Oxidation of Polymeric Terminal Diols with Iron(III) or Copper(II) Salts Mediated by the Nitroxyl Radical

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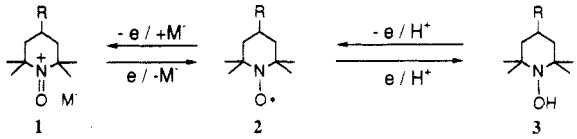
ABSTRACT: 4-Substituted-2,2,6,6-tetramethylpiperidine-1-oxyl (2) is a stable radical mediating a reversible redox reaction between oxoaminium salt (1) and hydroxylamine (3). The oxidation of polymeric terminal diols with Fe(III) or Cu(II) salts mediated by 2 was carried out to obtain the corresponding polymers containing carbonyl moieties. When 4 equiv of $Cu(NO_3)_2$, 1 equiv of $Cu(OH)_2$ as an acid-trapping agent, and 0.2 equiv of 2 (4-methoxy derivative) were used, a hydrogenated polybutadiene terminal diol (4) was efficiently and selectively oxidized to the corresponding polymer with aldehyde or ketone groups in both termini without any intermolecular reaction. Furthermore, 2 supported on cross-linked polystyrene beads catalyzed efficiently the oxidation of 4.

Introduction

Electron transfer catalysts dominate energy metabolism in animals and plants. NAD^+ (nicotinamide adenine dinucleotide), which is well-known as an electron transfer catalyst, is converted to NADH on accepting a proton and two electrons. This compound is an excellent model of electron transfer catalysts due to its high catalytic efficiency. In our research, the construction of redox systems of nicotinamides,[1] alloxan,[2] lipoic acids,[3,4] and viologens[4,5] and reduction of organic compounds mediated by them have been developed.

Hindered nitroxyl radical (e.g. 2,2,6,6-tetramethylpiperidine-1-oxyl, 2, R = H) is a well-known stable radical and forms the following reversible system:[6]



Selective oxidation of alcohols mediated by 2 in the indirect electrode oxidation has been described by Semmelhack and co-workers,[7] and redox systems of 2 combined with copper(I) and oxygen[8] have been reported. Oxidation of alcohols with chlorine gas catalyzed by 2[9] and the selective oxidation of benzyl alcohol to benzaldehyde with iron(III)[10] or copper(II)[11] mediated by 2 have also been reported.

Some polymeric terminal diols can be selectively and efficiently oxidized by 1-oxo-4-methoxy-2,2,6,6-tetramethylpiperidinium chloride (1), R = OMe, M = Cl) to corresponding polymeric terminal dialdehydes or ketones,[12] and hydrogenated polybutadiene terminal diol was oxidized by 1 in good yield to the corresponding polymer containing carbonyl groups in both termini.[13] This paper describes the oxidation of polymeric terminal diols by iron(III) or copper(II) salts mediated by 4-methoxy- and polymeric 2,2,6,6-tetramethylpiperidine-1-oxyls.

Experimental Section

Measurements. The infrared spectra (IR (neat and KBr)) were recorded with a JASCO FT/IR-Fourier transform infrared spectrometer. Gel permeation chromatography (GPC) was performed with a TOYO SODA CCP&8000 with a data processing system (columns, TSK gel, G $2000H_{XL}$, G $2500H_{XL}$, and G $3000H_{XL}$, eluent, THF; calibration, polystyrene standard).

Materials. 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (2) was prepared by the previously reported method.[14] Hydrogenated polybutadiene terminal diol (4, OH value = 0.877 mequiv/g) was obtained from Mitsubishi Kasei Co., Ltd., and used without further purification. Poly(tetrahydrofuran) terminal diol (OH value = 0.677 mequiv/g), polybutadiene terminal diol (OH value = 0.969 mequiv/g), and polybutylene adipate terminal diol (OH value = 0.988 meq/g) were obtained from Hodogaya Co., Ltd., Japan Synthetic Rubber Co., Ltd., and Japan Polyurethane Co., Ltd., respectively.

Typical Method of Oxidation. To a solution of 4 (1 g, OH group 0.877 mmol, $\overline{M}_n$ [$\overline{M}_w/\overline{M}_n$] = 3600 [1.4]) in 25 mL of dichloromethane were added copper(II) nitrate (trihydrate, 848 mg, 3.5 mmol), copper(II) oxide (86 mg, 0.88 mmol), and 33 mg (0.177 mmol) of 2 (R = OMe), and the mixture was kept at room temperature for 14 h. The resulting mixture was filtered to remove the copper salts, and extracted 3 times with 200 mL of ether and 100 mL of water. The ether layer was dried over anhydrous magnesium sulfate and evaporated to obtain the product (0.88 g, 88% in yield): IR (neat) 1725, 1461, 1380, 1110, 1100 cm^{-1}; $\overline{M}_n$ [$\overline{M}_w/\overline{M}_n$] 3800 [1.4].

