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An Aliphatic Bifunctional Free Radical Initiator. Synthesis of a Block Copolymer from an Azoperester by Sequential Thermal and Photochemical Initiation

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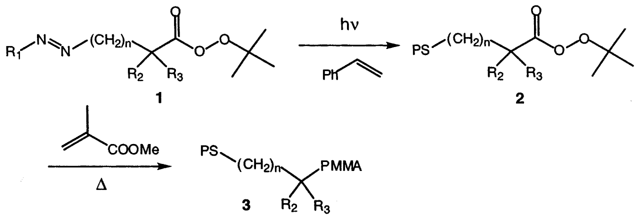
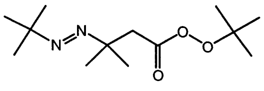
ABSTRACT: The azoalkaneperester *tert*-butyl 7-methyl-7-(*tert*-butylazo)peroxyoctanoate (**7**) has been found to be a viable bifunctional free radical initiator. Unlike the radicals from previously studied compounds **4**−**6**, those from **7** neither fragment nor cyclize, presumably on account of the medium ring that would be required. Thermolysis of **7** with styrene affords macroinitiator **21** while photolysis affords **22**. Photolysis of **21** with MMA yields block copolymer **23** while thermolysis of **22** with MMA affords block copolymer **24**. One advantage of **7** is that the photolysis−thermolysis sequence can be reversed, as can the order of addition of monomers.

Since azoalkanes and peroxides are the two most common initiators of free radical polymerization,[1] linking these groups should produce well-behaved bifunctional free radical initiators. A simple azoperester of general structure **1**, for example, could initiate polymerization of styrene (S) photochemically; then, thermolysis of the resulting end-functionalized polymer **2** could initiate polymerization of methyl methacrylate (MMA) to produce a block copolymer **3**. One advantage of a bifunctional initiator such as **1** is its flexibility, in that both the photolysis−thermolysis sequence and the styrene−MMA sequence could be reversed. Furthermore, the nature of R_2, R_3 could be varied to control the perester decomposition temperature[2] without affecting the more robust azo linkage. Finally, analogues of **1** bearing pendant groups that are relatively unreactive to radicals might be useful to prepare “link-functionalized” polymers.[3]



We have reported the decomposition of **4**, which incorporated a two-carbon link between the functional groups and a tertiary azoalkane to prevent tautomerization.[4] Both thermolysis and photolysis led to initiator-bearing radicals whose fragmentation rate turned out to be competitive with radical attack on styrene, so that much of the formed polystyrene (PS) would not contain an initiator end group. The much earlier studied compound **5** suffered from the same problem; moreover, its cyano group stabilized one incipient radical, causing the azo moiety to decompose at the same temperature as the perester. Thus, **5** could not have been used to generate a polymer containing just one type of end group.[5] A number of other bifunctional initiators have appeared in the literature, especially in recent years.[6−15]



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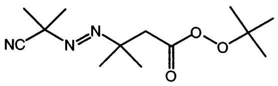

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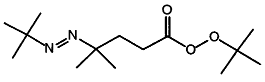
The γ-azo radical formed by thermolysis of **6**, unlike the β-azo radical from **4**, cannot undergo fragmentation. However, the γ-azo radical rapidly cyclized to the N=N bond, ruining any chance that **6** could be used to incorporate an azo group at the end of a polymer chain.[16] Increasing the separation between the two initiator moieties should slow intramolecular reactions, but it is not obvious how many methylene groups would be required to make radical addition to monomer the dominant reaction. We have chosen to study **7**, where cyclization is disfavored by the necessity of forming a seven- or eight-membered ring.[17] As it turns out, **7** does not suffer from intramolecular reactions and is a viable bifunctional free radical initiator.



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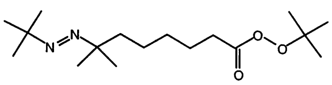

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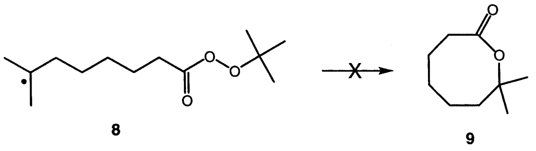
Results

Synthesis of 7. The anion of acetone *tert*-butylhydrazone was alkylated[18,19] with *tert*-butyl-6-iodohexanoate, and the ester was converted to the perester by the usual methods.[16] Compound **7** exhibited a UV λ_{max} of 370 nm ($\epsilon = 15.2$), typical of azoalkanes.

