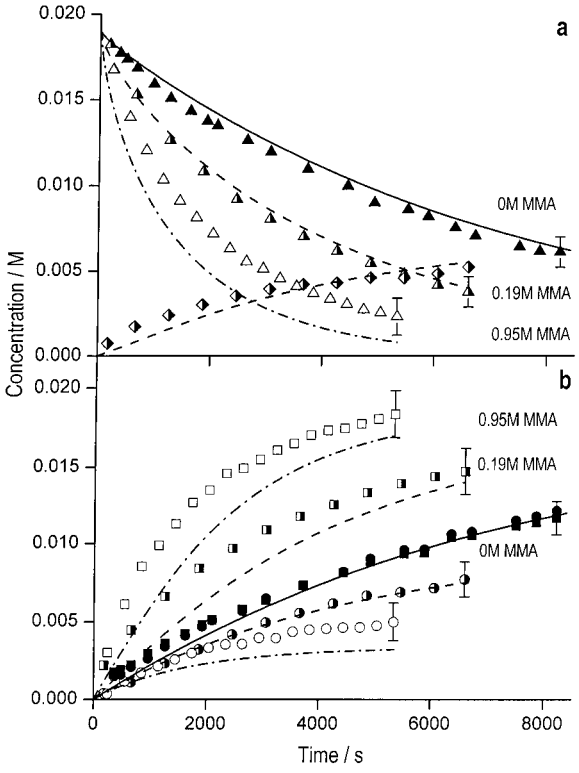


Figure 6. Time dependence of concentrations during the thermolysis of TEMPO–Cum at 100 °C in the absence and presence of methyl methacrylate-d_8. Solid, half-filled, and open symbols denote concentrations in the absence of monomer, the presence of a 10-fold monomer excess, and the presence of a 50-fold excess, respectively. Triangles, squares, circles, and diamonds represent initial alkoxyamine, TEMPOH, alkene, and unimeric alkene (V), respectively.

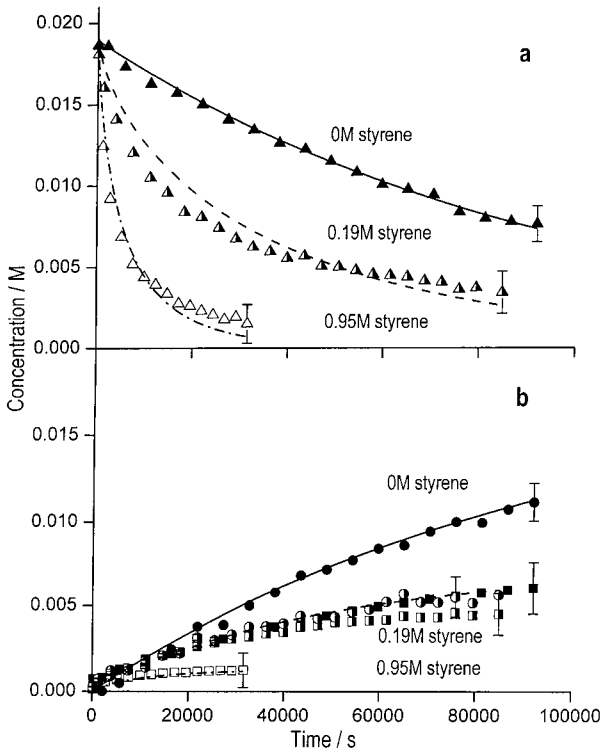


Figure 7. Time dependence of concentrations during the thermolysis of TEMPO–PhEt at 120 °C in the absence and presence of styrene-d_8. Solid, half-filled, and open symbols denote concentrations in the absence of monomer, the presence of a 10-fold monomer excess, and the presence of a 50-fold excess, respectively. Triangles, squares, and circles represent initial alkoxyamine, TEMPOH, and alkene, respectively.

equal concentrations at low conversions. At larger conversions, styrene appears in excess, and a signal at 1.06 ppm is observed that belongs to the four methyl groups of 2,2,6,6-tetramethylpiperidine (TEMPH). Moreover, line broadening is substantial, and it indicates considerable amounts of free TEMPO. Styrene was also the major product in the earlier work, but the formation of TEMPH was not mentioned.[9,11] We did not observe the self-termination products ethylbenzene and 2,3-diphenylbutane, presumably because we used a lower initial TEMPO–PhEt concentration. In the presence of styrene, the formation of TEMPH is suppressed, there is less line broadening, and the yields of styrene and TEMPOH are lower and more nearly equal. Apart from these products, one finds polymeric species with broad NMR signals of the terminal PhEt group at about 2.45 ppm (CH groups), but a unimer was not detected.

Figure 7 shows that the lifetime of TEMPO–PhEt and the yields of styrene and TEMPOH decrease with increasing styrene concentration, and this is because PhEt is scavenged by the addition to styrene. It explains the grossly different decay rates of TEMPO–PhEt reported by Priddy et al.[9] for the absence of styrene and by Hawker and coworkers[35] for the presence of styrene. The decreasing yields of styrene and TEMPOH render large contributions of a direct decay of TEMPO–PhEt[10] unlikely and indicate that the fractions of disproportionation in the reactions between PhEt or its styrene adduct with TEMPO are small. The absence of a detectable unimer and the observation of polymeric species mean that the rate constant for the decomposition of the unimeric alkoxyamine is equal or larger than that of the parent TEMPO–PhEt, in contrast to the cases of TEMPO–Cum and TEMPO–PEst.

It is not clear how the piperidine TEMPH and the considerable amount of free TEMPO are formed. The reaction probably is markedly temperature-dependent because TEMPH was not observed at a lower temperature. Moreover, it is catalyzed by impurities because the yields of TEMPH and TEMPO decreased with careful cleaning and preconditioning of the sample tubes, although their formation was never completely prevented in the absence of monomer. The products are explained by a reaction[37] between two TEMPOH molecules (reaction 12) to water, free TEMPO, and an aminyl radical (TEMP$^\bullet$). The aminyl radical will abstract a hydrogen atom from any donor and give TEMPH (reaction 13). This mechanism is speculative, but it explains the difference between the concentrations of styrene and TEMPOH plus TEMPH. It is balanced by the concentration of liberated TEMPO as estimated from the NMR line widths. In the presence of monomer, the reaction should be less important because the formation of TEMPOH is partly suppressed:

$$2\ \text{TEMPOH} \rightarrow \text{TEMPO}^\bullet + \text{TEMP}^\bullet + \text{H}_2\text{O} \quad (12)$$

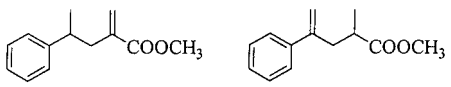
$$\text{R} - \text{H} + \text{TEMP}^\bullet \rightarrow \text{R}^\bullet + \text{TEMPH} \quad (13)$$

