Water Soluble Dialkyl Peroxides and Peroxyesters

Mary Y. Lu, Rong Bao, Wenqiu Liu, and Yuzhuo Li*

Department of Chemistry, Clarkson University, Potsdam, New York 13699-5810

Received October 12, 1994

Organic peroxides are widely used in areas ranging from polymerization initiators to new antibacterial agents.[1-7] For many purposes, peroxyesters, dialkyl and diaryl peroxides, are of particular interests due to the fact that they are relatively stable and easier to handle in comparison with peroxyacids and alkyl hydroperoxides.[3] Although these peroxides are widely used in organic media, their applications in aqueous and biological environments are limited because of their low solubility.[8]

In principle, an alkoxyl radical could be generated from an alkyl hydroperoxide, a dialkyl peroxide, or an alkyl peroxyester. Although peroxyesters and dialkyl peroxides give alkoxyl radicals readily upon decomposition, they are generally not soluble in water. Some alkyl hydroperoxides are soluble in water but a clean homolysis of their O–O bonds are not commonly observed except in some metal catalyzed decompositions.[3] It has been, therefore, difficult to generate an alkoxyl radical in water through peroxide decompositions.

Considering the applications of alkoxyl radicals in a wide range of areas such as initiation of polymerization, disinfection, antibacterial, and water-based cosmetics, a clean and easy scheme for the formation of alkoxyl radicals in water medium would be very useful. For this purpose, we have synthesized a group of water soluble dialkyl peroxides and peroxyesters that exemplify the advantages of incorporating a cationic functional group into organic peroxides (Figure 1). Specifically, *tert*-butoxyl radicals were generated from the prepared peroxides in a homogeneous water solution or the localized hydrophobic regions in micelles. To the best of our knowledge this is the first group of synthesized organic peroxides containing a cationic functional group.

Results and Discussion

Synthetic Design. 4-[[(*tert*-Butyldioxy)carbonyl]benzyl]triethylammonium chloride, Peroxide I, was synthesized as an analog of *tert*-butyl peroxybenzoate, a commercially available peroxyester that is capable of generating *tert*-butoxyl radical in organic solvent upon thermolysis or photolysis. Compounds **II-5** and **II-10** are the analogs of *tert*-butyl peroxyacetate (Lupersol 70), and compounds **III-3**, **III-4**, **III-5**, and **III-10** are dialkyl peroxides. These three types of compounds represent a range of peroxides with different thermal and photochemical stabilities. While the thermal reactivity of a peroxide is mainly dependent upon its O–O bond strength and the stability of its homolytic cleavage products, the photochemical reactivity is closely related to its molar absorptivity at the radiation wavelength. With a commonly used ultraviolet light source (254 nm), the decomposition rate is generally ranked in the order of aryl peroxyester, alkyl peroxyester, and dialkyl peroxide due to their UV absorption differences.

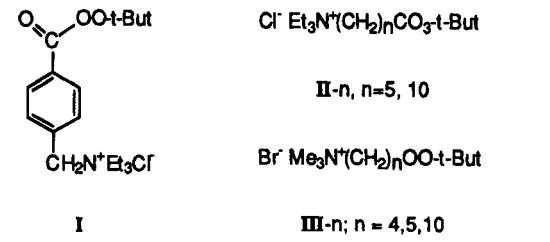

Figure 1. Organic peroxides containing a cationic functional group.

A peroxide with a short hydrocarbon chain (**I**, **II-5**, **III-3**, **III-4**, or **III-5**) between its dioxy group and cationic center is designed to be used in water solution directly. Although there may not be any specific requirement for the distance between the cationic center and the dioxy group, a shorter hydrocarbon chain usually provides higher solubility in water. A peroxide containing a long hydrocarbon chain between its dioxy group and cationic center, such as **II-10** or **III-10**, is designed to be used as a surfactant or cosurfactant to form micelles. The cationic functional group would be located in the water region, and the dioxy group would be in the hydrophobic or oil region. The decomposition of the dioxy group would give radicals and cause reactions in the hydrophobic region of a micelle. A potential application of such system is to initiate a polymerization in a micelle. The peroxide could also be used as a hydrophobic disinfectant in the micelles formed during cleaning processes or an amphiphilic antibacterial with the ability to penetrate into a hydrophobic area from a hydrophilic medium.

Synthesis of Peroxides I, II-5, and II-10. [4-[(*tert*-Butyldioxy)carbonyl]benzyl]triethylammonium chloride, compound **I**, was prepared from 4-(chloromethyl)benzoic acid via a simple and straight forward reaction sequence illustrated in Figure 2.