1-Oxo-4-methoxy-2,2,6,6-tetramethylpiperidinium Nitrate (Oxoaminium Nitrate, 5). To a solution of 500 mg (2.69 mmol) of 2 (R = OMe) in 40 mL of dry ether, 2 mL of 61% nitric acid was added, and the solution was stirred at room temperature for 15 min. The yellow precipitate was filtrated, washed several times with ether, and dried in vacuo to obtain 1-oxo-4-methoxy-2,2,6,6-tetramethylpiperidinium nitrate (630 mg, 94% in yield): mp 148.5–149.0 °C (dec); IR (KBr) 1626, 1356, 1390 cm^{-1}. Anal. Calcd for $C_{10}H_{20}N_2O_5$: H, 8.12; C, 48.37; N, 11.28. Found: H, 8.11; C, 48.32; N, 11.26.

Oxidation of 4 with Oxoaminium Nitrate (5). To a solution of 4 (250 mg, OH group 0.219 mmol, $\overline{M}_n$ [$\overline{M}_w/\overline{M}_n$] = 3800 [1.5]) in 6 mL of dichloromethane was added 109 mg (0.439 mmol) of 5, and the solution was kept at room temperature for 2 h in the dark. The reaction mixture was evaporated under reduced pressure to remove dichloromethane and was extracted 3 times with 50 mL of ether and 25 mL of water. The ether layer was dried over anhydrous magnesium sulfate, filtered, evaporated, and dried in vacuo to obtain the product (235.3 mg, 94% in yield): IR (neat) 2961, 2923, 1711, 1461, 1379 cm^{-1}; $\overline{M}_n$ [$\overline{M}_w/\overline{M}_n$] 3300 [1.5].

Polymeric Nitroxyl Radical (P-1). To a stirred solution of 6.00 g (34.88 mmol) of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl in 120 mL of anhydrous DMF was added 843 mg (35.12 mmol) of NaH. After stirring this suspension under N_2, 4.09 g (23.25 mmol) of cross-linked poly[styrene-*co*-*p*-(chloromethyl)-styrene] beads (styrene: *p*-(chloromethyl)styrene = 18:82) was added. After the mixture was stirred for 4 days at room

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Table I
Oxidation of Hydrogenated Polybutadiene Terminal Diol with Iron(III) Salts Mediated by Nitroxyl Radical 2[a]

oxidant	yield, %	conv,[b] %	turnover	$\bar{M}_n$ [$\bar{M}_w/\bar{M}_n$][c] before	after
$K_3Fe(CN)_6$	95	26	1	3600 [1.4]	3700 [1.4]
$Fe_2(SO_4)_3$[d]	100	26	1	4000 [1.4]	4100 [1.4]
$FeCl_3$	88	28	1	4000 [1.4]	4000 [1.7]
$Fe(NO_3)_3$[e]	95	100[f]	g	3600 [1.4]	5200 [2.3]

[a] Solvent, dichloromethane; catalyst, 0.2 equiv; $Fe(OH)_3$, 1 equiv; room temperature. [b] Conversion of hydroxyl to carbonyl group in the obtained polymer was estimated by IR. [c] Estimated by GPC based on PSt standards. [d] Hydrate. [e] Nonahydrate. [f] No OH absorption was observed in IR spectrum. [g] Not calculated.

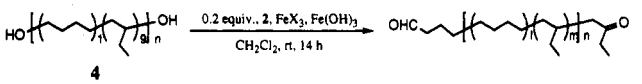
temperature, the suspension was filtered. The residue was washed with methanol, DMF, and water and dried in vacuo to give the red product (P-1), 4.88 g: IR (KBr) 2975, 2931, 1698, 1454, 1378, 1242, 1218, 1177, 1079, 1018, 856 cm^{-1}. Anal. Found: H, 8.48; C, 74.06; N, 3.78; Cl, 3.50.