In the presence of methyl methacrylate, TEMPO–PhEt yields styrene, TEMPOH, a little TEMPH, and small amounts of polymeric species. Furthermore, at large alkoxyamine conversions, two new olefinic compounds appear in small amounts. In comparison with literature data,[38] these are 2-methylene-4-phenylpentanoic acid methyl ester [olefinic protons at 6.10 ppm (dt, J = 1.6, 2.4 Hz)

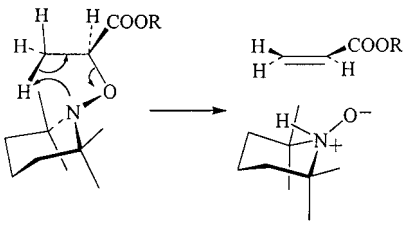
and 5.22 ppm (dt, J = 1.6, 1.2 Hz)] and 2-methyl-4-phenyl-4-pentenoic acid methyl ester [olefinic protons at 5.16 ppm (d, J = 1.5 Hz) and 5.01 ppm (m); Scheme 3]. The structure of the first alkene indicates that the reaction of the PhEt adduct to methyl methacrylate with TEMPO gives mainly alkene and TEMPOH by β-CH_3-hydrogen transfer because it was found before for the methyl methacrylate adducts of Cum and PEst. For the second alkene, there is no obvious explanation, and this also applies to small amounts of α-methylstyrene. Hence, with the exception of the minor formation of TEMPH, the reactions during the thermolysis of TEMPO–PhEt closely parallel those observed for TEMPO–Cum and TEMPO–PEst.

At first sight, the decay of TEMPO–EEst at 120 °C seems to follow the same route. For low conversions, there are only two products, *tert*-butylacrylate and TEMPOH. At higher conversions, TEMPH appears, and there is considerable line broadening. The calibration of the line broadening[30] yielded fairly accurate TEMPO concentrations. As expected from reactions 7–13, the sum of the concentrations [TEMPOH] + [TEMPH] + [TEMPO] was equal to the alkene (acrylate) concentration.

The decomposition of TEMPO–EEst in the presence of styrene and methyl methacrylate yields the same major products as in the absence, and there is only insignificant polymerization. However, in sharp contrast to TEMPO–Cum, TEMPO–PEst, and TEMPO–PhEt, the decay of TEMPO–EEst is only slightly accelerated by the addition of the monomers (Fig. 8). Also, the formations of the alkene and TEMPOH are less retarded. Obviously, the formation of the alkene and TEMPOH from TEMPO–EEst does not occur only by radical disproportionation in the bulk, but it must also be due to a reaction that competes with the homolysis. For TEMPO–Cum, TEMPO–PEst, and TEMPO–PhEt, such a reaction was found to be unimportant. For its explanation, we suggest an elimination via a five-member transition state that resembles the Cope elimination of *N*-oxides[39] (Scheme 4). A radical cage disproportionation cannot be ruled out completely, but it is unlikely because of the small fraction of bulk dis-



Scheme 3



Scheme 4

proportionation (discussed later) and the kinetic arguments (discussed previously).[10]

TEMPO–Acrylate-Cum

The observation of the direct decomposition of TEMPO–EEst prompted the study of the thermolysis of TEMPO–Acrylate-Cum in the absence and presence of styrene. Its homolysis rate constant is expected[21(a)] to be smaller than that of TEMPO–

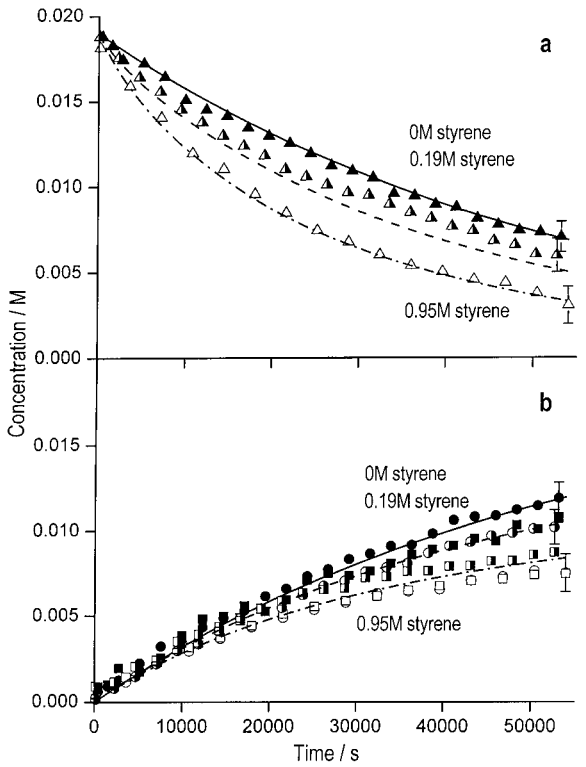


Figure 8. Time dependence of concentrations during the thermolysis of TEMPO–EEst at 120 °C in the absence and presence of styrene-d_8. Solid, half-filled, and open symbols denote concentrations in the absence of monomer, the presence of a 10-fold monomer excess, and the presence of a 50-fold excess, respectively. Triangles, squares, and circles represent initial alkoxyamine, TEMPOH, and alkene, respectively.

Cum; therefore, this unimer was easily synthesized by the heating of TEMPO–Cum in the presence of acrylate (see the Experimental section). At 120 °C and in the absence of monomer, the thermolysis leads to TEMPOH and several products that arise from the Acrylate-Cum residue, such as the expected alkene, α-methylstyrene, and further products without C—C-double bonds. The material balance between the decomposed alkoxyamine and the hydroxylamine is satisfactory (Fig. 9). As for TEMPO–Cum, TEMPO–PEst, and TEMPO–PhEt, but not TEMPO–EEst, the addition of styrene greatly accelerates the decay of starting compound (Fig. 9). Therefore, the decomposition of TEMPO–Acrylate-Cum follows the same pathway as TEMPO–Cum, TEMPO–PEst, and TEMPO–PhEt and does not involve much direct decay. Obviously, TEMPO–EEst is not a good model for longer chain TEMPO–acrylates.

BULK DISPROPORTIONATION BETWEEN TEMPO AND PEst AND BETWEEN TEMPO AND EEst FROM CIDNP

In the previous sections, we have shown that in the absence of monomer, the regeneration of the parent alkoxyamines TEMPO–Cum, TEMPO–PEst, TEMPO–PhEt, and TEMPO–Acrylate-Cum by radical coupling is the major reaction and that disproportionation between the carbon-centered radicals Cum, PEst, and PhEt and their adducts to styrene and TEMPO is a minor pathway, although the alkenes and TEMPOH are the major observable products. Cage reactions are unlikely. Only for TEMPO–EEst is a substantial concerted decay observed, and all radical adducts to methyl methacrylate react with TEMPO mainly by bulk disproportionation. To obtain more information on bulk disproportionation between ester-substituted radicals and TEMPO, we conducted CIDNP experiments. As for the TEMPO–Cum system,[22] the radicals PEst and EEst were generated by the photolysis of ketone precursors and reacted with TEMPO thereafter to form the alkoxyamines and/or the disproportionation products.

