(CDCl$_3$) (at 22 °C) δ 1.92 (3 H, s), 2.37 (3 H, br s), 2.51 (2 H, s), 3.07 (3 H, br s), 5.15 (1 H, s), 5.91 (1 H, s), 7.2–7.8 (8 H, m); ^{1}H NMR (CDCl$_3$) (at –50 °C) δ 1.92 (3 H, br s), 2.40/0.81 (3 H, s), 2.51 (2 H, br s), 3.00/3.84 (3 H, s), 5.19/4.78 (1 H, s), 5.95/5.66 (1 H, s), 7.2–7.8 (8 H, m) (the signals for the major and minor conformers are indicated before and after the slant lines, respectively); ^{13}C{^{1}H} NMR (CDCl$_3$) (at –45 °C) δ 20.1, 23.8, 37.8, 51.6, 53.9, 119.5, 119.6, 124.2, 126.6, 126.6, 126.8, 126.9, 141.4, 142.6, 147.3, 151.1; MS, m/z (%) 315 (M$^+$, 100), 300 (M$^+$ – CH$_3$, 26), 284 (M$^+$ – OCH$_3$, 15); found M$^+$ 315.1615. C$_{22}$H$_{21}$ON requires M$^+$ 315.1622. 1,3-Dimethyl-4b-aza-7H-benz[a]-indeno[c,d]azulene (16): orange granules; mp ca. 115 °C dec; ^{1}H NMR (CDCl$_3$) δ 2.37 (3 H, s), 2.76 (3 H, s), 3.70 (2 H, ddd, J = 4.7, 4.7, 1.8 Hz), 4.57 (1 H, tdd, J = 9.9, 4.7, 0.8 Hz), 6.14 (1 H, td, J = 4.7, 0.8 Hz), 6.58 (1 H, td, J = 1.8, 9.9 Hz), 6.69 (1 H, s), 6.82 (1 H, s), 6.8–7.6 (4 H, m); UV (CH$_3$OH–CH$_2$Cl$_2$, 9:1) λ_{max} (log ϵ) 325 nm (3.39), 359 (3.46), 375 (sh) (3.40), 424 (3.14); MS found M$^+$ 283.1317. C$_{21}$H$_{17}$N requires M$^+$ 283.1361.

(B) In Diethylamine. The photoreaction in diethylamine was carried out in a small photoreaction vessel (12 mL) with a pen-light under nitrogen bubbled continuously through the solution. The irradiated solution was evaporated and the residue was treated in the same manner described in methanol to give three photoproducts. The yield is shown in Table VIII. The amines 6 were identified by comparing with the authentic samples. 9-(2-Amino-4,6-dimethylphenyl)-9-diethylaminofluorene (20): oil; ^{1}H NMR (CDCl$_3$) δ 0.92 (6 H, t, J = 7.0 Hz), 1.08 (3 H, s), 2.14 (3 H, s), 2.16 (2 H, m), 2.69 (2 H, m), 6.05 (1 H, s), 6.39 (1 H, s), 7.2–7.8 (8 H, m); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 16.1, 20.5, 23.5, 44.8, 79.3, 116.3, 119.5, 120.5, 123.1, 126.2, 127.1, 128.0, 136.5, 138.0, 140.9, 147.4, 149.9; MS, m/z (%) 356 (M$^+$, 26), 284 (M$^+$ – Et$_2$N, 100), 282 (43); found M$^+$ 356.2270. C$_{25}$H$_{28}$N$_2$ requires M$^+$ 356.2253. 9-(3-Amino-2-(diethylamino)-4,6-dimethylphenyl)fluorene (21): colorless needles; mp ca. 235 °C dec; ^{1}H NMR (CDCl$_3$) δ 0.95 (3 H, s), 1.24 (6 H, t, J = 7.2 Hz), 2.15 (3 H, s), 3.33 (4 H, m), 4.13 (2 H, br s), 5.67 (1 H, s), 6.55 (1 H, s), 7.2–7.9 (8 H, m); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 15.7, 17.2, 17.8, 49.5, 49.5, 119.9, 121.3, 124.1, 126.6, 127.1, 127.5, 131.0, 136.5, 137.3, 140.9, 142.8, 148.1; MS, m/z (%) 356 (M$^+$, 100), 327 (M$^+$ – Et, 12), found M$^+$ 356.2268. C$_{25}$H$_{28}$N$_2$ requires M$^+$ 356.2253.

(C) In Acetonitrile in the Presence of TCNE. A solution of 20 mg (64 μmol) of the azide and 26 mg (200 μmol) of TCNE in 160 mL of

acetonitrile was irradiated. The photolyzed solution was evaporated and the residue was extracted with a small amount of chloroform. The extract was filtered through the tube packed with cotton. The two adducts, 24 and 25, were obtained by separation and purification in the same manner as described for methanol. The yield of the adducts shown in Table X was determined by the integration of ^{1}H NMR in the crude reaction mixture, based on the reacted material determined by HPLC. 1,3-Dimethyl-4c,7-tetracyanoethano-4c,12b-dihydro-4b-aza-7H-benz[a]indeno[c,d]azulene (24): colorless needles; mp ca. 190 °C dec; ^{1}H NMR (CDCl$_3$) δ 2.27 (3 H, s), 2.67 (3 H, s), 3.63 (1 H, dd, J = 8.5, 7.6 Hz), 4.97 (1 H, dd, J = 8.5, 8.5 Hz), 5.34 (1 H, s), 6.41 (1 H, s), 6.59 (1 H, d, J = 8.5 Hz), 6.70 (1 H, s), 6.86 (1 H, d, J = 7.6 Hz), 7.4–7.7 (4 H, m); MS, m/z (%) 411 (M$^+$, 36), 283 (M$^+$ – TCNE, 100), 282 (69), 268 (25); found M$^+$ 411.1480. C$_{27}$H$_{17}$N$_5$ requires M$^+$ 411.1483. 6,8-Dimethyl-9-(9-fluorenyl)-1,1,2,2-tetracyano-4-spiro[2,6]nona-4,6,8-triene (25): colorless granules; mp ca. 205 °C dec; ^{1}H NMR (CDCl$_3$) δ 1.02 (3 H, s), 2.28 (3 H, s), 4.96 (1 H, s), 6.79 (1 H, br s), 7.1–7.8 (8 H, m), 8.21 (1 H, d, J = 1.8 Hz); MS, m/z (%) 411 (M$^+$, 54), 347 (44), 346 (M$^+$ – HC(CN)$_2$, 100), 282 (35); found M$^+$ 411.1455. C$_{27}$H$_{17}$N$_5$ requires M$^+$ 411.1483.