A direct substitution on the α-chloromethyl group of 4-(chloromethyl)benzoic acid with triethylamine would yield very little desired ammonium product, **Ia**, because the competition from the carboxylate group as a nucleophile leads to a polymerization. Esterification of benzoic acid before the introduction of the triethylammonium group is therefore necessary. Alternatively, a slightly more expensive reagent, methyl 4-(bromomethyl)benzoate could be used as the starting material. The acid chloride of the ammonium compound **Ia** is easily prepared from its acid precursor and thionyl chloride in the presence of pyridine, which then in turn reacts with *tert*-butyl hydroperoxide to give the desired peroxide, **I**.

[5-[(*tert*-Butyldioxy)carbonyl]pentyl]triethylammonium chloride, compound **II-5**, and [10-[(*tert*-butyldioxy)-carbonyl]decyl]triethylammonium chloride, compound **II-**

* Author to whom correspondence should be addressed.

(1) Benson, S. W.; Shaw, R. In *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1970, Vol. I.
(2) Hiatt, R. In *Organic Peroxides*; Swern, D. Ed.; Wiley-Interscience: New York, 1971; Vol. II.
(3) Ando, W., Ed. *Organic Peroxides*; John Wiley & Sons, Inc.: New York, 1992.
(4) Liu, J. M.; Ni, M. Y.; Fan, Y. F.; Tu, Y. Y.; Wu, Z. H.; Wu, Y. L.; Chou, W. S. *Acta. Chim. Sin.* **1979**, *37*, 129.
(5) Manes, L. V.; Bakus, G. J.; Crews, P. *Tetrahedron Lett.* **1984**, *25*, 931.
(6) Kligman, A. M., Leyden, J. J.; Stewart, R. *Int. J. Dermatol.* **1977**, *16*, 413.
(7) Cavallo, J. J.; Reynolds, R. A. U.S. Pat. 3 622 351, 1969.
(8) Sheppard, C. S. *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; John Wiley and Sons, Inc.: New York, 1988; Vol. II, pp 1–21.

0022-3263/95/1960-5341$09.00/0

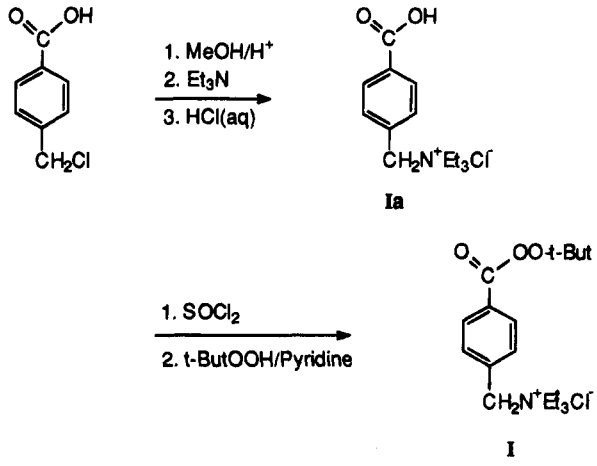

Figure 2. Synthetic sequence for peroxide **I**.

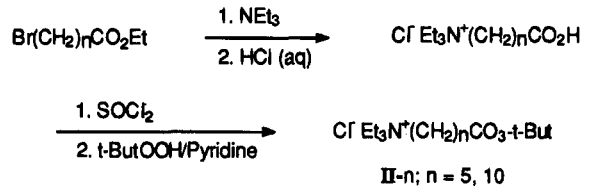

Figure 3. Synthetic sequence for peroxides **II-5** and **II-10**.

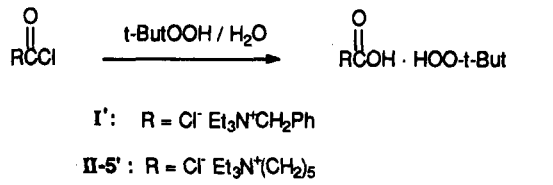

Figure 4. Formation of complexes **I'** and **II-5'**.

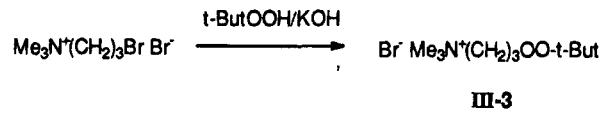

Figure 5. Synthetic sequence for peroxide **III-3**.

10, were prepared according to a reaction sequence that is illustrated in Figure 3.

In each synthetic sequence leading toward peroxides **I** and **II-n**, the acid chloride used in the last step is destroyed by hydrolysis during workup. It was found that a premature termination of the final step by hydrolysis would give stable complexes such as **I'** and **II-5'**, respectively (Figure 4). The complexes are most likely stabilized by the interaction between the ammonium center and the dioxy group. The complexes have similar physical and chemical properties compared to peroxides **I** and **II-5**. For example, they give similar test results with iodide solution as oxidants and their proton NMR spectra in D_2O are extremely similar. In their MS spectra, unlike **I** and **II-5**, **I'** and **II-5'** give parent peaks that correspond to their carboxylic acid moieties, respectively. Therefore, precautions must be taken to ensure the completion of the final step of the reaction.