Photolysis Products of 7. A C_6D_6 solution of 0.02 M **7** was irradiated at 25 °C and 366 nm where only the azo moiety absorbs light, and the product mixture was examined by ^{13}C NMR and CI/GC/MS. Although cyclization of radical **8** could lead to **9**, we find no evidence for this lactone. The ^{13}C NMR spectrum of the



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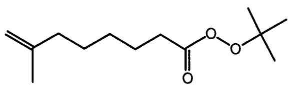
product mixture clearly showed disappearance of the α-azo carbons at 68.61 and 66.62 ppm along with appearance of new peaks at 82.65 and 170.35 ppm. However, this carbonyl signal is too far upfield to be **9**. For comparison, the ^{13}C=O chemical shift of **9** lacking one and both methyl groups in $CDCl_3$ is 176.7 and 176.6 ppm, respectively.[20,21] Since changing solvent from C_6D_6 to $CDCl_3$ causes a downfield shift of only 0.76 ppm for **7**, it is very unlikely that **9** is present. Because the new ^{13}C peaks are very close to those of **7** (82.96, 170.59 ppm), we assign them to perester **10**. The olefinic carbons of **10** appeared at 110.35 and 145.60 ppm and the protons fell at 4.75−4.79 ppm. ^{13}C signals in the photolyzate at 141.97 and 111.11 ppm were attributed to isobutene, an assignment supported by GC/MS. The CI/GC/MS showed no peaks with a pseudo-molecular ion at the mass of **9** + H, neither in irradiated **7** nor in a solution containing 1,4-cyclohexadiene (1,4-CHD). Thus, **8** does not cyclize to **9** but instead disproportionates with *tert*-butyl radical in a reaction typical of tertiary radical pairs.[22]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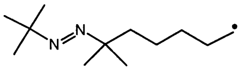
Thermolysis Products of 7. In an experiment complementary to the irradiation of **7**, we sought to determine whether radical **11** would cyclize to the azo group, a facile reaction in the case of **6**. The resulting cyclic hydrazyl radicals might abstract hydrogen to afford **12** or **13**, or they might ring open or lose *tert*-butyl radical to yield azo compounds **14** or **15**. Thermolysis of **7** (benzene, 120 °C, 3 h) afforded CO_2 in 104% yield and methane in 42% yield, according to GC analysis of the evolved gases. To look for products **12**−**15**, we prepared three C_6D_6 solutions containing 0.05 M **7**: one with no scavenger, one with 0.1 M *tert*-butyl mercaptan, and a third containing 0.1 M 1,4-CHD. These were degassed, sealed, and heated at 120 °C for 3.5 h; then the products were examined by NMR and CI/GC/MS. Because *t*-BuSH reacted slowly with **7** at room temperature, the freshly prepared sample was placed immediately into the hot oil bath. The ^{13}C NMR spectra of all samples clearly showed disappearance of the carbonyl and the perester *tert*-butoxy carbon of **7**. The unscavenged thermolyzed sample of **7** exhibited a GC peak at 14.06 min whose CI mass spectrum consisted mostly of M+1 = 199. Although this peak could be **14**, its yield increased when scavenger was added, not the behavior expected for a rearrangement product of **11**. No other GC/MS peak in the scavenged runs exhibited a peak at *m*/*e* = 199. Compounds **12** and **13** are ruled out because no new ^{13}C NMR peak was found in the region expected for the *tert*-butyl group (compare *tert*-butylhydrazine in C_6D_6, δ = 53.28, 26.61 ppm.) Finally, the absence of a GC/MS peak at M + 1 = 141 argues against the presence of **15**.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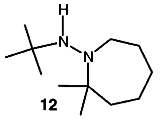
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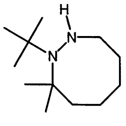
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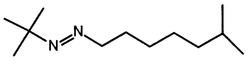
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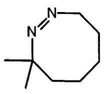
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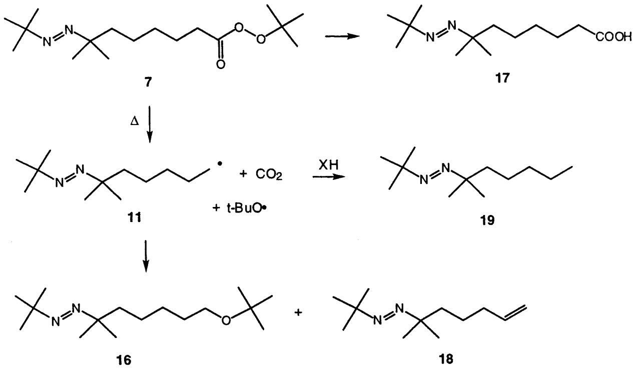
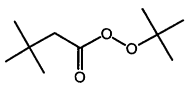
Turning to the products that *were* formed, we found that all samples contained acetone, *tert*-butyl alcohol, ether **16**, carboxylic acid **17**, and an alkene assigned as **18** on the basis of its GC retention time and GC/MS spectrum. These types of products, including carboxylic acids, are typical for peresters studied in this laboratory.[23] Since carboxy radicals lose CO_2 very rapidly,[24] it is unlikely that **17** arises by O−O homolysis of **7**. Instead, we attribute **17** to hydrolysis of **7** by adventitious water, based on our observation that thermolysis of another perester in scrupulously dried benzene greatly reduced the yield of carboxylic acid. The 14.06 min peak was assigned to **19** on the basis of its CI/MS fragmentation pattern and the observation that its area increased significantly relative to that of **16** and **18** upon inclusion of hydrogen donors. These product studies demonstrate that radical **11** has no tendency to cyclize but instead behaves like a typical primary alkyl radical.