Time-Resolved Absorption Spectroscopy. An undegassed solution of the azide (4.8 × 10^{-5} M) in methanol–ether (92:8) was irradiated at 25 °C in a 1 × 1 × 4 cm quartz cell with a 248-nm pulse from an excimer laser with a pulse width of 12 ns and output energy of 50 mJ/cm^2. In the observation of decomposition rate of the o-quinoid species 11, a steady light source was used as a monitor light.

Calculation of Spin Densities with the INDO–UHF Method. Calculations were carried out on a Hitach-M-200H computer of the Computer Center of the Institute for Molecular Science. The program used was the following, CNINDO: CNDO and INDO molecular orbital program (FORTRAN IV), which was originally programmed by J. A. Pople, D. L. Beveridge, and P. A. Dobosh (QCPE No. 141).

Methyl-Substituted Poly(vinylnaphthalene) as a Reversible Singlet Oxygen Carrier

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Abstract: Methyl-substituted poly(vinylnaphthalenes) (5a–c) were prepared by radical polymerization of the corresponding vinylnaphthalenes 4a–c. Polymers 5a and 5b have been shown to bind and release singlet molecular oxygen (^{1}O$_2$) reversibly at temperatures between 0 and 35 °C. Methylene blue sensitized photooxygenation of polymers 5 at 0 °C produced the corresponding polymer endoperoxides 6 in nearly quantitative yields. Generation of ^{1}O$_2$ from the thermolysis of polymer endoperoxide 6b at 35 °C was confirmed by trapping experiments using typical ^{1}O$_2$ acceptors. Kinetic parameters for the thermolyses of 6a and 6b were compared with those for the corresponding monomer endoperoxides. The yield of ^{1}O$_2$ generated from polymer 6b was determined to be as high as 66 ± 5%. The synthetic utility of these polymeric endoperoxides as a ^{1}O$_2$ source has been demonstrated in the oxidation of a series of representative substrates. Advantages of using these polymer ^{1}O$_2$ sources are the following: (1) the mild condition for generation of ^{1}O$_2$, (2) utility in nonsolvent systems, and (3) easy removal and reuse.
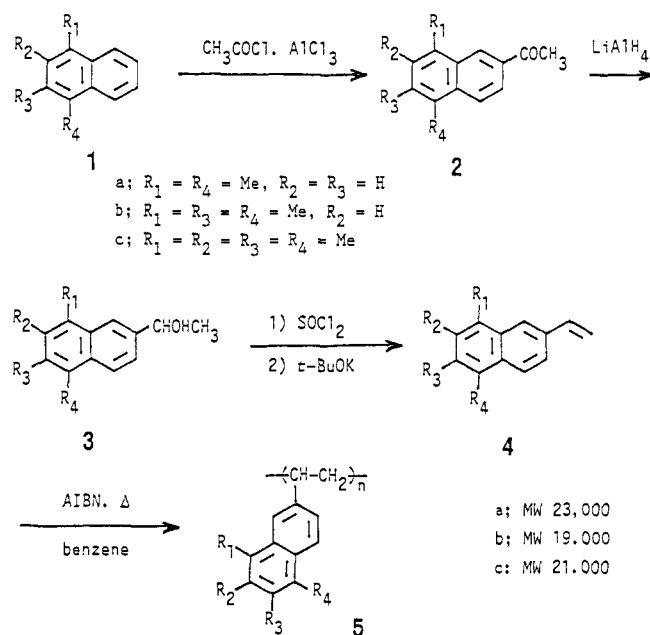
Since singlet oxygen (^{1}O$_2$) was shown to be involved in a variety of chemical and biochemical phenomena, there has been a surge of interest in chemical methods of producing ^{1}O$_2$.[1] One major advantage of the use of chemical ^{1}O$_2$ sources over the photosensitization method is to avoid secondary interactions of photoexcited sensitizers with substrates or products which sometimes complicate

the mechanisms of photosensitized oxygenations.[2] Mechanistically less complicated chemical ^{1}O$_2$ sources that can generate ^{1}O$_2$ at ordinary temperature are extremely useful for ^{1}O$_2$ reactions of organic substrates and biological systems, particularly for their

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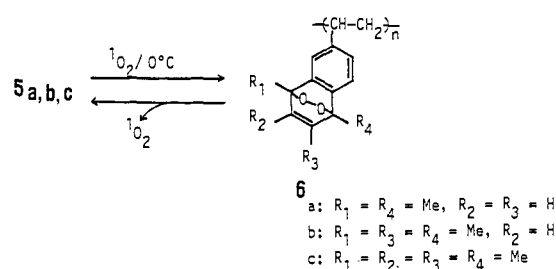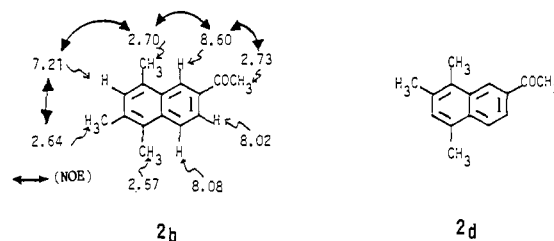
Scheme I

Scheme II

polymer reagents. We describe here the details of the preparation and properties of polymer endoperoxides derived from methyl-substituted polyvinylnaphthalenes.[4]

Results and Discussion

Synthesis of Poly(vinylnaphthalene) and Polymeric Endoperoxides. Methyl-substituted vinylnaphthalenes **4a, 4b,** and **4c** were prepared in a straightforward fashion from the corresponding polymethylnaphthalenes **1a, 1b,** and **1c,** respectively, as outlined in Scheme I. 2-Acetyl-5,8-dimethylnaphthalene (**2a**) and 2-acetyl-5,6,7,8-tetramethylnaphthalene (**2c**) were prepared by Friedel–Crafts acetylation.[8]   In the case of 1,2,4-trimethyl-naphthalene (**1b**), a single acetylated product was obtained in 66% yield after recrystallization from ethyl acetate. Examination of the 400-MHz ^{1}H NMR, including NOE–FID difference technique, allowed full assignment of all protons of the acetylated product. The observed NOE is fully consistent with structure **2b,** as shown eliminating an alternative structure, **2d.** The methyl-

mechanistic investigations. In this context, we recently demonstrated the usefulness of a water-soluble $^1O_2$ source for the oxidation of biological substrates.[3]   We are interested also in developing a new polymer $^1O_2$ carrier[4] that can bind and release $^1O_2$ reversibly near room temperature for use as a synthetic reagent as well as for the potential application to insect-repellent systems owing to the toxicity of $^1O_2$ toward cells.