Synthesis of Peroxides III-3 and III-10. Four dialkyl peroxides each containing a cationic functional group and a different chain length were prepared according to sequences illustrated in Figures 5 and 6.

Monosubstitution of an α,ω-dibromoalkane can be accomplished by a careful control of the stoichiometric

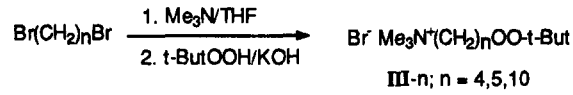

Figure 6. Synthetic sequence for peroxide **III-10**.

ratio of the two reagents, their overall concentrations, and temperature. The nucleophilic substitution of the second bromine by *tert*-butyl peroxide ion may be interfered with by the elimination of the α-hydrogen. This is a common problem during the synthesis of dialkyl peroxides under basic conditions.[9] Several approaches have been reported to reduce such competition.[10-12] The examples include the use of trifluoroacetic silver salt as a condensation reagent and the use of a phase-transfer reagent. We have found, however, the dialkyl peroxides (**III-n**; n = 3, 4, 5, 10) can be synthesized from the reaction of (n-bromoalkyl)trimethylammonium bromide and *tert*-butyl hydroperoxide at room temperature in the presence of potassium hydroxide without any significant complication from elimination if it is conducted under a careful control of the amount of the base and the use of an excess amount of *tert*-butyl hydroperoxide as a solvent. When n equals 2, however, the electronwithdrawing group at the β-position to oxygen–oxygen bond does cause elimination and yields a complex mixture. Therefore, the attempt to prepare peroxide **III-2** was not successful. In all cases, the reagent *tert*-butyl hydroperoxide can be recovered via distillation and reused.

Solubilities and Reactivities of the Prepared Peroxides. Representative peroxides, **III-3** and **III-10**, were modeled with the AM1 method[13] for their properties including O–O bond lengths, dihedral angles, dipole moments, and distances between the ammonium center and the dioxy group (Table 1). Compared to their counterparts that do not have a cationic group (a dimethylamino group was used to replace the trimethylammonium group), the dipole moment is significantly increased as expected when the third methyl group is introduced. It translates to a significant increase in water solubility for the peroxides in reality. Table 2 lists their relative solubilities in water, chloroform, methylene chloride, and hexadecane at room temperature. The results indicate that the prepared peroxides are readily soluble in polar organic solvents as well as in water. The solubility of **III-3** in water is greater than its analog with a longer hydrocarbon chain, **III-10**, while its solubility in a nonpolar solvent such as hexadecane is less than **III-10**. This solubility change follow the trend set by their calculated solvation energies as shown in Table 1. The solubilities of peroxides **I** and **II-n** in water and organic solvents were further improved by converting them into their bromide analogs.

Both peroxyesters and dialkyl peroxides show oxidizing properties when they are tested with potassium iodide.[14] Their relative oxidization reaction rates are summarized in Table 2. A peroxide with a long hydrocarbon chain such as **III-10** was found to have a higher reactivity than

(9) Huang, H. H. *J. Chem. Soc., Chem. Commun.* **1969**, 815.
(10) Cookson, P. G.; Davies, A. G.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1976**, 1022.
(11) Salomon, M. F.; Salomon, R. G. *J. Org. Chem.* **1976**, *41*, 3983–3987.
(12) Bourgeois, M. J. *Synthesis* **1989**, 700.
(13) AM1 calculations were performed on RS6000 workstations with Spartan software available through Wavefunction, Inc., Riverside, CA.
(14) Altshuller, A. P.; Schwab, C. M.; Bare, M. *Anal. Chem.* **1959**, *31* (12), 1987–1990.

Table 1. Molecular Modeling Results for Selected Peroxides with AM1 Approach

peroxide	O–O (Å)[c]	-O–O-(deg)[d]	ΔH_f (kcal/mol)[e]	DP (Debye)[f]	ΔE_{sol} (kcal/mol)[g]
III-3a[a] in vacuum	1.2895	−111.3785	−41.100	1.736	
III-3 in vacuum	1.2889	−109.4583	−26.091	8.278	
III-3 in water	1.2881	−104.3378	−59.637	8.613	33.546
III-3 in hexadecane	1.2861	−103.806	−39.946	8.631	13.855
III-10a[b] in vacuum	1.2986	−111.4870	−88.023	1.353	
III-10 in vacuum	1.2897	−111.5083	−70.152	9.437	
III-10 in water	1.2922	−112.2422	−96.472	9.782	26.320
III-10 in hexadecane	1.2897	−111.113	−88.759	9.534	18.607

[a] III-3a: *tert*-Butyl 3-(dimethylamino)propyl peroxide, analog of **III-3**. [b] III-10a: *tert*-butyl 10-(dimethylamino)decyl peroxide, analog of **III-10**. [c] O-O: Bond distance between the dioxy oxygens. [d] -O–O-: Dihedral angle with the dioxy oxygens as center. [e] ΔH_f: Standard heat of formation. [f] DP: Dipole moment. [f] ΔE_{sol}: Calculated solvation energy.