Formation of Macroinitiators from 7. To find conditions favoring formation of low molecular weight polymers and thus to facilitate NMR end group analysis, a series of experiments with various concentrations of styrene and MMA was carried out at several temperatures using the model perester **20** as initiator. It was found that 0.02 M **20** with 1.0 M monomer in benzene at 132 °C would produce manageable polymer molecular weights in a short time.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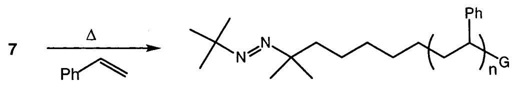
Thermolysis of 7 with Styrene. A solution of 0.02 M **7** with 1.0 M styrene in benzene was heated at 132 °C for 20 min. The PS was isolated, reprecipitated twice with methanol, dried, and dissolved in *p*-xylene-d_{10}. The ^{1}H NMR spectrum exhibited the characteristic broad PS signals plus many smaller peaks in the region 0.5−1.2 ppm, attributed to aliphatic end groups. The obvious ^{13}C signals at 66.90 and 69.04 ppm, comparable to those for the quarternary azo carbons of **7** at 66.9 and 68.9 ppm in *p*-xylene-d_{10}, suggest that a major polymer from **7** is **21** (the nature of G is discussed below). A quantita-



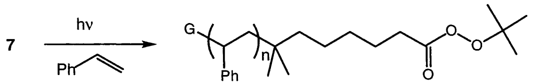
21

tive UV spectrum of **21** (98 mg in 3 mL of benzene) exhibited the broad 366 nm absorption typical of the azo group. From its absorbance (0.083) and the assumption that each PS contained one azo group, we computed the M_n of **21** as 5980. The value of M_n for another PS sample made exactly the same way was determined by GPC to be 3990. The higher M_n computed by UV is readily understood if part of the PS arises from initiation by methyl radicals and therefore contains no azo group (see below). Comparison of the molecular weight determined by UV vs GPC will not detect PS terminated at each end with azo groups because both the molecular weight and the extinction coefficient would be doubled.

Because thermolysis of **7** produces a *tert*-butoxy radical, one would also expect *tert*-butoxy-terminated PS, whose ^{13}C−O NMR signal should lie in the vicinity of 80 ppm. We were therefore surprised initially that the ^{13}C spectrum of the isolated polymer was clear from 50 to 120 ppm, except for the above-mentioned α-azo carbons. Nakamura et al.[25] reported that *tert*-butyl perpivalate in neat styrene at 60 °C gave 98.6% addition of *t*-BuO$^\bullet$ to styrene and only 1.4% β-scission. Similar results have been reported by Watanabe et al.[26] However, our use of benzene solvent[27] and the fact that our temperature was 72 °C higher and our styrene concentration was 8.7 times lower than Nakamura's would raise the ratio of β-scission to *t*-BuO$^\bullet$ addition by 2 orders of magnitude.[28] While this calculation predicts a major role for *t*-BuO$^\bullet$ fragmentation, it does not account for the complete absence of *t*-BuO groups in the isolated PS. The prevalence of fragmentation during thermolysis of **7**, supported by our sizable methane yield, and the fact that the methyl affinity of styrene is 2700 times greater than that of benzene[29,30] both predict methyl addition to styrene. However, the spectrum of the isolated PS was too complex in the region of 20−30 ppm to verify the presence of such a methyl end group.