Scheme 5 shows the major reactions (PEst, R = CH_3; EEst, R = H). After excitation of the $n\pi^*$ transition, the ketones rapidly cross to the triplet state, from which they cleave into pairs of ester-substituted alkyl and acyl radicals (reaction 14). In the geminate (cage) phase (reaction 15), radical coupling regenerates the parent ketone, and disproportionation provides an aldehyde and an alkene. By analogy with $(CH_3)_3COOCCH_2\dot{C}O$,[40] the escaping acyl radicals should decarbonylate on a microsecond timescale and provide a second alkyl radical (reaction 16). Hence, the slower bulk reactions take place only between the ester-substituted alkyl radicals (reaction 17). In the presence of TEMPO, these reactions are replaced by the coupling and disproportionation of the carbon-centered radicals with the nitroxide (reaction 18).

The upper part of Figure 10 shows a CIDNP spectrum taken at room temperature 100 μs after the laser pulse photolysis of 6 mM PEst ketone $[CH_3OOCC(CH_3)_2COC(CH_3)_2COOCH_3]$ in toluene-d_8. From the g factors and hyperfine coupling constants of the radicals and Kaptein's rules,[41] one expects enhanced absorption for the β-CH_3 protons of the alkyl radical $CH_3OOC\dot{C}(CH_3)_2$ that contribute to the geminate products. This is, in fact, observed (parent ketone, VIa; CH_3 and CH_2 protons of methyl methacrylate, VIIIa and VIIIb; and aldehyde proton, VII). The corresponding protons of the escaping PEst radicals carry emissive polarization.[41] Therefore, their dimer (X) and the disproportionation product $CH_3OOCC(CH_3)_2H$ (IX) exhibit emission. From the ratio of these emissions, a ratio of disproportionation to combination close to 1 is obtained for the self-termination of two PEst radicals ($f_D = 0.5$). This agrees with earlier findings for the propagating radical of methyl methacrylate.[42] Methyl methacrylate is formed in geminate and bulk disproportionations. Therefore, it carries

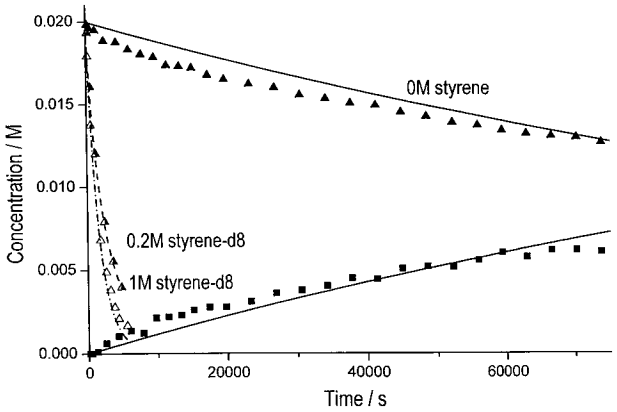
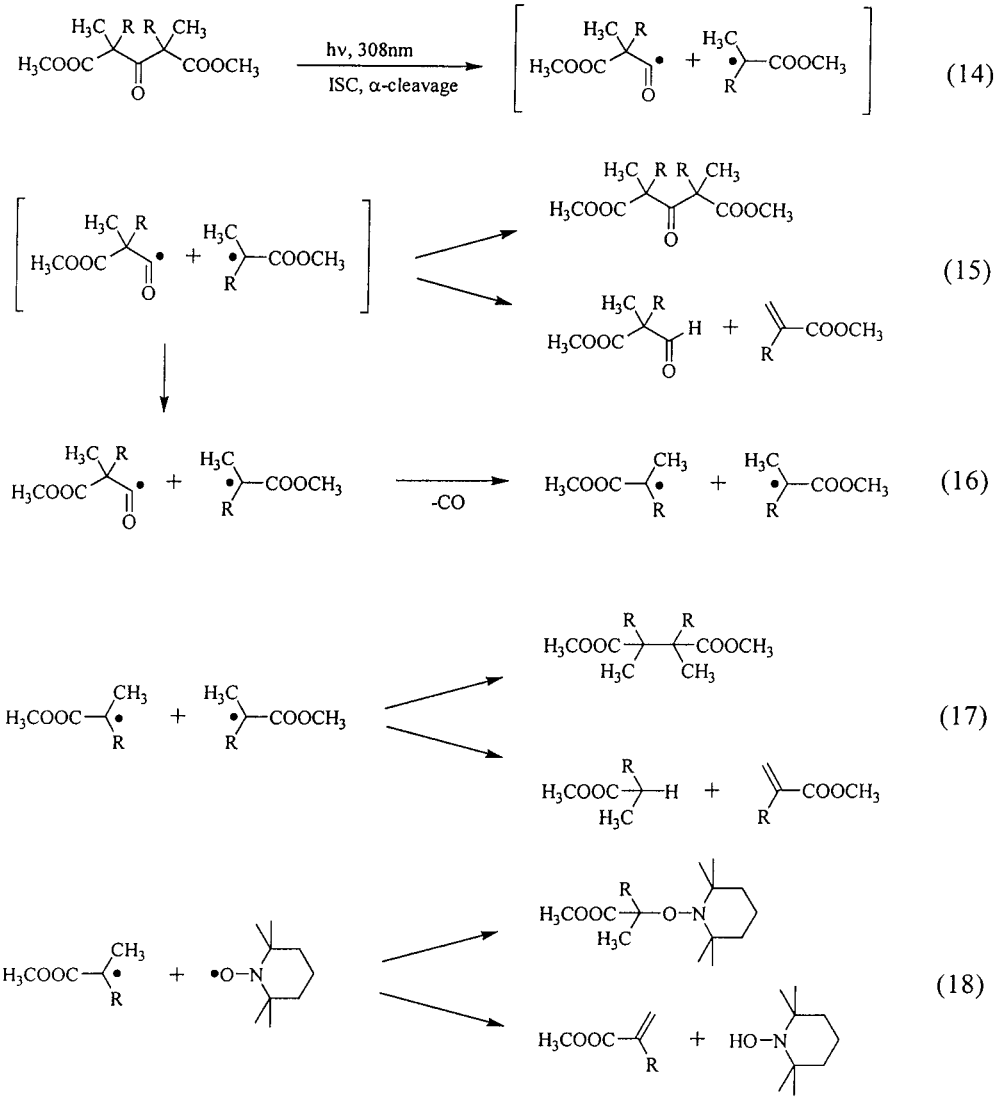


Figure 9. Time dependence of concentrations during the thermolysis of TEMPO–Acrylate-Cum at 120 °C in the absence and presence of styrene-d_8. Solid, half-filled, and open symbols denote concentrations in the absence of monomer, the presence of a 10-fold monomer excess, and the presence of a 50-fold excess, respectively. Triangles and squares represent initial alkoxyamine and TEMPOH, respectively.