Since Wasserman and Scheffer reported the use of 9,10-diphenylanthracene endoperoxide as a chemical $^1O_2$ source,[5] endoperoxides derived from a number of aromatic and heteroaromatic compounds have been shown to dissociate to parent aromatics with a concomitant generation of $^1O_2$ upon their thermal decompositions.[6]   Among these endoperoxides alkyl-substituted naphthalene endoperoxides are known to release $^1O_2$ under extremely mild conditions.[6,7]   For example, endoperoxides derived from 1,4-dimethyl- and 1,2,4-trimethylnaphthalenes produce $^1O_2$ efficiently at 25 °C with half-lives of 5 and 70 min, respectively.[7] Moreover, the half-lives of the decomposition of naphthalene endoperoxides giving $^1O_2$ can be controlled by alkyl substituents.[6,7] However, a serious disadvantage often encountered in singlet oxygenation using such an aromatic hydrocarbon endoperoxide is the difficulty in separating oxidation products from the reaction mixture containing a large excess of aromatic hydrocarbon. We therefore prepared the polymer $^1O_2$ sources which contain methyl-substituted naphthalenes as pendant groups. These polymers react with $^1O_2$ smoothly at 0 °C to produce the corresponding endoperoxide polymers which on warming to room temperature revert to parent polymers with a concomitant generation of $^1O_2$. These polymers containing naphthalene endoperoxide units are effective reagents for $^1O_2$ generation and have several advantages over monomeric $^1O_2$ sources. These include (1) utility in $^1O_2$ reaction in nonsolvent systems such as polymer films; (2) easy removal by simple precipitation; (3) reuse of these

substituted acetylnaphthalenes **2** were then converted to the corresponding alcohols **3** by reduction with LiAlH$_4$. The desired methyl-substituted vinylnaphthalenes **4** were prepared in good yields from **3** by treatment with SOCl$_2$ followed by dehydro-chlorination with *t*-BuOK in dimethyl sulfoxide. Radical polymerization of monomers **4** was carried out in degassed benzene at 70 °C in the presence of azobisisobutyronitrile (AIBN) to give the corresponding polymers **5** in high yields. These polymers are soluble in aromatic and halogenated solvents such as benzene, toluene, dichloromethane, and 1,2-dichloroethane but are insoluble in alcohols. After repeated precipitations by adding methanol, molecular weights of polymers **5a, 5b,** and **5c** were determined as 23 000, 19 000, and 21 000, respectively, by means of gel permeation chromatography.

When a solution of polymer **5b** was irradiated in dichloromethane with a tungsten–bromine lamp at 0 °C in the presence of methylene blue under oxygen atmosphere, approximately 0.9 mol equiv of oxygen with respect to a naphthalene unit in the polymer was consumed within 3.5 h. The progress of the photooxygenation was monitored by oxygen absorption and the disappearance of UV absorption at 290 nm of the naphthalene ring. After concentration under reduced pressure below 5 °C, the mixture was poured into methanol to give **6a** as white powder in almost quantitative yield. Polymeric endoperoxides **6a** and **6c** were prepared by a similar procedure (Scheme II).

Thermal Decomposition of Polymeric Endoperoxides. When a solution of **5a** was photooxygenated in dichloroethane at 0 °C, the absorption at 290 nm gradually disappeared owing to the formation of the endoperoxide groups. Warming the solution to

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(7) (a) Wasserman, H. H.; Larsen, D. L. *J. Chem. Soc., Chem. Commun.* **1972,** 253. (b) Larsen, D. L. Dissertation, Yale University, New Haven, Conn.

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Table I. Activation Parameters, Half-Lives, Activation Enthalpies, and Activation Entropies for Thermolyses of Naphthalene Endoperoxides[a]

compd	E_a, kcal/mol	ln A	$\tau_{1/2}$ (at 30 °C), min	$\Delta H^{\ddagger,b}$ kcal/mol	$\Delta S^{\ddagger}$, eu[b]
6a	25.8 ± 0.2	34.0 ± 0.3	80	25.2 ± 0.2	7.0 ± 0.6
7	26.6 ± 0.4	35.0 ± 0.7	116	26.0 ± 0.2	9.0 ± 1.4
6b	26.9 ± 0.04	34.2 ± 0.1	419	26.3 ± 0.04	7.4 ± 0.2
8	27.6 ± 0.2	34.2 ± 0.1	589	27.0 ± 0.2	8.9 ± 0.6

[a] In dichloromethane at temperature range of 25–40 °C. [b] Obtained at 30 °C.
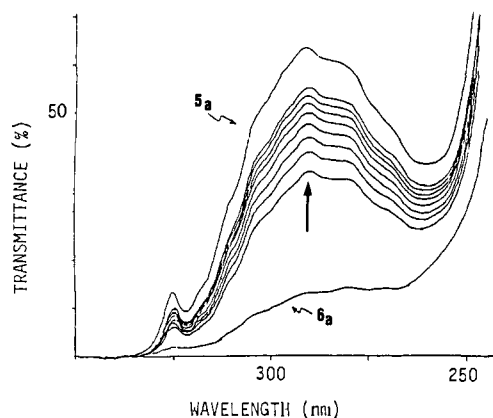

Figure 1. Progressive UV spectral change in the thermolysis of polymeric endoperoxide **6a** at 30 °C in dichloromethane.