Table 2. Solubilities and Relative Reaction Rates of Some Peroxides with KI in Water

	solubility				rel ox rate[c]	
peroxide	water	CH_3Cl	CH_2Cl_2	hexa-decane	without SDS[b]	with SDS[c]
tert-ButOOH	vs	vs	s	i	1.000	1.032
I	vs	vs	s	i	0.251	<0.002
II-5	vs	vs	vs	i	0.202	<0.002
II-10	s	vs	vs	ss	0.578	<0.002
III-3	vs	s	s	i	0.105	0.051
III-10	s	s	s	ss	0.974	<0.002

[a] [Peroxide] = 1×10^{-3} M, [KI] = 5×10^{-3} M, [SDS] = 1×10^{-2} M. [b] vs: very soluble, > 1 g/mL; s: soluble, >0.1 g/mL; ss: slightly soluble; i: insoluble. [c] Rel Ox. rate: relative oxidation rate of an iodide solution in water with or without a surfactant, SDS.

its short chain analogs. As shown in Table 1, the O–O bond lengths and dihedral angles are relatively the same for all peroxides. Therefore, the difference in their oxidization rates is unlikely due to the O–O bond strengths. As the computational results indicate, a peroxide with a longer chain, when dissolved in water, receives less stabilization than those with shorter chains. This decrease in solvation energy translates to a instability for a peroxide with a longer chain length. As shown in Table 2, while the reactivity of a peroxide with a short hydrocarbon chain, **III-3**, was relatively insensitive to the addition of a surfactant, the reactivity of a peroxide with a longer chain decreases significantly. This trend can be explained by the formation of micelles or strong aggregates among the long chain peroxide molecules. It is common for a long chain hydrocarbon with a polar end, an amphiphile, to form micelles at and above a certain concentration in water. The critical micelle concentration (CMC) is a function of the chain length.[15] For example, decyltrimethylammonium bromide has a CMC of 65 mM in water at 25 °C while dodecyltrimethylammonium bromide has a CMC of 14 mM.[16] When these peroxides are incorporated into micelles, the dioxy group is located at the inside of the micelle and the interaction between the dioxy groups and iodide becomes less and less frequent. Since there is practically no water molecules in the center of the micelle, the *tert*-butoxy radicals must react with the iodide during the collision and reformation of the micelles.

Like all peroxides in general, the peroxides are susceptible to decomposition in the presence of acids or electron-donating compounds such as amines.[17] Therefore, the removal of triethylamine from the very first step during the introduction of ammonium functional group is crucial. It has been found that these peroxyesters and dialkyl peroxides are stable in water for days without triethylamine whereas they decompose readily in hours in the presence of triethylamine.

The prepared peroxides have been successfully used to initiate a polymerization process. For example, emulsion polymerization of styrene in water using peroxide **II-10** as initiator and SDS as surfactant at 60 °C gives monodispersed spherical polystyrene particles. The particle size and molecular weight can be adjusted by varying the ratios of initiator, surfactant, monomer, and other reaction conditions. The advantages of these water soluble organic dialkyl peroxides and alkyl peroxyester over conventional water soluble polymer initiators such as potassium persulfate will be presented in a separate paper.

Conclusion

A range of water soluble dialkyl peroxides and peroxyesters are synthesized using simple and straightforward reaction sequences. Their solubilities and reactivities are directly related to their solvation energies and environment. The strategy of introducing a cationic functional group into organic peroxides can be extended to other types of peroxides for the delivery of needed peroxide functional groups to the desired medium.

Experimental Section

All chemicals were obtained from Aldrich and used without further purification except styrene. Styrene was distilled under reduced pressure to remove the inhibitor and stored at 4 °C until use. Mass spectra were recorded on a VG ZAB-SE spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Broker AC 250 Hz spectrometer. SEM photographs were taken with a JOEL JSM6300 scanning electron microscope.