To assess the degree of *tert*-butoxy radical fragmentation independently, a 0.02 M solution of model perester **20** was heated at 102 °C for 5 h in 1.0 M styrene in benzene. The ^{13}C NMR spectrum of the purified PS was once again completely clear in the region 50−120 ppm. Since the temperature of this experiment was 30 °C lower than the one used to make **21**, the absence of *tert*-butoxy-initiated PS from **7** is less surprising.

Photolysis of 7 with Styrene. Having demonstrated that thermolysis of **7** can produce azo-terminated PS, we then showed that photolysis of this initiator could produce perester-terminated PS. A 0.02 M solution of **7** and 1.0 M styrene in benzene was irradiated at 366 nm and 80 °C for 50 min. After isolation and reprecipitation of the PS, its ^{1}H NMR spectrum in *p*-xylene-d_{10} showed sharp singlets at 83.2 and 170.7 ppm. Since these peaks disappeared in a DEPT-135 experiment, they are quarternary carbons, which we assign to the Me$_3$C−O and carbonyl groups, respectively. The initiator **7** exhibits these peaks at 82.96 and 170.59 ppm, indicating that at least part of the polymer has structure **22**, the remainder being *t*-Bu$^\bullet$-initiated PS. A sample of **22** made from 0.02 M **7**, and 2.0 M styrene irradiated at 85 °C for 50 min gave a GPC M_n of 5000.



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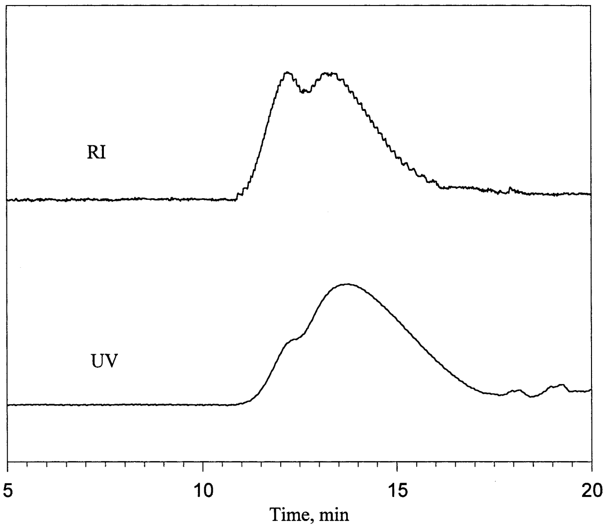
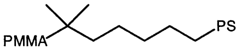


Figure 1. GPC trace of the copolymer from irradiating **21** with MMA at 80 °C.

Generation of Block Copolymers 23 and 24 from Macroinitiators 21 and 22. To determine whether **21** and **22** could serve as macrointiators to polymerize MMA, we irradiated **21** at 366 nm and 80 °C with 3 M MMA in benzene for 50 min. The polymer, referred to as the second stage polymer, was isolated by precipitation with methanol and showed both PS and PMMA peaks in the ^{1}H NMR spectrum. While this result is encouraging, it does not prove that we made the expected block copolymer **23** since the *tert*-butyl radical from **21** could have been mainly responsible for polymerization of MMA. Even the larger M_n of the second stage polymer (14 500) than that of **21** (M_n = 8500 from 0.02 M **7** and 2.0 M styrene) could merely indicate that the *t*-Bu radical from **21** polymerized MMA to a higher degree than **7** polymerized styrene.



23

Evidence that **23** was actually formed was uncovered in both GPC and silica gel chromatography experiments. The second stage polymer from **21** was analyzed by GPC using two columns in series (50−100K then 500−20K) and two detectors, RI and UV (280 nm). By RI, M_n = 14 500, M_w = 31 200 while by UV, M_n = 7000, M_w = 15 200. Both detectors showed a bimodal molecular weight distribution (cf. Figure 1), which we interpret as a mixture of **23** and PS. The higher molecular weight material gave a stronger signal by RI relative to UV, indicating that it contains a greater proportion of PMMA and therefore that **21** added MMA.