30 °C in turn reproduced the absorption of the naphthalene chromophore at 290 nm. Finally, the UV spectrum perfectly overlapped with that of the original **5a** (Figure 1), showing the absence of side reactions during photooxygenation of polymer **5a**. Such a completely reversible oxygenation–deoxygenation process was also observed with **5b** but not with **5c** (vide infra). The rates of appearance of the naphthalene chromophore from polymeric endoperoxides **5a,b** were measured in dichloromethane by monitoring the increase of the absorption at 290 nm as a function of time at various temperatures. Additionally, the rate constants of the decompositions of the corresponding monomer endoperoxides **7**[7b] and **8** were measured for comparison. In each case excellent first-order kinetics were obtained.
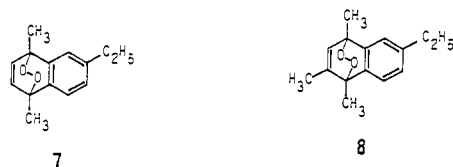

7   **8**

Figure 2 shows a plot of the log of the first-order rate constants vs. reciprocal of the absolute temperature. The activation parameters (E_a, A) and the associated activation enthalpies ($\Delta H^{\ddagger}$) as well as the activation entropies ($\Delta S^{\ddagger}$) derived from Eyring plots for the decomposition of **6a**, **6b**, **7**, and **8** are listed in Table I. The results of Table I indicate that the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the thermolyses of polymer endoperoxides **6a,b** are ca. 1 kcal/mol and 2 eu smaller respectively than those for the thermolyses of the corresponding monomer endoperoxides, implying a participation of a so-called polymer effect in the thermal decomposition of the polymer endoperoxides. Turro et al. have reported the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the thermolyses of endoperoxides derived from 9,10-diphenyl- and 1,4-dimethyl-9,10-diphenylanthracenes in various solvents.[9] They observed that the use of aromatic solvents such as toluene or chlorobenzene lowers the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values a few kilocalories/mole and several entropy units, respectively, compared to those obtained in nonaromatic solvents.[9] Our observation that the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values obtained for polymers **6a** and **6b** are smaller than those for monomer endoperoxides **7** and **8**, respectively, suggests the existence of a similar interaction between the endoperoxide groups and the neighboring aromatic
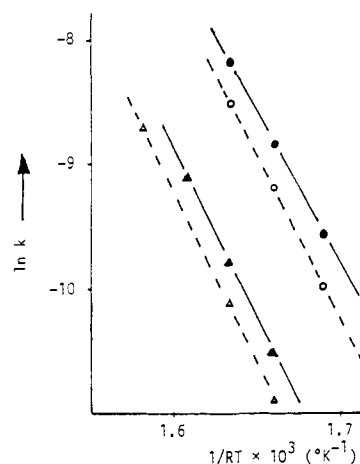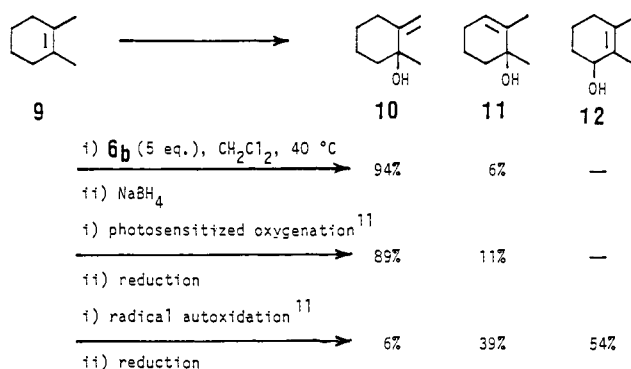

Figure 2. Plots of the log of the rate constants in thermolyses of endoperoxides as a function of temperature in dichloroethane. Polymeric endoperoxides (—), **6a** (●); **6b** (▲). Naphthalene endoperoxides (---), **7** (○); **8** (△).

Scheme III

rings within the polymer chains.

Thermal decomposition of **6c** requires higher temperatures for the decomposition, and the decomposition rate did not fit with first-order kinetic. In addition, reversibility was not observed with **6c** as apparent from the UV spectral change due to the occurrence of a side reaction, probably diepoxide formation,[6b,10] during the decomposition process. Therefore, **6c** cannot be used as a $^1O_2$ generator. In contrast, polymeric endoperoxides **6a,b** would be highly suitable as $^1O_2$ generators because of their high reversibility. Half-lives at 30 °C of **6a** ($\tau_{1/2}$ 80 min) and **6b** ($\tau_{1/2}$ 419 min) are also ideal as $^1O_2$ sources. The generation of $^1O_2$ from **6b** was confirmed by the following experiments.

The product distribution from 1,2-dimethylcyclohexene (**9**) has been generally used as a criterion for the participation of $^1O_2$.[11] A solution of **9** and **6b** (5 equiv of naphthalene endoperoxide unit) in dichloromethane was allowed to warm to 40 °C. After removal of resulting polymer **5b** by precipitation, the mixture was reduced with NaBH₄ to yield **10** and **11** in a ratio of 94:6. The ratio is very close to that observed in dye-sensitized photooxygenation and

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Table II. Oxidation of Singlet Oxygen Acceptors with Polymer Endoperoxide **6b**

| entry	substrate	mol ratio[a] of 6b vs. acceptor	condition[b]			product (yield, %)
			phase	temp, °C	time, h	
1	**13**	3:1	c	40	6	**14** (77)
2	**13**	3:1	d	40	6	**14** (36)
3	**16**	5:1	e	40	6	**17** (29)
4	**16**	5:1	c	40	6	**17** (16)
5	**18**	5:1	e	35	15	**19 + 20** (50) (5:4)
6	**18**	5:1	c	35	15	**19 + 20** (47) (5:4)

[a] Based on a naphthalene unit of **6b**. [b] See Experimental Section. [c] In a polymer film. [d] Suspension in methanol. [e] In a solution of dichloromethane.

Scheme IV
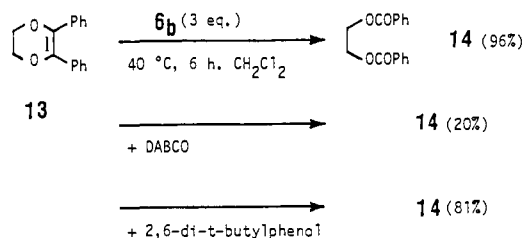
Scheme V

quite different from the product ratio in radical autoxidation (Scheme III).[11] 2,3-Diphenyl-*p*-dioxene (**13**) undergoes 1,2-addition with $^1O_2$ to give **14**.[12] Under thermolysis of **6b**, **13** was converted to **14** in 96% yield. When a small amount of 1,4-diazabicyclo[2.2.2]octane (DABCO), a $^1O_2$ quencher, was added to the reaction system, the production of **14** was drastically reduced. In contrast, addition of 2,6-di-*tert*-butylphenol, a free radical inhibitor, did not affect the yield of **14** appreciably (Scheme IV). These results undoubtedly indicate that the reactive species generated from **6b** is $^1O_2$.