Preparation of [4-(Methoxycarbonyl)benzyl]triethylammonium Chloride.[19] To a solution of methyl 4-(chloromethyl)benzoate (33 g, 180 mmol) in toluene (100 mL), acetone (100 mL), and *N,N*-dimethylformamide (10 mL) at 50 °C was added triethylamine (30.3 g, 300 mmol) dropwise in 1 h. The mixture was refluxed for 20 h. TLC analysis indicted that the reaction was completed. The mixture was concentrated under a reduced pressure and a slight yellow residue was obtained. The residue was washed with ether (2 × 50 mL) to obtain 30 g of a white solid, the [4-(methoxycarbonyl)benzyl]triethylammonium chloride. Yield: 59%. Mp: 73–75 °C. IR: 1721 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ 8.03 (d, 2H, J = 8 Hz), 7.75 (d, 2H, J = 8 Hz), 5.05 (s, 2H), 3.30 (q, 6H), 2.94 (s, H), 1.45 (t, 9H). ^{13}C NMR (D_2O) δ 170.73 (s, C=O), 134.99 (s, C_3), 134.61 (s, C_1),

(15) Clint, J. H. *Surfactant Aggregation*; Chapman and Hall: New York, 1992; p 108.
(16) Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; Nat. Bur. Stand. (U.S.): Washington, DC, 1971.
(17) Keaveney, W. P.; Berger, M. G.; Pappas, J. J. *J. Org. Chem.* **1967**, *32*, 1537.
(18) Harald, N.; Hans, M. P.; Gunter, N. Ger. (East) DD 283, 497, 1990.
(19) Thanei-Wyss, P.; Waser, P. G. *Helv. Chim. Acta* **1983**, *66*, 2198.

133.68 (s, C_4), 132.30 (s, C_2), 61.59 (s, PhCH_2N), 55.21 (s, OCH_3), 54.92 (s, NCH_2CH$_3$), 9.39 (s, NCH$_2$$CH_3$). HRMS m/z: (M − Cl) calcd for $C_{15}H_{24}NO_2$ 250.1807, found 250.1810.

Preparation of (4-Carboxybenzyl)triethylammonium Chloride. A solution of [4-(methoxycarbonyl)benzyl]triethylammonium chloride (0.5 g, 1.75 mmol) in hydrochloride (24%, 30 mL) was heated to reflux for 5 h. The mixture was concentrated under a reduced pressure, and a slight yellow residue was obtained. The residue was washed with diethyl ether/acetone (10%) to obtain a 0.45 g white solid. Yield: 94%. Mp: 127−129 °C. IR: 1712 cm^{-1} (C=O). ^{1}H NMR (D_2O) δ 8.14 (d, 2H, J = 8 Hz), 7.71 (d, 2H, J = 8 Hz), 4.55 (s, 2H), 3.31 (q, 6H), 1.47 (t, 9H). ^{13}C NMR (D_2O) δ 169.99 (s, C=O), 133.40 (s, C_3), 133.06 (s, C_1), 132.17 (s, C_4), 130.96 (s, C_2), 60.05 (s, PhCH_2N), 53.43 (s, NCH_2CH$_3$), 7.93(s, NCH$_2$$CH_3$). HRMS m/z: (M − Cl) calcd for $C_{14}H_{22}NO_2$ 236.1651, found 236.1650.

Preparation of [4-[(*tert*-Butyldioxy)carbonyl]benzyl]triethylammonium Chloride, I. (4-Carboxybenzyl)trimethylammonium chloride (0.5 g, 1.7 mmol) was mixed with thionyl chloride (20 mL) at 0 °C. The mixture was heated and kept at 60 °C for 10 h. The mixture was concentrated under a reduced pressure, and a slight yellow residue was obtained. The residue was washed with absolute anhydrous ether to get 0.5 g of a white solid of [4-(chloroformyl)benzyl]triethylammonium chloride. A mixture of the chloride (0.2 g, 0.7 mmol), 5.5 M *tert*-butyl hydroperoxide in 2,2,4-trimethylpentane (0.36 mL, 2 mmol), methylene chloride (2 mL), and pyridine (180 mg, 2.3 mmol) was stirred at 0 °C for 8 h and then stirred at room temperature for 10 h. The reaction mixture was then stirred at 50 °C for a period of 4 h. The mixture was concentrated under a reduced pressure, and a colorless residue was obtained. The residue was washed with anhydrous diethyl ether (2 × 40 mL) to obtain a white solid. A saturated sodium bicarbonate solution (20 mL) was added to the solid, and the mixture was stirred at room temperature for 10 min. The mixture was concentrated under reduced pressure to yield a colorless solid, which was extracted with chloroform (3 × 40 mL). The extract was evaporated under reduced pressure to obtain 0.15 g of [4-[(*tert*-butyldioxy)carbonyl]benzyl]triethylammonium chloride. Yield: 65%. ^{1}H NMR ($CDCl_3$) δ 7.74 (d, 2H, J = 8 Hz), 7.84 (d, 2H, J = 8 Hz), 4.99 (s, 2H), 3.47 (q, 6H), 1.48 (t, 9H), 1.42 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 163.11 (s, C=O), 132.97 (s, C_1), 132.65 (s, C_4), 129.43 (s, C_2), 129.21 (s, C_3), 84.13 (s, O-O-C), 60.35 (s, NCH_2Ph), 53.11 (s, NCH_2CH$_3$), 26.10 (s, O-O-C-(Me)$_3$), 8.49 (s, N-CH$_2$-CH_3). High-resolution (FAB) MS m/z: (M − Cl) calcd for $C_{18}H_{30}NO_3$ 308.2226, found 308.2222.