Polymeric Nitroxyl Radical (P-2). To a stirred solution of 2.00 g (11.63 mmol) of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl in 50 mL of anhydrous tetrahydrofuran was added 280 mg (11.67 mmol) of NaH. The suspension was stirred under N_2, and 2.04 g (11.62 mmol) of poly[styrene-*co*-*p*-(chloromethyl)styrene] beads (styrene: *p*-(chloromethyl)styrene = 18:82) was added. The reaction mixture was stirred at 50 °C for 2 days. The beads were filtered off, washed with methanol, tetrahydrofuran, and water, and dried in vacuo at 100 °C for several hours to yield the red product (P-2), 2.12 g: IR (KBr) 2906, 1510, 1446, 1421, 1362, 1265, 1081 cm^{-1}. Anal. Found: H, 6.07; C, 73.02; N, 0.91; Cl, 17.75.

Estimation of Conversion of OH Group. The conversion of the OH group by oxidation was estimated from the ratio of the amount of the produced carbonyl group to that of the original hydroxyl group of polymeric terminal diol using a calibration curve. The calibration curve was obtained by plotting intensity ratio of OH absorption of anise alcohol to C=O absorption of benzaldehyde vs molar ratio of them.

Results and Discussion

Oxidation of Hydrogenated Polymeric Terminal Diols with Iron(III) or Copper(II) Salts Mediated by Monomeric Nitroxyl Radical. Oxidation of hydrogenated polybutadiene terminal diol (4, $\bar{M}_n$ = 2280 based on hydroxyl content) with iron(III) and copper(II) salts was carried out in the presence of 0.2 equiv of nitroxyl radical 2 in dichloromethane under heterogeneous condition. Fe-



4

$(OH)_3$ or $Cu(OH)_2$ (1.0 equiv) was added as an acid scavenger to the reaction mixture. Some iron(III) salts (4 equiv to OH) were used in the presence of 2 (R = OMe, 0.2 equiv to OH) in dichloromethane. The reactions were carried out at room temperature for 14 h. Results are listed in Table I. Although $K_3Fe(CN)_6$, $Fe_2(SO_4)_3$, or $FeCl_3$ could oxidize 4 to some degree, $Fe(NO_3)_3$ oxidized 4 efficiently (isolated yield, 95%; conversion of OH group of the isolated product, 100%). However, both the number-average molecular weight ($\bar{M}_n$) and the molecular weight distribution ($\bar{M}_w/\bar{M}_n$) increased after the oxidation, and a bimodal GPC curve was observed, being indicative of the formation of higher molecular weight polymer by an intermolecular reaction, probably acetalization. Therefore, Cu(II) salts with a redox potential lower than that of Fe(III)[15] were used as oxidants. The results are shown in Table II. $Cu(ClO_4)_2$, $CuCl_2$, or $CuBr_2$ oxidized

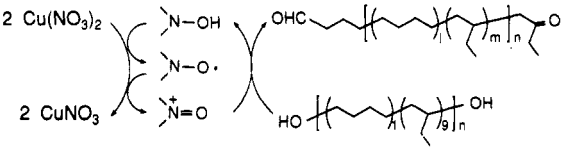
Table II
Oxidation of Hydrogenated Polybutadiene Terminal Diol with Copper(II) Salts Mediated by 2[a]

oxidant	yield, %	conv,[b] %	turnover	$\bar{M}_n$ [$\bar{M}_w/\bar{M}_n$][c] before	after
$Cu(OH)_2$	90	0	0	3200 [1.5]	3600 [1.4]
$Cu(OAc)_2$	97	0	0	3200 [1.5]	3600 [1.4]
$CuSO_4$[d]	95	0	0	3200 [1.5]	3600 [1.4]
$Cu(ClO_4)_2$[e]	88	29	1	3600 [1.4]	3600 [1.4]
$CuCl_2$	93	27	1	3600 [1.4]	3800 [1.4]
$CuBr_2$	94	33	1.5	3600 [1.4]	4300 [1.9]
$Cu(NO_3)_2$[f]	88	100[g]	5	3600 [1.4]	3800 [1.4]

[a] Solvent, dichloromethane; oxidant, 4 equiv; catalyst, 0.2 equiv; $Cu(OH)_2$, 1.0 equiv; room temperature. [b] Conversion by hydroxy to carbonyl group in the obtained polymer was estimated by IR. [c] Estimated by GPC based on PSt standards. [d] Pentahydrate. [e] Hexahydrate. [f] Trihydrate. [g] No OH absorption was observed in IR spectrum.