2,5-Di-*tert*-butylfuran (**15**)[6b,13] was next employed as a $^1O_2$ acceptor in order to measure the yield of $^1O_2$ generated from **6b**, since **15** has a large second-order rate constant (1.5×10^8 M^{-1} s^{-1} in dichloromethane[13a]) with $^1O_2$ and the physical quenching component of the rate has been shown to be negligible.[13a,14] The yield of $^1O_2$ was determined by the ratio of disappearance of acceptor **15** to the appearance of naphthalene chromophore from **6b** by measuring UV absorption at 290 nm. The disappearance of **15** was determined by integration of the *tert*-butyl signal of **15** by ^{1}H NMR. When **6b** was decomposed in dichloromethane at 35 °C in the presence of excess **15** as $^1O_2$ trap, the yield of $^1O_2$ was determined as high as 66 ± 5%. This value is very close to the $^1O_2$ yields obtained from monomer naphthalene endoperoxides,[7b,9] e.g., 69% from 1,4,5-trimethylnaphthalene endoperoxide.[9]

Synthetic Utility of Polymeric Endoperoxides. As already mentioned, polymeric endoperoxides (**6a,b**) were used for singlet oxygenation of known $^1O_2$ acceptors (Scheme V). Usually, the reaction was conducted in homogeneous solution such as dichloromethane solution at 35–40 °C. The mole ratio of endoperoxide unit to acceptor ranged from 3:1 to 5:1. In cases where the polymeric endoperoxide is insoluble, the oxidation can be carried out in a suspension (entry 2). When a solution of **6b** and acceptor in dichloromethane was gradually evaporated to dryness under reduced pressure, a film of the polymer endoperoxide-containing acceptor was formed. Warming this film to 35 °C resulted in the oxidation of the acceptor (entries 1, 4, and 6). We expected a different regioselectivity in singlet oxygenation of citronellol (**18**) in a polymer film. However, almost the same product distribution was observed in singlet oxygenation of **18** both
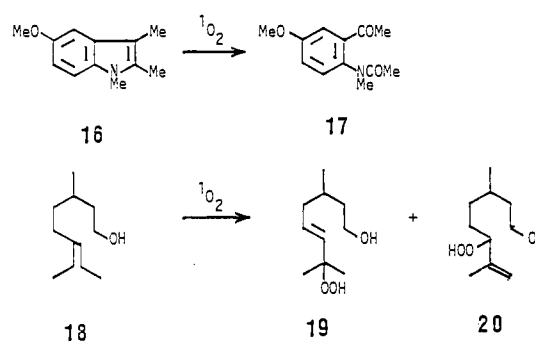
in solution and film (entries 5 and 6). These results, including product structures and reaction conditions, are listed in Scheme V and Table II. After oxygenation, the resulting poly(vinyl-naphthalene) **5b** was recovered quantitatively by adding methanol.

The use of such polymeric endoperoxides may prove superior to existing methods for chemical generation of $^1O_2$. Thermal decomposition of 9,10-diphenylanthracene endoperoxide requires drastic conditions such as prolonged refluxing (over 1 day) in benzene.[5b] In addition, alcoholic solvents cannot be used for 9,10-diphenylanthracene endoperoxide since they react with this endoperoxide.[5b] In contrast, the present polymeric endoperoxide **6b** can be used in a suspension in alcoholic solvents. We already noted that a water-soluble naphthalene endoperoxide can be effectively used as a $^1O_2$ source in aqueous solvents.[3] Thus, the polymer reagent would be usable as a suspension in aqueous solvents as well. The strong basic solution and stringent solvent requirement of the sodium hypochlorite–hydrogen peroxide[11a] and bromine–alkaline hydrogen peroxide[15] methods for $^1O_2$ generation are avoided. The special low-temperature techniques and accompanying solubility problems of the triphenyl phosphite–ozone method[16] are eliminated. Notable features of the present method using polymer reagents are as follows: (1) $^1O_2$ is generated under extremely mild neutral conditions; (2) oxidation is carried out under a variety of conditions such as in a solution, suspension, polymer film, and solid; (3) the polymers are easily removable and reusable. One major problem in using such polymeric endoperoxides for the purpose of synthetic oxygenation is the necessity of using a large excess (more than 3 equiv) of the polymer reagents for the completion of singlet oxygenation.

In conclusion, we have prepared a new type of polymeric $^1O_2$ generator. In particular, polymer **5b** has been demonstrated to bind and release $^1O_2$ reversibly at near room temperature. These polymeric endoperoxides will find important applications in a variety of systems which require pure singlet molecular oxygen.

Experimental Section

Melting points were determined on a Yanagimoto micro-melting-point apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a Varian T-60, HA-100, or JEOL JNM-GX 400 spectrometer employing Me$_4$Si as an internal standard. Mass spectra were obtained on a Hitachi RMS-4 or JEOL JMS-DX 300 spectrometer. UV spectra were recorded on a Shimadzu UV-200. Molecular weights were determined by gel

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permeation chromatography on a Toyasoda HLC 802UR. GLC analyses were performed on a Shimadzu GC-2C using a 6-ft column ($^1/_8$ in. round) packed with silicon DC 550. Silica gel chromatography was performed with Wako gel C-200. TLC was performed on Merck silica gel 60 F_{254}. Ether was distilled from LiAlH₄. Benzene was distilled from sodium metal. Dichloromethane was distilled from CaH₂. Spectrophotometric grade 1,2-dichloroethane was used without further purification.

Materials. 1,4-Dimethylnaphthalene (**1a**) was prepared by chloromethylation of 1-methylnaphthalene followed by reduction with Zn–AcOH.[17] 1,2,4-Trimethylnaphthalene (**1b**) was prepared by chloromethylation of 1,2-dimethylnaphthalene followed by reduction as described above. 1,2,3,4-Tetramethylnaphthalene (**1c**) was prepared according to the method described in the literature.[18] 2-Acetyl-5,8-dimethylnaphthalene (**2a**) and 2-acetyl-4,6,7,8-tetramethylnaphthalene (**2c**) were prepared by Friedel–Crafts acetylation.[8] 2-Ethyl-5,8-dimethylnaphthalene was prepared from **2a** by reduction with LiAlH₄–AlCl₃ in 79% yield. 2-Ethyl-5,6,8-trimethylnaphthalene was prepared from **2b** by reduction with LiAlH₄–AlCl₃ in 92% yield. 2,5-Di-*tert*-butylfuran (**15**) was prepared from 2,2′,7,7′-tetramethyloctanedione by the method of Ito et al.[19] 5-Methoxy-1,2,3-trimethylindole (**16**) was prepared according to the procedure described previously.[20] 2,3-Diphenyl-*p*-dioxene (**13**) was prepared by condensation of benzoin with ethylene glycol. 1,2-Dimethylcyclohexene (**9**) was prepared by dehydration of 1,2-dimethylcyclohexanol with iodine. Oxidation products **10**,[21] **11**,[21] **14**,[12] **17**,[22] **19**,[23] and **20**[23] were independently prepared by dye-sensitized photooxygenation as described in the literatures.