Preparation of [5-(Ethoxycarbonyl)pentyl]triethylammonium Bromide. A mixture of ethyl 6-bromohexanoate (17.84 g, 80 mmol), toluene (120 mL), acetone (60 mmol), and *N*,*N*-dimethylformamide (6 mL) was heated to 50 °C. Then triethylamine (16.16 g, 160 mmol) was added to the mixture during 1 h. The mixture was refluxed for a period of 36 h, evaporated under reduced pressure, and washed with diethyl ether to obtain 18 g of light colored solid. Yield: 69%. Mp: 98−100 °C; IR: 1728 cm^{-1} (O=C); ^{1}H NMR (D_2O) δ 4.14 (q, 2H), 3.26 (q, 6H), 3.14 (m, 2H), 2.38 (t, 2H), 1.65 (m, 4H), 1.35−1.20 (m, 14H). ^{13}C NMR (D_2O) δ 177.54 (s, C=O), 64.48 (s, OCH_2), 57.27 (s, RCH$_2$N), 53.41 (s, NCH_2CH$_3$), 34.53 (s, C_5), 25.93 (s, C_3), 24.66 (s, C_4), 21.55 (s, C_2), 14.26 (s, OCH$_2$$CH_3$), 7.57 (s, NCH$_2$$CH_3$). HRMS m/z: (M − Br) calcd for $C_{14}H_{30}NO_2$ 188.1651, found 188.1653.

Hydrolysis of [5-(Ethoxycarbonyl)pentyl]triethylammonium Bromide. A solution of [5-(ethoxycarbonyl)pentyl]triethylammonium bromide (18 g, 56 mmol) in hydrochloric acid (24%, 240 mL) was refluxed for a period of 24 h. The solvent was evaporated under reduced pressure to obtain a residue. The residue was washed with diethyl ether to yield 16 g of a yellow solid. Yield: 94%. Mp: 87−89 °C; IR: 1723 cm^{-1} (O=C); ^{1}H NMR (D_2O) δ 3.27 (q, 6H), 3.15 (m, 2H), 2.40 (t, 2H), 1.63 (m, 4H), 1.44−1.21 (m, 11H). ^{13}C NMR (D_2O) δ 179.34 (s, C=O), 57.28 (s, RCH$_2$N), 53.41 (s, NCH_2CH$_3$), 34.30 (s, C_5), 25.92 (s, C_3), 24.59 (s, C_4), 21.55 (s, C_2), 7.55 (s, NCH$_2$$CH_3$). High-resolution (FAB) MS m/z: (M − Cl) calcd for $C_{12}H_{26}NO_2$ 216.1963, found 216.1962.

Preparation of [5-[(*tert*-Butyldioxy)carbonyl]pentyl]triethylammomium Chloride, II-5. 5-(Carboxypentyl)triethylammonium chloride (5 g, 20 mmol) was mixed with thionyl chloride (50 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and at 50 °C for 24 h. The mixture was concentrated under reduced pressure and then washed with absolute anhydrous diethyl ether to give a brown residue. The residue was mixed with 3 M *tert*-butyl hydroperoxide in 2,2,4-trimethylpentane (30 mL, 90 mmol), and the mixture was stirred at 0 °C for 1 h. To the reaction mixture at 0 °C was added pyridine (1.6 g, 20.1 mmol) dropwise during 10 min. The mixture was stirred at 0 °C for 1 h and at room temperature for 10 h. After removal of the excess reagents under reduced pressure, the residue was washed with anhydrous diethyl ether. A saturated sodium bicarbonate solution (50 mL) was added to the residue, and the mixture was stirred at 0 °C for 1 h and concentrated in vacuo. The residue was extracted with chloroform (3 × 40 mL). The solvent of the reaction mixture was evaporated in vacuo to obtain 5.5 g of [5-[(*tert*-butyldioxy)carbonyl]pentyl]triethylammonium chloride. Yield: 85%. ^{1}H NMR ($CDCl_3$) δ 3.51(q, 6H), 3.33 (t, 2H), 2.38 (t, 2H), 1.77−1.32 (m, 24H). ^{13}C NMR ($CDCl_3$) δ 170.88 (s, C=O), 83.56 (s, COO), 53.41 (s, NCH_2CH$_3$), 25.89 (br s, C_2−5 and OCH$_2$$CH_3$), 8.33 (br s, NCH$_2$$CH_3$). High-resolution MS m/z: (M − 1) calcd for $C_{16}H_{33}ClNO_3$ 322.2148, found 322.2144.