Scheme 5

enhanced absorption and emission, and the enhanced absorption from the geminate process dominates.

In the presence of 5 mM TEMPO, the formations of the dimer (X) and $CH_3OOCC(CH_3)_2H$ (IX) are suppressed. Therefore, the corresponding lines are missing in the lower part of Figure 10. The emissive radical polarization is now transferred by the bulk coupling reaction to the CH_3 groups of TEMPO–PEst [XI, $(CH_3)_2$, 1.50 ppm, s]. The enhanced absorptions of the geminate products are not affected, and it is particularly noteworthy that the ratio of the enhanced absorptions of methyl methacrylate and the geminate aldehyde product are practically the same in the absence and presence of the nitroxide. If there was considerable disproportionation in the reaction of PEst with TEMPO, one would expect a large emission of methyl methacrylate for the coupling product TEMPO–PEst, and this is not found. Hence, disproportionation between TEMPO and PEst must be a minor pathway, and this confirms the conclusions from the NMR product study. From the polarizations, we estimate that the bulk fraction of disproportionation for PEst and TEMPO must be smaller than 3%.

The upper part of Figure 11 shows CIDNP effects 50 μs after the laser pulse photolysis of 6 mM EEst ketone [$CH_3OOCCH(CH_3)COCH(CH_3)COOCH_3$; two diastereoisomers in a 1:1 ratio] in toluene-d_8 and in the absence of TEMPO. These effects are again easily explained in terms of Scheme 5. En-

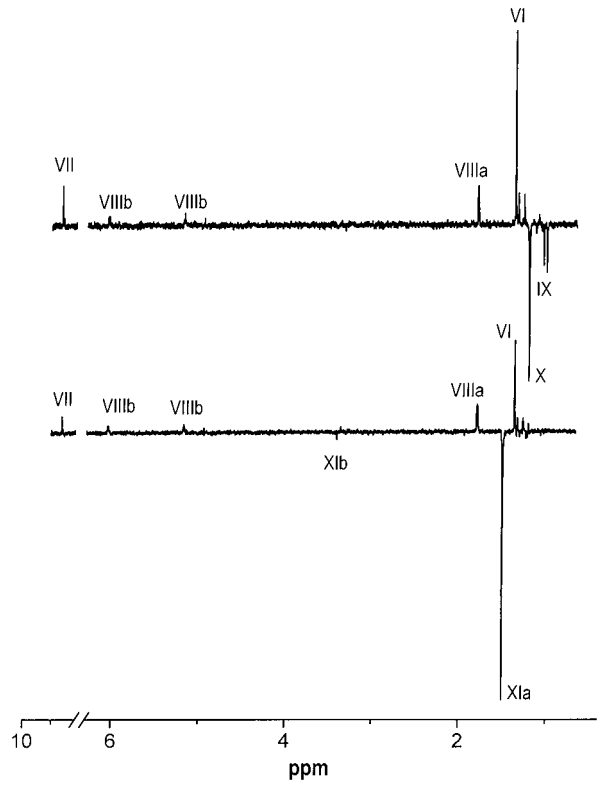


Figure 10. CIDNP spectrum taken 100 μs after the pulse photolysis of PEst ketone in the absence (top) and presence (bottom) of TEMPO: (VI) MeOOC—C(CH_3)$_2$—CO—C(CH_3)$_2$—COOMe, (VII) MeOOC—C(CH_3)$_2$—C*H*O, (VIII) MeOOC—C(CH_3^a)=$CH_2^{b,b'}$, (IX) MeOOC—CH(CH_3)$_2$, (X) MeOOC—C(CH_3)$_2$—C(CH_3)$_2$—COOMe, and (XI) H_3^bCOOC—C(CH_3^a)$_2$—TEMPO.

hanced absorption is expected for the β-CH_3 protons, and an emission is expected for the CH proton of the EEst group of the geminate products. These polarizations are found for the regenerated ketone (XIIIa and XIIIb), the aldehyde (XIV), and the corresponding alkene methylacrylate (XVa and XVb). The bulk self-termination of the EEst radical forms two stereoisomers of 2,4-dimethylbutanedioic acid dimethyl ester, methyl acrylate, and methyl propionate (XVIIa and XVI). From the emissive signals of dimethylbutanedioic acid dimethyl ester and methyl propionate, one now deduces a disproportionation/combination ratio for the self-termination of EEst of 0.7 (f_D = 0.4). In the presence of 5 mM TEMPO, the formation of the self-termination products is suppressed, and there is a dominant emission of TEMPO–EEst (XVIIIa). As in the absence of TEMPO, the CH_2 protons of methyl acrylate remain in enhanced absorption. Hence, little emissive radical polarization is transferred to this product by a bulk reaction between EEst and TEMPO. From the signal intensities of TEMPO–EEst and the acrylate, one now estimates about 4% as the upper limit of the fraction of bulk disproportionation.

These results show that the self-termination of PEst and EEst radicals involves considerable fractions of disproportionation, whereas the bulk cross disproportionation/combination ratios of TEMPO reacting with PEst and EEst are small. This agrees with the common notion that persistent radicals favor combination.[42] There is no significant difference in the fractions of disproportionation in the bulk for the pairs TEMPO/PEst and TEMPO/EEst. They do not exceed about 3–4% but may be slightly larger than for TEMPO/Cum and TEMPO/PhEt, where 1% is more likely. The small fraction of bulk disproportionation for TEMPO/EEst also excludes a large cage dispro-

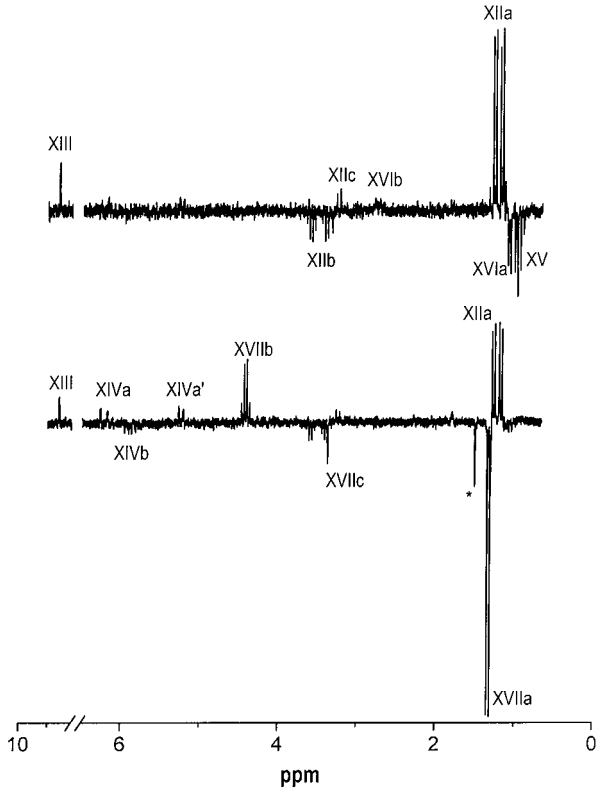


Figure 11. CIDNP spectrum taken 50 μs after the pulse photolysis of EEst ketone in the absence (top) and presence (bottom) of TEMPO: (XII) H_3^cCOOC—CH^b(CH_3^a)—CO—CH(CH_3)—COOCH_3, (XIII) MeOOC—CH(CH_3)—C*H*O, (XIV) MeOOC—CH^b=$CH_2^{a,a'}$, (XV) MeOOC—CH_2—CH_3, (XVI) MeOOC—CH^b(CH_3^a)—CH^b(CH_3^a)—COOMe (two isomers), and (XVII) H_3^cCOOC—CH^b(CH_3^a)—TEMPO. The asterisk denotes compound XIa, which arises from the photolysis of a trimethylated ketone impurity.

portionation during the thermolysis of TEMPO–EEst and supports the concerted decay.