2-Acetyl-5,6,8-trimethylnaphthalene (2b). To a stirred solution of anhydrous AlCl₃ (16 g, 0.12 mol) and acetyl chloride (10 mL, 0.14 mol) in dichloroethane (100 mL) was added dropwise 1,2,4-trimethylnaphthalene (**1b**) (17 g, 0.1 mol) in dichloroethane (100 mL). The mixture was stirred overnight and poured into ice–water containing hydrochloric acid. The organic layer was separated and the water layer was extracted with chloroform. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated. The precipitate was recrystallized from ethyl acetate to yield 14.2 g of **2b** (66%): mp 96.5–97.5 °C; ¹H NMR (CDCl₃) δ 2.46 (s, 3 H), 2.57 (s, 3 H), 2.70 (s, 3 H), 2.73 (s, 3 H), 7.21 (bs, 1 H), 8.02 (dd, 1 H, *J* = 2, 9 Hz), 8.08 (d, 1 H, *J* = 9 Hz), 8.60 (d, 1 H, *J* = 2 Hz); MS, *m/e* 212 (M⁺). Anal. Calcd for C₁₅H₁₆O: C, 84.87; H, 7.60. Found: C, 84.62; H, 7.56.

2-(1-Hydroxyethyl)-5,8-dimethylnaphthalene (3a). To a stirred solution of 2-acetyl-5,8-dimethylnaphthalene (**2a**) (3.6 g, 18 mmol) in ether (100 mL) was added slowly a suspension of LiAlH₄ (520 mg, 13.5 mmol) in ether (50 mL) at room temperature. The mixture was stirred for 3 h and poured into an ice–water mixture. Hydrochloric acid was added to the contents until the white solid was dissolved. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated. The crude product was purified by washing with *n*-hexane to yield 3.4 g of **3a** (93 %): mp 69–71 °C; ¹H NMR (CDCl₃) δ 1.54 (d, 3 H, *J* = 6.5 Hz), 2.02 (bs, 1 H, OH), 2.40 (s, 3 H), 4.99 (q, 1 H, *J* = 6.5 Hz), 7.07 (s, 2 H), 7.36 (dd, 1 H, *J* = 2 Hz, 9 Hz), 7.78 (d, 1 H, *J* = 2 Hz), 7.83 (d, 1 H, *J* = 9 Hz). Anal. Calcd for C₁₄H₁₆O: C, 83.96; H, 8.05. Found: C, 84.19; H, 8.19.

2-(1-Hydroxyethyl)-5,6,8-trimethylnaphthalene (3b). A similar procedure as described for preparation of **3a** was carried out with **2b** (10.6 g, 50 mmol) and LiAlH₄ (1 g, 26 mmol). The crude product was purified by column chromatography on silica gel with benzene and successively dichloromethane as eluents to give 8.74 g of **3b** (82%): mp 63.5–65 °C; ¹H NMR (CDCl₃) δ 1.53 (d, 3 H, *J* = 6 Hz), 2.12 (bs, 1 H, OH), 2.39 (s, 3 H), 2.49 (s, 3 H), 2.58 (s, 3 H), 4.92 (q, 1 H, *J* = 6 Hz), 6.64 (bs, 1 H), 7.30 (dd, 1 H, *J* = 2 Hz, 9 Hz), 7.68 (d, 1 H, *J* = 2 Hz), 7.81 (d, 1 H, *J* = 9 Hz). Anal. Calcd for C₁₅H₁₈O: C, 84.07; H, 8.47. Found: C, 83.93; H, 8.45.

2-(1-Hydroxyethyl)-5,6,7,8-tetramethylnaphthalene (3c). A similar procedure as described for **3a** was carried out with **2c** (12 g, 53 mmol) and LiAlH₄ (1 g, 26 mmol). The crude product was purified by washing with cold ether to give 11.06 g of **3c** (91%): mp 118.5–120 °C; ¹H NMR (CDCl₃) δ 1.53 (d, 3 H, *J* = 7 Hz), 1.88 (bs, 1 H, OH), 2.37 (s, 6 H), 2.57 (s, 6 H), 4.99 (q, 1 H, *J* = 7 Hz), 7.29 (dd, 1 H, *J* = 9, 2 Hz), 7.83 (d, 1 H, *J* = 2 Hz), 7.88 (d, 1 H, *J* = 9 Hz). Anal. Calcd for C₁₆H₂₀O:

C, 84.16; H, 8.83. Found: C, 83.89; H, 8.79.

1,4-Dimethyl-6-vinylnaphthalene (4a). To a stirred solution of alcohol **3a** (3 g, 15 mmol) in dichloromethane (10 mL) was added SOCl₂ (2.2 mL, 30 mmol) at 0 °C. The reaction mixture was stirred for 3 h and excess SOCl₂ and the solvent were removed in vacuo. The residue was dissolved in dimethyl sulfoxide (30 mL). To the solution was added *t*-BuOK (2.53 g, 22.5 mmol) in small portions at ice–water bath temperature with stirring. The mixture was stirred for 3 h, poured into ice–water, and extracted three times with ether. The combined ether layers were washed three times with water and dried over Na₂SO₄; the solvent was evaporated. The residue was purified by column chromatography on silica gel with hexane as eluent to give 2.21 g of **4a** (81%) as white crystals: mp 48–49 °C; ¹H NMR (CDCl₃) δ 2.62 (s, 6 H), 5.31 (dd, 1 H, *J* = 11, 2 Hz), 5.83 (dd, 1 H, *J* = 17, 2 Hz), 6.93 (dd, 1 H, *J* = 11, 17 Hz), 7.13 (bs, 1 H), 7.63 (dd, 1 H, *J* = 9, 2 Hz), 7.88 (bs, 1 H), 7.96 (d, 1 H, *J* = 9 Hz). Exact MS. Calcd for C₁₄H₁₄: *m/e* 182.10948. Found: 182.11013.