Silica gel chromatography allowed partial purification of **23**. Preparative TLC (elution three times with benzene, then once with 5% MeOH in CHCl$_3$) gave a faster moving band that proved to be PS and a slower band assigned to **23**, which could not be separated from PMMA. The continued presence of PS ^{1}H NMR signals even though PS itself had been removed signifies formation of block copolymer **23**.

A sample of **22** was then used to initiate the polymerization of 3 M MMA at 132 °C for 15 min. Two column GPC analysis revealed a bimodal distribution by RI and a trimodal one by UV (cf. Figure 2). By RI, M_n = 11 600, M_w = 27 300 while by UV, M_n = 5100, M_w = 14 300. Once again, the RI response was greater than the UV

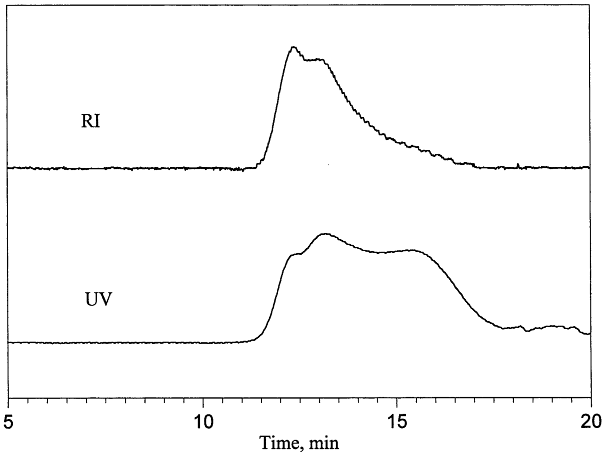
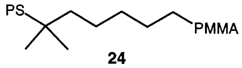


Figure 2. GPC trace of the copolymer from heating **22** with MMA at 132 °C.

one for the highest molecular weight peak, indicating that **22** had added MMA units to yield **24**. The large size of the latest UV peak suggests the presence of low MW PS arising from the preparation of **22**.



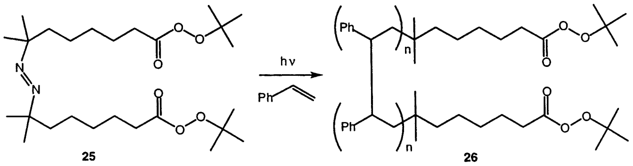
24

Column chromatography of **24** (elution with benzene for the first 12 fractions, then with CHCl$_3$, and finally with 1−2% MeOH/CHCl$_3$) allowed removal of PMMA, which was isolated pure in the later fractions; however, PS was still present. Since PMMA itself was removed, the PMMA^{1}H NMR signals in this polymer mixture must arise from block copolymer **24**.

Discussion

A careful search for cyclization of radicals **8** and **11** failed to turn up any evidence for this process. Thus, the longer chain in **7** compared to **6** successfully prevented cyclization. The thermal and photochemical reactions of **7** are similar to those of azo and azoxy peresters that we studied earlier[16,23] where disproportionation of the *tert*-butoxy−alkyl radical pair and formation of *tert*-butyl ethers were dominant processes. In the thermolysis of **7**, the sizable yield of methane indicates substantial fragmentation of the *tert*-butoxy radical and indeed, when **7** was thermolyzed with styrene, the polymer did not contain any detectable *tert*-butoxy end groups.

^{13}C NMR analysis of the PS produced thermally and photochemically from **7** revealed azo and perester end groups, respectively, thus supporting the formation of **21** and **22**. However, these structures do not specify the nature of G, which is usually another PS chain because styrene terminates 92% by recombination at 80 °C.[31] As with any unsymmetrical initiator,[9] both the azo and perester moieties of **7** produce two different radicals (t-Bu$^\bullet$ + **8** and Me$^\bullet$ + **11**, respectively), each of which initiates styrene polymerization. Random recombination of growing chains then yields a mixture of terminal monofunctional, bifunctional, and unfunctionalized PS. Given that **7** produces **21** and **22** as mixtures of macroinitiators, the second stage polymers must be even more heterogeneous. For example, **21** will lead to PMMA homopolymer from t-Bu$^\bullet$ initiation, to a diblock copolymer if the propagating PMMA chain disproportionates ($k_d/k_c = 0.6$), and to a triblock copolymer if the propagating chain recombines. Although we elected to study **7** because of its synthetic accessibility and because it is a homologue of **6**,[16] photolysis of symmetrical azoalkane **25** with styrene would be an improvement, as it would afford mainly bifunctional PS **26**. The second stage polymer from **26** + MMA would then be largely free of PS.