SIMULATIONS AND RATE CONSTANTS

The time dependencies of alkoxyamine decay and product formation shown in Figures 2, 4, 6, 7 and 8 were simulated on the basis of the reactions of Scheme 2, which neglects the possible but not detected addition of TEMPO to the monomers.[27] The scheme involves more rate constants than could conceivably be obtained from simulations. Therefore, the number of these free parameters was reduced. First, the rate constants of the alkoxyamine decays (reaction 1) were measured from the appearance of TEMPO by ESR spectroscopy in chlorobenzene and in the presence of oxygen (air) as a alkyl radical trap as in earlier work.[21(a,b),22] The rate constants were larger by about a factor of 2 in the more polar chlorobenzene than in *tert*-butyl-benzene, which was used earlier. They are given as k_{ESR} in column 2 of Table I. Oxygen converts TEMPOH to TEMPO; therefore, the ESR data can include contributions to TEMPOH from geminate disproportionation and/or the nonradical alkoxyamine decay. However, for most of the alkoxyamines, these processes were found to be unimportant as previously, and for TEMPO–EEst, an appropriate separation is made (Table I).

Second, all rate constants were assumed to be independent of chain length. Thus, for the unimers and higher styrene- and methyl methacrylate-containing compounds, the rate constant of the alkoxyamine decay (reaction 1) was assumed to be the same as for TEMPO–PhEt and TEMPO–PEst, respectively. Of course, this is a very crude approximation. However, the reactions involving the unimeric and polymeric alkoxyamines do not influence the overall kinetics to large degrees, and the use of modified decay constants of these species did not change the main results. Therefore, the self-termination constants of all transient species were also set equal to common estimated diffusion limited values of $2k_t = 5 \times 10^9$ $M^{-1}\,s^{-1}$ at 100 °C and 7×10^9 $M^{-1}\,s^{-1}$ at 120 °C.

All other rate constants were varied within reasonable restricting limits. For the cross-reaction rate constant (k_c) between the carbon-cen-

Table I. Kinetic Parameters Used for the Product Yield Simulations during the Thermolysis of Alkoxyamines TEMPO–R at 100 °C for R = Cum and PEst and at 120 °C for R = PhEt, EEst, and Cum-Acrylate in the Presence and Absence of Styrene (Sty) and Methyl Methacrylate (MMA)[a]

R—	k_{app} (s^{-1})[b]	k_{ESR} (s^{-1})[c]	k_c ($M^{-1}\,s^{-1}$)[d]	k_a (Sty) ($M^{-1}\,s^{-1}$)[e]	k_a (MMA) ($M^{-1}\,s^{-1}$)[e]	f_D (%)
Cum—	1.7×10^{-4}	2.1×10^{-2}	2.0×10^{8}	1.3×10^{3}	2.3×10^{3}	0.6
Cum—Sty—		1.4×10^{-4}	3×10^{8}	1.5×10^{3}		0
Cum—MMA—		4.3×10^{-3}	2×10^{7}		1.7×10^{3}	20[f]
PEst—	1.2×10^{-4}	4.3×10^{-3}	6.5×10^{8}	2.5×10^{4}	8×10^{3}	2.2
PEst—Sty—		1.4×10^{-4}	3×10^{8}	1.5×10^{3}		0
PEst—MMA–		4.3×10^{-3}	2×10^{7}		1.7×10^{3}	20
PhEt—	1.0×10^{-5}	1.2×10^{-3}	3.5×10^{8}	3.5×10^{3}	1.8×10^{3}	0.8
PhEt—Sty—		1.2×10^{-3}	3×10^{8}	2.5×10^{3}		0
PhEt—MMA—		5×10^{-2}	2×10^{7}		2.5×10^{3}	20[f]
EEst—	1.5×10^{-5}	7×10^{-5}[g]	5×10^{9}	1×10^{5} [48]	5×10^{4} [48]	3[h]
EEst—Sty—		1.2×10^{-3}	3×10^{8}	2.5×10^{3}		0
EEst—MMA—		5×10^{-2}	2×10^{7}		2.5×10^{3}	20[f]
Cum—Acrylate—	5.6×10^{-6}	7.4×10^{-4}	5×10^{8} [1]	1×10^{5}		0.8
Cum—Acrylate—Sty—		1.2×10^{-3}	3×10^{8}	2.5×10^{3}		0

[a] For abbreviations of the radicals, see Scheme 1.
[b] Observed apparent decay rate constant of the alkoxyamine in the absence of monomer.
[c] Decay constant as observed by ESR. For unimeric species, the values were adopted from similar low molecular weight model compounds.
[d] Similar to published data.[21(c)]
[e] Similar to published data.[41]
[f] Used for Figures 2, 4, and 6–9.
[g] $k_{dd} = 1.8 \times 10^{-5}\ s^{-1}$, $k_d = 5.2 \times 10^{-5}\ s^{-1}$, where k_{dd} represents the direct decomposition.
[h] Upper limit from CIDNP.

tered radicals and TEMPO (reaction 2), these limits are known,[21(c)] and for the rate constants (k_a) of the first and subsequent monomer additions (reaction 3), we also used data from earlier work.[43] Finally, the mechanism was simplified with respect to alkene and TEMPOH formation. For TEMPO–Cum, TEMPO–PEst, and TEMPO–PhEt and their adducts to monomers, only alkene formation by bulk disproportionation was considered, but for TEMPO–EEst, nonradical decomposition was included. The final rate parameters used are collected in Table I. From the quality of the simulations, we estimate that they should be correct within a factor of 2.

As shown in part in the figures, the time dependence of the concentrations could be simulated rather well for TEMPO–Cum, TEMPO–PEst, TEMPO–PhEt, and TEMPO–Acrylate-Cum without us resorting to any nonradical alkoxyamine decay. In these cases, good simulations also required rather low fractions of bulk disproportionation between the carbon-centered radicals and TEMPO (Table I). Small values of f_D below 1% were equally necessary for TEMPO reacting with all radical adducts to styrene, and they were set to zero. However, for the reactions between the unimeric radical adducts to methyl methacrylate and TEMPO, large fractions were required, and the value of 20% given in Table I and used for the figures presents a minimum value because even higher fractions could be used if the other parameters were changed but somewhat beyond the reasonable limits.