1,2,4-Trimethyl-6-vinylnaphthalene (4b). The title compound **4b** was obtained in 85% yield from **3b** (7.5 g, 35 mmol) by a similar procedure as described for **4a**. **4b**: mp 40.5–41 °C; ¹H NMR (CDCl₃) δ 2.38 (s, 3 H), 2.47 (s, 3 H), 2.56 (s, 3 H), 5.24 (dd, 1 H, *J* = 11, 2 Hz), 5.78 (dd, 1 H, *J* = 18, 2 Hz), 6.89 (dd, 1 H, *J* = 18, 11 Hz), 7.03 (bs, 1 H), 7.51 (dd, 1 H, *J* = 9, 2 Hz), 7.78 (d, 1 H, *J* = 9 Hz), 7.89 (d, 1 H, *J* = 9 Hz); MS, *m/e* 196 (M⁺), 186 (M⁺ – CH₃), 165, 153.

1,2,3,4-Tetramethyl-6-vinylnaphthalene (4c). The title compound **4c** was obtained in 86% yield from **3c** (10 g, 44 mmol) by a similar procedure as described above: mp 47–47.5 °C; ¹H NMR (CDCl₃) δ 2.40 (s, 6 H), 2.58 (s, 6 H), 5.25 (dd, 1 H, *J* = 11, 2 Hz), 5.78 (dd, 1 H, *J* = 17, 2 Hz), 6.89 (dd, 1 H, *J* = 17, 11 Hz), 7.53 (dd, 1 H, *J* = 9, 2 Hz), 7.89 (bs, 1 H), 7.96 (d, 1 H, *J* = 9 Hz); MS, *m/e* 210 (M⁺). Anal. Calcd for C₁₆H₁₈: C, 91.37; H, 8.63. Found: C, 91.08; H, 8.59.

Poly(1,4-dimethyl-6-vinylnaphthalene) (5a). A solution of monomer **4a** (1.20 g, 6.6 mmol) in dry benzene (20 mL) containing AIBN (30 mg) was transfered into a glass tube and degassed with three freeze-thaw cycles. The tube was sealed in vacuo and allowed to stand at 70 °C for 12 h. The resulting mixture was cooled and poured into methanol (400 mL). The polymer precipitated was collected and purified by reprecipitation by adding benzene solution into methanol to give 1.06 g of **5a** (88%): MW 23 000; UV (1,2-dichloroethane) λmax 292 nm (ε 5070), 326 (720). Anal. Calcd for (C₁₄H₁₄)ₙ: C, 92.26; H, 7.74. Found: C, 92.24; H, 7.67.

Poly(1,2,4-trimethyl-6-vinylnaphthalene) (5b). The title compound **5b** was obtained in 92% yield from **4b** (5 g) by a similar procedure as described for **5a**: MW 19 000; UV (1,2-dichloroethane) λmax 286 nm (ε 4950), 314 (1810), 330 (1400). Anal. Calcd for (C₁₅H₁₆)ₙ: C, 91.37; H, 8.63. Found: C, 91.69; H, 8.19.

Poly(1,2,3,4-tetramethyl-6-vinylnaphthalene) (5c). The title compound **5c** was obtained in 74% yield from **4c** by a similar procedure: MW 21 000; UV (1,2-dichloroethane) λmax 295 nm (ε 4460), 330 (600). Anal. Calcd for (C₁₆H₁₈)ₙ: C, 91.37; H, 8.63. Found: C, 91.52; H, 8.73.

Photooxygenation of Polymers 5a, 5b, and 5c. The photooxygenation was carried out under circulation of oxygen in a closed system. The progress of the reaction was monitored by oxygen consumption by means of a gas buret. A solution of polymer (**5a**, **5b**, or **5c**, each 2 mmol) in dichloromethane (250 mL) containing methylene blue (5 × 10⁻⁶ M) was irradiated with a 650-W tungsten–bromine lamp at 0 °C under oxygen bubbling until oxygen uptake ceased. The completion of the photooxygenation took 10 h for **5a**, 3.5 h for **5b**, and 1.5 h for **5c**. The resulting mixture was concentrated to 10 mL under reduced pressure at 0 °C and poured into methanol (200 mL). The polymeric endoperoxides (**6a**, **6b**, or **6c**) which precipitated were collected and dried in vacuo. Nearly theoretical amounts of polymeric endoperoxides were obtained in each case. Before the use of these polymeric endoperoxides, the content of each endoperoxide unit in the whole polymer was determined by means of UV spectroscopy. Usually the contents was estimated to be nearly 90%. These polymeric endoperoxides (**6a,b,c**) were stored in the freezer (ca. 0 °C) for several months without any decomposition.

Determination of the Rates for Thermolyses of Endoperoxides 6a, 6b, 7, and 8. A solution of polyvinylnaphthalene **5a** or **5b** (4 × 10⁻³ M of a naphthalene unit) and methylene blue (5 × 10⁻⁶ M) in dichloroethane (20 mL) was irradiated with a tungsten–bromine lamp externally through 5% K₂Cr₂O₇ aqueous filter solution at 0 °C under oxygen bubbling. The resulting solution was diluted 50 times with dichloroethane and allowed to stand at given temperatures. The UV spectra were recorded at appropriate time intervals. The rates for the thermolyses of these endoperoxides were calculated according to the following equation:

$$\ln (A_0 - A_n) - \ln (A_0 - A_m)/t_n - t_m = k$$

where A_0 is the initial absorbance at 290 nm, whereas A_n and A_m are the absorbances at 290 nm at time t_n and t_m, respectively.

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Rates for the thermolysis of **6a**: $k = 6.99 \times 10^{-5}$ s^{-1} at 25.0 °C (correlation coefficient $r = 0.99992$) (for the values, t (min), $A_0 - A$): 0, 0.2709; 20, 0.2500; 40, 0.2301; 60, 0.2115; 80, 0.1943; 100, 0.1789; 120, 0.1636); $k = 1.45 \times 10^{-4}$ s^{-1} at 30.0 °C ($r = 0.99991$): 0, 0.2308; 15, 0.2026; 30, 0.1796; 45, 0.1579; 60, 0.1375; 75, 0.1208; 90, 0.1061; 105, 0.0928); $k = 2.88 \times 10^{-4}$ s^{-1} at 35.0 °C ($r = 0.99989$): 0, 0.2308; 10, 0.1943; 20, 0.1661; 30, 0.1384; 40, 0.1162; 50, 0.0976; 60, 0.0821).