Preparation of [10-(Methoxycarbonyl)decyl]triethylammonium Bromide. A mixture of methyl 11-bromoundecanoate (11.12 g, 40 mmol), toluene (80 mL), acetone (40 mL), and *N*,*N*-dimethylformamide (4 mL) was heated to 50 °C. Then triethylamine (99%, 8.16 g, 80 mmol) was added to the mixture during 1 h. The mixture was refluxed for a period of 39 h, evaporated under reduced pressure, and washed with diethyl ether to obtain 8.9 g of light brown solid. Yield: 56%. Mp: 67−69 °C. IR: 1734 cm^{-1} (O=C). ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 3H), 3.53 (q, 6H), 3.33 (m, 2H), 2.31 (t, 2H), 1.61−1.28 (m, 25H). ^{13}C NMR ($CDCl_3$) δ 173.68 (s, C=O), 57.02 (s, RCH$_2$N), 53.02 (s, NCH_2CH$_3$), 50.90 (s, OCH_3), 33.51 (s, C_{10}), 28.55 (m, C_{4-8}), 25.89 (s, C_3), 24.33 (s, C_9), 21.54 (s, C_2), 7.64 (s, NCH$_2$$CH_3$).

Hydrolysis of [10-(Methoxycarbonyl)decyl]triethylammonium Bromide. A solution of [10-(methoxycarbonyl)decyl]triethylammonium bromide (2 g, 5.26 mmol) in hydrochloric acid (24%, 30 mL) was refluxed for a period of 24 h. The solvent was evaporated under reduced pressure to obtain a residue. The residue was washed with diethyl ether to yield 1.4 g of a brown solid. Yield: 82.8%. Mp: 77−79 °C; IR: 1722 cm^{-1} (O=C). ^{1}H NMR (D_2O) δ 3.25 (q, 6H), 3.11 (m, 2H), 2.35 (t, 2H), 1.58 (m, 8H), 1.27−1.20 (m, 17H). ^{13}C NMR (D_2O) δ 181.90 (s, C=O), 59.15 (s, RCH$_2$N), 54.92 (s, NCH_2CH$_3$), 36.38 (s, C_{10}), 30.38 (m, C_{4-8}), 28.04 (s, C_3), 26.83 (s, C_9), 23.34 (s, C_2), 9.22 (s, NCH$_2$$CH_3$).

[10-[(*tert*-Butyldioxy)carbonyl]decyl]triethylammomium Chloride, II-10, was prepared according to a similar procedure for compound **II-5**. Yield: 67.8%. ^{1}H NMR ($CDCl_3$) δ 3.48 (q, 6H), 3.24 (t, 2H), 2.31 (t, 2H), 1.70 (m, 8H), 1.44−1.32 (m, 26H). ^{13}C NMR ($CDCl_3$) δ 171.11 (s, C=O), 83.23 (s, $(CH_3)_3$COO), 57.41 (s, RCH$_2$N), 53.37 (s, NCH_2CH$_3$), 31.20 (s, C_{10}), 29.07 (m, C_{4-9}), 26.39 (s, br, OCCH_3 and C_3), 21.90 (s, C_2), 7.99 (s, NCH$_2$$CH_3$). High-resolution MS m/z: (M − Cl) calcd for $C_{21}H_{44}NO_3$ 358.3321, found 358.3315. (M − 1) calcd for $C_{21}H_{43}NO_3Cl$ 392.2931, found 392.2932.

Preparation of [3-(*tert*-Butyldioxy)propyl]trimethylammonium Bromide, III-3. A mixture of *tert*-butyl hydroperoxide (90%, 20 mL) and potassium hydroxide (0.32 g, 4.97 mmol) was stirred at 0 °C for 4 h until a clear solution was obtained. (3-Bromopropyl)trimethylammonium bromide (1 g, 3.8 mmol) was added to the solution. The mixture was stirred at room temperature under nitrogen for a period of 36 h and concentrated under reduced pressure. The residue was washed with anhydrous diethyl ether (3 × 20 mL) to obtain a white solid, which was extracted with chloroform (3 × 40 mL) to remove potassium bromide. The solvent was evaporated reduced pressure to obtain 0.8 g of [3-(*tert*-butyldioxy)propyl]triethylammonium chloride. Yield: 78%. Mp: 84−86 °C. ^{1}H NMR (D_2O) δ 4.09 (t, 2H), 3.42 (m, 2H), 3.11 (s, 9H), 2.14 (m, 2H), 1.23 (s, 9H). High-resolution MS m/z: (M − Br) calcd for $C_{10}H_{24}NO_2$ 190.1807, found 190.1808.