For TEMPO–EEst, satisfactory simulations of the experimental data could also be obtained without the inclusion of nonradical decomposition, but then a high fraction of bulk disproportionation between TEMPO and EEst of about 28% had to be applied. This is ruled out by the CIDNP results, and so $f_D = 3\%$ was adopted, which is compatible with these. Simulations with the inclusion of the direct decomposition (k_{dd}) to alkene and TEMPOH revealed that this reaction contributes about 25% to the decay of TEMPO–EEst.

In addition to the parameters resulting from the simulations, Table I also contains apparent rate constants (k_{app}) for the alkoxyamine decomposition as taken from the nearly exponential decays. For TEMPO–PhEt and in the absence of monomer, this constant corresponds to a lifetime of 1.0×10^5 s in chlorobenzene at 120 °C, which is close to the value reported for a 1,3,5-trichlorobenzene solution.[9] In the absence of monomer and a direct decomposition pathway, the ratio k_{app}/k_{ESR} should be nearly equal to the fraction of bulk disproportionation[12,20] that resulted from the simulations. This is the case for TEMPO–Cum ($k_{app}/k_{ESR} = 0.8\%$ vs $f_D = 0.6\%$ from the simulation), TEMPO–PEst ($k_{app}/k_{ESR} = 2.8\%$ vs $f_D = 2.2\%$), TEMPO–PhEt ($k_{app}/k_{ESR} = 0.8\%$ vs $f_D = 0.8\%$), and TEMPO–Acrylate-Cum ($k_{app}/k_{ESR} = 0.8\%$ vs $f_D = 0.8\%$). This agreement further confirms the very small values of f_D for TEMPO–Cum and TEMPO–PhEt in contrast to the earlier claim.[10] Except for TEMPO–EEst, k_{app} increases markedly in the presence of monomer because the reformation of the alkoxyamines is quenched.

The unimeric coupling products TEMPO–Styrene–R were observed for R = Cum and R = PEst but not for R = PhEt and R = EEst. The simulations reveal the reason. The parameters k_d of Table I decrease in the order TEMPO–Cum > TEMPO–PEst > TEMPO–PhEt ≈ TEMPO–Styrene–R > TEMPO–Acrylate-Cum > TEMPO–EEst. Hence, only the first two alkoxyamines decay faster than the corresponding styrene unimers, so the unimer can accumulate. The ordering also allows the easy synthesis of TEMPO–Acrylate-Cum.

At the same temperature, TEMPO–Acrylate-Cum decomposes approximately 10 times faster than TEMPO–EEst. This agrees with a generally faster NO—R bond cleavage of alkoxyamines with longer chain radicals R, but in view of other findings,[21(a)] the difference seems rather large and may be due to steric effects of the neighboring bulky Cum group.

Finally, we note that the experimental data do not reveal any evidence for the possible addition of TEMPO to styrene[27] and for the hydrogen abstraction from TEMPOH by transient radicals.[44] Obviously, these processes do not interfere with the major reactions under our experimental conditions.

CONCLUDING REMARKS

This work has concentrated on the formation of alkenes and the hydroxylamine TEMPOH during the thermolysis of several alkoxyamines (TEMPO–R) that may hinder TEMPO-mediated living polymerizations. In most cases, the alkenes and TEMPOH are formed by bulk disproportionations between the carbon-centered radicals and free TEMPO, but TEMPO–EEst gives these products also via a substantial nonradical elimination reaction. The latter process certainly demands a

special transition-state geometry, and it seems to be disfavored for most of the leaving groups R considered here. However, the relatively large alkene yields reported by Studer[13] for other TEMPO-based compounds support its principal occurrence. Furthermore, Hawker et al.[45] reported that the thermolysis of low molecular weight and polymeric alkoxyamines in the presence of excess maleic anhydride and maleimide derivatives leads to an insertion of these compounds into the alkyl—nitroxide bond followed by the elimination of the hydroxylamine under the formation of an unsaturated maleic anhydride or maleimide end group. Although the mechanism was not disclosed in detail, it is very likely just the concerted process (reaction 6) observed here for TEMPO–EEst, and it is noteworthy that it was found for a nitroxide group with a structure that differs markedly from TEMPO. Hawker et al. also showed that the reaction can be used for end-group functionalizations and that this offers the additional advantage of improved thermal stability of the resulting polymer chain. Hence, reaction 6 may hinder living and controlled polymerizations, but it can also be put to good use.

In relation to coupling, the extent of the bulk disproportionation between TEMPO and carbon-centered radicals is much smaller than that found for the self-terminations of the transient species. Disproportionation/combination ratios of radicals are not yet well understood, and they depend on various factors.[42] First, the extent of disproportionation increases often with an increasing number of transferable β-hydrogen atoms. This explains the larger f_D for the self-disproportionation of PEst (50%) than for EEst (40%), but it is not observed for the cross-disproportionation of the carbon-centered radicals with TEMPO (Table I). Second, disproportionation/combination ratios are usually small in the self-terminations of radicals with extended spin delocalization, and, in fact, Cum and PhEt radicals more strongly prefer self-termination by coupling (Cum, $f_D = 5\%$[29]) than the ester-derived radicals. Their cross reactions with TEMPO also follow this trend (Table I). The unpaired electron spin of nitroxide radicals is about equally distributed over the NO group. Besides the general propensity of persistent radicals for coupling, this may also contribute to the smaller disproportionation/combination ratio for the cross reactions between TEMPO and the carbon-centered radicals in comparison to the self-terminations of the latter. Finally, steric substituent factors are important, and disproportionation is favored if the coupling leads to a sterically strained bond. Probably, and in agreement with the termination step in polymerization,[42] sterical constraints on the transition state for coupling make the unimeric adduct radicals of methyl methacrylate react with TEMPO with a large f_D ($\geq$20%), although f_D is small for the electronically similar PEst radical. Some nonradical decomposition of the unimeric alkoxyamine TEMPO–methyl methacrylate–R is not ruled out by our findings, although it appears to be not likely.