Rates for the thermolysis of **6b**: $k = 2.76 \times 10^{-5}$ s^{-1} at 30.0 °C ($r = 0.9998$) (for the values, t (min), $A_0 - A$): 0, 0.3460; 30, 0.3271; 60, 0.3125; 90, 0.2968; 120, 0.2833; 150, 0.2699; 180, 0.2561; 210, 0.2436); $k = 5.68 \times 10^{-5}$ s^{-1} at 35.0 °C ($r = 0.9999$): 0, 0.3460; 20, 0.3226; 40, 0.3021; 60, 0.2827; 80, 0.2636; 100, 0.2448; 120, 0.2321; 140, 0.2150); $k = 1.10 \times 10^{-4}$ s^{-1} at 39.7 °C ($r = 0.9999$): 0, 0.2908; 15, 0.2659; 30, 0.2418; 45, 0.2189; 60, 0.1987; 75, 0.1796; 90, 0.1633).

Rates for the thermolysis of **7**: $k = 4.65 \times 10^{-5}$ s^{-1} at 25.0 °C ($r = 0.9997$); $k = 9.97 \times 10^{-5}$ at 30.0 °C ($r = 0.9988$); $k = 2.00 \times 10^{-4}$ s^{-1} at 35.0 °C ($r = 0.9995$).

Rates for the thermolysis of **8**: $k = 1.96 \times 10^{-5}$ s^{-1} at 30.0 °C ($r = 0.994$); $k = 4.06 \times 10^{-5}$ s^{-1} at 35.0 °C ($r = 0.9998$).

Oxygenation of 1,2-Dimethylcyclohexene (9) with Polymeric Endoperoxide (6b). A solution of **9** (11 mg, 0.089 mmol) and polymeric endoperoxide **6b** (peroxide content 94%) (108 mg, 0.445 mmol equiv of endoperoxide) in dichloromethane (1 mL) was allowed to stand at 40 °C for 5 h. Methanol (10 mL) was added to the mixture and the polymer precipitated was removed by filtration. The methanolic filtrate was treated with NaBH$_4$ (20 mg) and concentrated. The residue was treated with three drops of 15% H$_2$SO$_4$ and extracted with ether. The ether layer was dried over Na$_2$SO$_4$ and carefully evaporated. Analysis by GLC showed the production of **10** and **11** in a ratio of 94:6.

Oxygenation of 2,3-Diphenyl-*p*-dioxene (13) with Polymeric Endoperoxide (6b). A solution of **13** (15 mg, 0.063 mmol) and **6b** (peroxide content 92%) (47 mg, 0.189 mmol endoperoxide equiv) in dichloromethane (1 mL) was allowed to stand at 40 °C for 6 H. Methanol (10 mL) was added to the mixture and the polymer precipitated was removed by filtration. The filtrate was evaporated in vacuo. Analysis by ¹H NMR of the residue revealed the presence of **14** (96%). The reaction was conducted in a solution of **13** (0.063 mmol), **6b** (0.189 mmol equiv of endoperoxide), and Dabco (0.7 mg) under the same conditions. ¹H NMR spectrum of the residue showed the presence of **13** (80%) and **14** (20%).

The reaction was conducted in a solution of **13** (0.063 mmol), **6b** (0.189 mmolequiv of endoperoxide), and 2,6-di-*tert*-butylphenol (0.7 mg) under the same conditions. ¹H NMR of the residue showed that 81% of **13** was oxygenated to **14**.

Trapping of Singlet Oxygen by 2,5-Di-*tert*-butylfuran (15). A sealed tube containing a solution of **6b** (0.072 mmol equiv endoperoxide) and **15** (0.15 mmol) in dichloromethane (5 mL) was prepared. The sample tube was allowed to stand at 35 °C for 8 h. After evaporation at 0 °C, the residue was treated with CD$_3$OD. Precipitated polymer was separated by filtration. The filtrate was directly analyzed by ¹H NMR and the amount of consumed **15** was calculated by disappearance of the *tert*-butyl signal of **15**. After being washed with methanol and dried in vacuo, the polymer was analyzed by UV spectroscopy to reveal the amount of naphthalene unit regenerated in the reaction. The amount of consumed **6b** was also calculated from the data obtained in the decomposition rate of **6b**. The yield of ¹O$_2$ per naphthalene unit regenerated in the polymer **6b** was calculated to be 66 ± 5%.

Oxygenation of 5-Methoxy-1,2,3-trimethylindole (16) with 6b in Solution. A solution of **16** (20 mg, 0.1 mmol equiv of endoperoxide) in dichloromethane (1 mL) was allowed to stand at 40 °C for 6 h. Methanol (10 mL) was added to the mixture, and the polymer precipitated was removed by filtration. The filtrate was evaporated in vacuo and analyzed by ¹H NMR, showing the formation of **17** (29%) together with recovery of **16** (71%).

Oxygenation of Citronellol (18) with 6b in Solution. A solution of **18** (31 mg, 0.2 mmol) and **6b** (1 mmol equiv of endoperoxide) in dichloromethane (1 mL) was allowed to stand at 35 °C for 15 h. After similar workup, ¹H NMR of the residue revealed the formation of a mixture of hydroperoxides **19** and **20** in a ratio of 5:4 in ~50% yield together with unreacted **18** (50%).

Oxygenation of 13 with 6b in a Film. A solution of **13** (30 mg, 0.126 mmol) and **6b** (0.38 mmol equiv of endoperoxide) in dichloromethane (2 mL) was rotary-evaporated under reduced pressure at 0 °C. The resulting film was allowed to warm to 40 °C for 6 h and dissolved in dichloromethane. After removal of the polymer by usual workup, the residue was analyzed by ¹H NMR to reveal the formation of **14** (77%).

Oxygenation of 16 with 6b in a Film. A film consisting of **16** (0.1 mmol) and **6b** (0.5 mmol equiv of endoperoxide) prepared as described above was allowed to warm to 40 °C for 6 h. After removal of the polymer in a usual manner, the residue was analyzed by ¹H NMR, showing the production of **17** (16%).

Oxygenation of 18 with 6b in a Film. A film consisting of **18** (0.2 mmol) and **6b** (1 mmol equiv of endoperoxide) was allowed to warm to 35 °C for 15 h. After the usual workup, ¹H NMR of the mixture revealed the production of **19** and **20** in a ratio 5:4 in 47% yield.

Oxygenation of 13 with 6b in a Suspension. To a solution of **13** (30 mg, 0.126 mmol) in methanol (2 mL) was added **6b** (0.38 mmol equiv of endoperoxide). The resulting suspension was stirred for 6 h at 40 °C; the polymer was removed by filtration. The filtrate was concentrated and the residue was analyzed by ¹H NMR, showing the formation of **14** (36%) together with **13** (64%).