In summary, the simple bifunctional initiator **7** does not suffer from intramolecular reactions of the initially formed radicals, unlike previously studied azoperesters. Instead the formed radicals polymerize styrene to produce macroinitiators **21** and **22**, which in turn can be thermolyzed with methyl methacrylate to yield block copolymers such as **23** and **24**.

Experimental Section

NMR spectra (250 MHz) were run in CDCl$_3$ unless otherwise specified. All chemical shifts are in ppm. Gel permeation chromatography was carried out on a Waters instrument using polystyrene standards (Polysciences) to generate the molecular weight calibration curve.

***tert*-Butyl 6-bromohexanote** was obtained in 71% yield by esterification of 6-bromohexanoic acid. ^{1}H NMR: 3.36−3.42 (t, 2H), 2.18−2.24 (t, 2H), 1.80−1.91 (m, 2H), 1.54−1.66 (m, 2H), 1.37−1.50 (m, 11H).

***tert*-Butyl 6-iodohexanote** was prepared from *tert*-butyl 6-bromohexanote according to the literature[32] in 97% yield. ^{1}H NMR: 3.16−3.21 (t, 2H), 2.19−2.25 (t, 2H), 1.78−1.89 (m, 2H), 1.54−1.66 (m, 2H), 1.36−1.47 (m, 11H).

***tert*-Butyl 7-Methyl-7-(*tert*-butylazo)octanoate.** To a solution of acetone *tert*-butyl hydrazone (1.0 g, 7.8 mmol)[33] in THF (20 mL) at −78 °C was added MeLi (8.2 mmol, 5.1 mL of 1.5 M in hexane). After the solution had been stirred for 1.5 h at −78 °C, HMPA (1.4 g, 7.8 mmol) was added; then a solution of *tert*-butyl 6-iodohexanote (2.4 g, 8.0 mmol) in THF (5 mL) was added. The solution was stirred for another 30 min at −78 °C, slowly warmed to room temperature, and stirred for 3 h more. Ether (40 mL) was added, and the organic solution was washed with water and then brine. After drying over Na$_2$SO$_4$ and filtering, the solvent was removed by rotary evaporatation. The product (1.2 g, 52%) was obtained by flash column chromatography on silica gel (ethyl acetate−hexanes, 1:20). ^{1}H NMR: 1.07 (s, 6H), 1.14 (s, 9H), 1.15−1.30 (m, 4H), 1.43 (s, 9H), 1.50−1.62 (m, 4H), 2.15−2.21 (t, 2H). ^{13}C NMR: 23.85, 24.83, 25.37, 27.14, 28.47, 30.08, 35.90, 40.72, 66.31, 68.27, 80.24, 173.62.

7-Methyl-7-(*tert*-butylazo)octanoic acid was prepared in 97% yield by hydrolysis of *tert*-butyl 7-methyl-7-(*tert*-butylazo)-octanoate using trifluoroacetic acid in methylene chloride.[34,35] ^{1}H NMR: 1.07 (s, 6H), 1.14 (s, 9H), 1.18−1.39 (m, 4H), 1.57−1.65 (m, 4H), 2.30−2.36 (t, 2H). ^{13}C NMR: 23.78, 24.84, 24.92, 27.14, 30.00, 34.32, 40.63, 66.40, 68.29, 180.33.

***tert*-Butyl 7-methyl-7-(*tert*-butylazo)peroxyoctanoate** (**7**) was made according to the method of Staab et al.[35] in 71% yield. ^{1}H NMR: 1.05 (s, 6H), 1.12 (s, 9H), 1.15−1.34 (m, 4H), 1.30 (s, 9H), 1.54−1.67 (s, 4H), 2.24−2.30 (t, 2H). ^{13}C NMR: (CDCl$_3$, δ): 23.66, 24.81, 25.18, 26.45, 27.10, 29.98, 31.53, 40.57, 66.30, 68.16, 83.50, 171.35.

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