It is tempting to address the role of the alkene and TEMPOH formation in TEMPO-mediated polymerizations on the basis of these results. According to theory, f_D causes an end of the conversion at $t_D = 2/k_d f_D$ and leads to a maximum monomer conversion $C_{max} = 1 - \exp(-1.62 k_p([I]_0/3k_t k_c k_d f_D^2)^{1/3})$ if a low molecular alkoxyamine is used as an initiator and self-initiation is ignored.[20] The dissociation constant of TEMPO–polystyryl is $k_d = 0.0016\ s^{-1}$ at 125 °C.[47] For reasonable rate constants, $k_t = 5 \times 10^8\ M^{-1}\ s^{-1}$, $k_c = 7.6 \times 10^7\ M^{-1}\ s^{-1}$ (Table I), $k_p = 2300\ M^{-1}\ s^{-1}$ at 125°C,[46] $[I]_0 = 0.1$ M, and $f_D = 0.8\%$ as for the reaction of PhEt with TEMPO, theory predicts that the styrene conversion should end after about 43 h and at a final value of about 53%. Larger conversions have been obtained[2,3] with longer conversion times. Of course, this may be due to self-initiation, but it is also compatible with f_D for TEMPO–polystyryl being even smaller than 0.8% at 125 °C. The latter view is supported by the absence of disproportionation during the thermolysis of a TEMPO-based alkoxyamine that is a better model for TEMPO–polystyryl than TEMPO–PhEt.[10] Further support is the fact that $f_D = 0$ could be applied in all our simulations involving TEMPO–styryl–R (Table I).

For nitroxide-mediated polymerizations of methyl methacrylate, the detrimental influence of radical disproportionation is established,[7,18] and it is further supported by our data. TEMPO mediation of acrylate polymerizations has met little success, although some copolymerizations are possible.[3] On the basis of the small value $f_D = 0.8\%$ found during the reactions of TEMPO–Acrylate-Cum and for reasonable rate constants of the other reactions, disproportionation does not seem to limit the acrylate polymerizations severely. However, in this case f_D may well be larger for polymeric acrylate radicals than for unimeric acrylate radicals, and the nonradical decay may also play a role.

Finally, there are clear indications that the fractions of disproportionation to combination for

carbon-centered radicals reacting with nitroxides depend strongly on the nitroxide and especially on steric effects of the nitroxide substituents.[7,18] Therefore, we have studied the extent of disproportionation during the thermolysis of alkoxyamines based on other nitroxides and will report the results in a subsequent publication.

The authors thank the Swiss National Foundation for Scientific Research for its financial support, Mrs. I. Verhoolen for the synthesis of some alkoxyamines and PEst ketone, Dr. S. Marque (Marseille) for the synthesis of EEst ketone, and Marque and T. Kothe together for their help with the ESR experiments.

REFERENCES AND NOTES

1. Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Patent 4,581,429; Chem Abstr 1985, 102, 221335q.
2. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 2987.
3. An overview is provided by articles in (a) Controlled/Living Radical Polymerization; Matyjaszewski, K., Ed.; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000. Recent important references include (b) Rodlert, M.; Harth, E.; Rees, I.; Hawker, C. J. J Polym Sci Part A: Polym Chem 2000, 38, 4749; (c) Lacroix-Desmazes, P.; Delair, T.; Pichot, C.; Boutevin, B. J Polym Sci Part A: Polym Chem 2000, 38, 3845; (d) Boutevin, B. J Polym Sci Part A: Polym Chem 2000, 38, 3235; and (e) Otsu, T. J Polym Sci Part A: Polym Chem 2000, 38, 2121.
4. (a) Johnson, C. H.; Moad, G.; Solomon, D. H.; Spurling, T. H.; Vearing, D. J. Aust J Chem 1990, 43, 1215; (b) Wayland, B. B.; Pozmik, G.; Mukerjee, S. L. J Am Chem Soc 1994, 116, 7943; (c) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y. S.; Miyamoto, T.; Kobatake, S.; Yamada, B. Macromolecules 1996, 29, 6393; (d) Greszta, D.; Matyjaszewski, K. Macromolecules 1996, 29, 7661.
5. (a) Fischer, H. Macromolecules 1997, 30, 5666; (b) Fischer, H. J Polym Sci Part A: Polym Chem 1999, 37, 1885; (c) Souaille, M.; Fischer, H. Macromolecules 2000, 33, 7378.
6. (a) Bachmann, W. E.; Wiselogle, F. Y. J Org Chem 1936, 1, 354; (b) Perkins, M. J. J Chem Soc 1964, 5932; (c) Fischer, H. J Am Chem Soc 1986, 108, 3925; (d) Ruegge, D.; Fischer, H. Int J Chem Kinet 1989, 21, 703; (e) Kothe, T.; Martschke, R.; Fischer, H. J Chem Soc Perkin Trans 2 1998, 503; (f) Wagner, P. J.; Thomas, M. J.; Puchalski, A. E. J Am Chem Soc 1986, 108, 7739; (g) Walling, C. J Am Chem Soc 1988, 110, 6846; (h) Daikh, E.; Finke, R. G. J Am Chem Soc 1992, 114, 2939; (i) MacFaul, P. A.; Arens, I. W. C. E.; Ingold, K. U.; Wayner, D. D. M. J Chem Soc Perkin Trans 2 1997, 135; (j) Bravo, A.; Bjorsvik, H.-R.; Fontana, F.; Liguori, L.; Minisci, F. J Org Chem 1997, 62, 3849; (k) Karatekin, E.; O'Shaughnessy, B.; Turro, N. J. J Chem Phys 1998, 108, 9577; (l) Studer, A. Chem Eur J 2001, 7, 1159; (m) Fischer, H. Chem Rev, submitted for publication, and references therein, 2001.
7. Moad, G.; Anderson, A. G.; Ercole, F.; Johnson, C. H. J.; Krstina, J.; Moad, C. L.; Rizzardo, E.; Spurling, T. H.; Thang, S. H. ACS Symp Ser 1998, 685, 332.
8. He, J.; Li, L.; Yang, Y. Macromolecules 2000, 33, 2286.
9. Li, I.; Howell, B. A.; Matyjaszewski, K.; Shigemoto, T.; Smith, P. B.; Priddy, D. B. Macromolecules 1995, 28, 6692.
10. Skene, W. G.; Scaiano, J. C.; Yap, G. P. A. Macromolecules 2000, 33, 3536 and references therein.
11. Moffat, K. A.; Hamer, G. K.; Georges, M. K. Macromolecules 1999, 32, 1004.
12. Ohno, K.; Tsujii, Y.; Fukuda, T. Macromolecules 1997, 30, 2503.
13. Studer, A. Angew Chem Int Ed 2000, 39, 1108.
14. Goto, A.; Terauchi, T.; Fukuda, T.; Miyamoto, T. Macromol Rapid Commun 1997, 18, 673.
15. Goto, A.; Fukuda, T. Macromolecules 1999, 32, 618.
16. Bon, S. A. F.; Chambard, G.; German, A. L. Macromolecules 1999, 32, 8269.
17. Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J.-P.; Tordo, P.; Gnanou, Y. J Am Chem Soc 2000, 122, 5929.
18. Chong, B. Y. K.; Ercole, F.; Moad, G.; Rizzardo, E.; Thang, S. H.; Anderson, A. G. Macromolecules 1999, 32, 6895.
19. (a) Engel, P. S.; Duan, S.; Arhancet, G. B. J Org Chem 1997, 62, 3537; (b) Fischer, A.; Brembilla, A.; Lochon, P. Macromolecules 1999, 32, 6069.
20. Souaille, M.; Fischer, H. Macromolecules 2001, 34, 2830.
21. (a) Marque, S.; Le Mercier, C.; Tordo, P.; Fischer, H. Macromolecules 2000, 33, 4403; (b) LeMercier, C.; LeMoigne, F.; Tordo, P.; Lutz, J.-F.; Lacroix-Desmazes, P.; Boutevin, B.; Couturier, J.-L.; Guerret, O.; Marque, S.; Martschke, R.; Sobek, J.; Fischer, H. ACS Symp Ser 2000, 768, 108; (c) Sobek, J.; Martschke, R.; Fischer, H. J Am Chem Soc 2001, 123, 2849.
22. Kothe, S.; Marque, S.; Martschke, R.; Popov, M.; Fischer, H. J Chem Soc Perkin Trans 2 1998, 1553.
23. Woodworth, B. E.; Zhang, X.; Metzner, Z.; Gaynor, S. G.; Matyjaszewski, K. Macromolecules 1998, 31, 5955.
24. Schaffner, E.; Kweton, M.; Vesel, P.; Fischer, H. Appl Magn Reson 1993, 5, 127.
25. (a) Bowry, V. W.; Ingold, K. U. J Am Chem Soc 1992, 114, 4992; (b) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. J Am Chem Soc 1992, 114, 4983; (c) Beckwith, A. L. J.; Bowry, V. W.; Moad, G. J Org Chem 1988, 53, 1632; (d) Baldovi, M. V.;