Preparation of [10-(*tert*-Butyldioxy)decyl]trimethylammonium Bromide, III-10. (10-Bromodecyl)trimethylammonium bromide was prepared from 1,10-dibromodecane according to literature procedure.[19] Yield: 76%. Mp: 135−137 °C. ^{1}H NMR (D_2O) δ 3.50 (t, 2H), 3.30 (m, 2H), 3.10 (s, 9H), 1.78 (m, 4H), 1.32 (m, 12H). Anal. Calcd for $C_{13}H_{29}NBr_2$: C,

43.47%; H, 8.14%; N, 3.90, Br, 44.49%. Found: C, 43.39%; H, 8.19%; N, 3.90.

tert-Butyl hydroperoxide (90%, 4 mL) was mixed with potassium hydroxide (0.56 mmol, 40 mg) at 0 °C. The temperature of solution was allowed to rise to room temperature. The solution was stirred at room temperature for 4 h. (10-Bromodecyl)trimethylammonium bromide (202 mg, 0.56 mmol) was added to the solution. The mixture was stirred at room temperature for 20 h and then concentrated in vacuo. The residue was washed with diethyl ether (2 × 10 mL) to obtain a white solid, which was extracted with chloroform (3 × 20 mL) to remove potassium bromide. The solvent was evaporated under reduced pressure to give 0.11 g of [10-(*tert*-butyldioxy)-decyl]trimethylammonium bromide. Yield: 55%. ^{1}H NMR (D_2O) δ 4.0 (t, 2H), 3.30 (m, 2H), 3.09 (s, 9H), 1.77 (m, 2H), 1.58 (m, 2H), 1.31−1.21 (m, 21H). ^{13}C NMR (D_2O) δ 84.74(s, R*C*H_2N), 69.27 (s, OO*C*$(CH_3)_3$), 55.27 (s, NCH_3), 30.94 (m, C_{4-7}), 27.88 (m, $C_{3,9}$ and OC(*C*$H_3)_3$), 24.00 (s, C_2). HRMS *m*/*z*: (M − Br) calcd for $C_{17}H_{38}NO_2$ 288.2902, found 288.2900.

[4-(*tert*-Butyldioxy)butyl]trimethylammonium Bromide, III-4, and [5-(*tert*-Butyldioxy)pentyl]trimethylammonium Bromide, III-5, were prepared according to a similar procedure for compound **III-3**. **III-4**, Yield: 75%. ^{1}H NMR (D_2O) δ 4.06 (t, 2H), 3.33 (m, 2H), 3.10 (s, 9H), 1.87 (m, 2H), 1.67 (m, 2H), 1.24 (s, 9H); High-resolution MS *m*/*z*: (M − Br) calcd for $C_{11}H_{26}NO_2$ 204.1964, found 204.1965. **III-5**, Yield: 55%. ^{1}H NMR (D_2O) δ 4.04 (t, 2H), 3.32 (m, 2H), 3.10 (s, 9H), 1.80 (m, 2H), 1.71 (m, 2H), 1.57 (m, 2H), 1.24 (s, 9H); High-resolution MS *m*/*z*: (M − Br) calcd for $C_{12}H_{28}NO_2$ 218.2120, found 218.2125.

Emulsion Polymerization of Styrene with Peroxide II-10 as an Initiator. A styrene emulsion was prepared by stirring a 30.0 mL aqueous solution of SDS (0.160 g, 0.56 mmol) in a 100 mL three neck round bottom flask for 30 min at 60 °C. The emulsion was added with distilled styrene (10.0 g, 96.1 mmol) and stirred for an additional 30 min. The initiator, **II-10** (50.0 mg, 0.13 mmol), was then added into the emulsion as a water (1 mL) solution. The reaction mixture was kept at 60 °C for 2 h, elevated to 90 °C, and then kept for 8 h. The solvent was removed under reduced pressure just before the SEM analysis. The SEM photograph showed monodispersed spherical polystyrene particles with an average size of 80 nm.

Acknowledgment. We wish to thank Professor Stig E. Friberg of Clarkson University for the extremely valuable discussions.

Supporting Information Available: ^{1}H NMR spectra of new compounds (10 pages) *in lieu* of combustion analysis. This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9417075