Mohtat, N.; Scaiano, J. C. Macromolecules 1996, 29, 5497; (e) Skene, W. G.; Scaiano, J. C.; Listigovers, N. A.; Kazmaier, P. M.; Georges, M. K. Macromolecules 2000, 33, 5065.

26. We express the relative yields of the two reactions in terms of fractions, but the use of separate rate constants for coupling and disproportionation is completely equivalent.
27. (a) Moad, G.; Rizzardo, E.; Solomon, D. H. Polym Bull 1982, 6, 589; (b) Connolly, T. J.; Scaiano, J. C. Tetrahedron Lett 1997, 38, 1133; (c) Aldabbagh, F.; Busfield, W. K.; Jenkins, I. D.; Thang, S. H. Tetrahedron Lett 2000, 41, 3673; (d) Devonport, W.; Michalak, L.; Malmström, E.; Mate, M.; Kurdi, B.; Hawker, C. J.; Barclay, G. G.; Sinta, R. Macromolecules 1997, 30, 1929.
28. Dourges, M.-A.; Charleux, B.; Vairon, J.-P; Blais, J.-C.; Bolbach, G.; Tabet, J.-C. Macromolecules 1999, 32, 2495.
29. Skinner, K. J.; Hochster, H. S.; McBride, J. M. J Am Chem Soc 1974, 96, 4301.
30. In separate experiments, NMR line broadening above the instrumental minimum of 0.35 Hz (line broadening factor = 0) was observed for TEMPO concentrations greater than 5×10^{-4} M. Plots of the line width versus the TEMPO concentration served for the estimation of nitroxide concentrations, and for TEMPO–Cum, an upper limiting concentration of 10^{-3} M at large conversions was deduced.
31. δ: 4.51 (dd, J = 10.6, 3.2 Hz, 1H, CH), 2.71 (dd, J = 1 3.7, 3.2 Hz, 1H, H-1 in CH_2), 2.28 (dd, J = 13.7, 10.6 Hz, 1H, H-2 in CH_2), 1.31, 1.10 (each broad s, 12H, $4CH_3$ of the TEMPO moiety), 1.20, 1.01 [each broad s, 6H, $(CH_3)_2$—C—Ph].
32. That is, 2,2-dimethyl-4-phenyl-4-(2,2,6,6-tetramethylpiperidinyloxy)butyric acid *t*-butylester. δ (in the reaction with deuterated styrene): 1.35, 1.21 (broad s, 12H, $4CH_3$ in TEMPO moiety), 1.07, 0.97 [each broad s, 6H, $(CH_3)_2$—C—C═O)].
33. Fallon, G. D.; Holland, K. A.; Rae, I. D. Aust J Chem 1990, 43, 521.
34. δ: 6.16 (d, J = 1.7 Hz, 1H, ═CH), 5.48 (dd, J = 1.7, 1.0 Hz, 1H, ═CH), 3.50 (s, 3H, $COOCH_3$), 2.66 (d, J = 1.0 Hz, 2H, CH_2), 1.39 (s, *t*-Bu), 1.14 [s, ~6H, $2CH_3$)].
35. (a) Hawker, C. J.; Barclay, G. G.; Devonport, W. Macromolecules 1996, 29, 5245; (b) Hawker, C. J.; Barclay, G. G.; Dao, J. J Am Chem Soc 1996, 118, 11467.
36. Bizilj, S.; Kelly, D. P.; Serelis, A. K.; Solomon, D. H.; White, K. E. Aust J Chem 1985, 38, 1657.
37. (a) Brownlie, I. T.; Ingold, K. U. Can J Chem 1967, 45, 2427; (b) Grattan, D. W.; Carlsson, D. J.; Howard, J. A.; Wiles, D. M. Can J Chem 1979, 57, 2834.
38. (a) Nash, G.; Warring, A. J. J Chem Res Miniprint 1988, 8, 1811; (b) Fouquet, E.; Pereyre, M.; Rodriguez, A. L. J Org Chem 1997, 62, 5242.
39. Cope, C.; Trumbull, E. R. Org React 1960, 11, 317.
40. Wu, J. Q.; Beranek, I.; Fischer, H. Helv Chim Acta 1995, 78, 194.
41. Kaptein, R. Chem Commun 1971, 732.
42. Moad, G.; Solomon, D. H. The Chemistry of Free Radical Polymerization; Pergamon: Oxford, 1995.
43. (a) Walbiner, M.; Wu, J.-Q.; Fischer, H. Helv Chim Acta 1995, 78, 910; (b) Zytowski, T.; Knuehl, B.; Fischer, H. Helv Chim Acta 2000, 83, 658; (c) Buback, M; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kucha, F. D.; Manders, B. G.; O'Driscoll, K. F.; Russel, G. T.; Schweer, J. Macromol Chem Phys 1995, 196, 3267; (d) Hutchinson, R. A.; Beuermann, S.; Paquet, D. A., Jr.; McMinn, J. H.; Jackson, C. Macromolecules 1998, 31, 1542.
44. Gridnev, A. A. Macromolecules 1997, 30, 7651.
45. Harth, E.; Hawker, C. J.; Fan, W.; Waymouth, R. M. Macromolecules 2001, 34, 3856.
46. (a) Fukuda, T.; Goto, A.; Ohno, K. Macromol Rapid Commun 2000, 21, 151; (b) Fukuda, T.; Goto, A. ACS Symp Ser 2000, 768, 27.
47. Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kutcha, F. D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. Macromol Chem Phys 1995, 196, 3267.