4 to some degree, although no oxidation proceeded at all with oxidants such as $Cu(OH)_2$, $Cu(OAc)_2$, or $Cu(SO_4)_2$. $Cu(NO_3)_2$ was particularly efficient in oxidizing 4 (isolated yield, 88%; conversion of OH of the isolated product, 100%). In this oxidation $\bar{M}_n$ [$\bar{M}_w/\bar{M}_n$]s before and after the oxidation were 3600 [1.4] and 3800 [1.4], respectively, suggesting little change in the polymer chain length. In this oxidation, oxoaminium nitrate would oxidize the hydroxyl groups of 4. Then, 1-oxo-4-methoxy-2,2,6,6-tetramethylpiperidinium nitrate (oxoaminium nitrate, 5), which is thought to be the intermediary actual oxidant for the hydroxy groups, was prepared and used for the oxidation of 4 ($\bar{M}_n$ [$\bar{M}_w/\bar{M}_n$] = 3800 [1.5]). Actually, 5 efficiently oxidized 4 to the corresponding terminal dialdehyde or ketone (94% in yield; 100% conversion; $\bar{M}_n$ [$\bar{M}_w/\bar{M}_n$] = 3300 [1.5]), indicating that the actual oxidant of the OH group is the oxoaminium nitrate when $Cu(NO_3)_2$ is used as the oxidant. This probably suggests that in the oxidations with other copper salts intermediary actual oxidant and copper(I) species formed from copper(II) salt is unstable to oxidize OH groups[16-20] and that the bond between the corresponding hydroxyl amine and the generated acid may be so tight that $Cu(OH)_2$ cannot trap the acid.

As described above, when $Cu(NO_3)_2$ was used as an oxidant, the oxidation of 4 proceeded most efficiently. Therefore, the oxidation with $Cu(NO_3)_2$ was studied in detail. The results are shown in Table III. No oxidation took place without 2, indicating that $Cu(NO_3)_2$ cannot directly oxidize 4. The following catalytic cycle may be suggested:



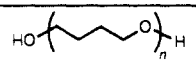
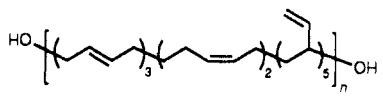
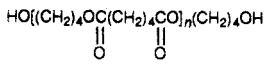
In the absence of the acid trapping agent $Cu(OH)_2$, 96% yield and 100% conversion of hydroxyl groups were achieved, but $\bar{M}_n$ considerably increased after the oxidation. The polymer produced showed a bimodal GPC curve. These results seem to indicate intermolecular reactions, e.g. acetalization between the produced carbonyl compound and the starting alcohol (4) catalyzed by the generated HNO_3. In contrast, 80% yield and 73% conversion of OH groups were achieved without a change of $\bar{M}_n$ in the presence of $Cu(OH)_2$. When anhydrous magnesium sulfate was added to remove water formed in

Table III
Oxidation of Hydrogenated Polybutadiene Terminal Diol with $Cu(NO_3)_2$ Mediated by 2[a]

expt no.	$Cu(NO_3)_2$,[b] equiv	acid-trapping agent (equiv)	time, h	yield, %	conv,[c] %	turnover	$\bar{M}_n$ [$\bar{M}_w/\bar{M}_n$][d] before	$\bar{M}_n$ [$\bar{M}_w/\bar{M}_n$][d] after
1[e]	4	$Cu(OH)_2$ (1)	14	90	0	0	3200 [1.5]	3600 [1.4]
2	4		145	96	100[f]	[g]	3300 [1.3]	10600 [1.0], 4800 [1.1]
3	4	$Cu(OH)_2$ (1)	65	80	73	8	3300 [1.3]	3800 [1.7]
4[h]	4	$Cu(OH)_2$ (1)	7	92	100[f]	[g]	3300 [1.5]	5100 [2.2]
5[h]	2	$Cu(OH)_2$ (1)	7	97	80	[g]	3300 [1.5]	19200 [2.4], 3200 [1.4]
6	8	$Cu(OH)_2$ (1)	14	91	100[f]	10	3600 [1.4]	4000 [1.5]
7	4	$Cu(OH)_2$ (2)	14	93	100[f]	10	3600 [1.4]	4000 [1.5]

[a] Solvent, dichloromethane; catalyst, 0.1 equiv; room temperature. [b] Trihydrate. [c] Conversion of hydroxy to carbonyl group in the obtained polymer was estimated by IR. [d] Estimated by GPC based on PSt standards. [e] No catalyst. [f] No OH absorption was observed in IR spectrum. [g] Not calculated. [h] $MgSO_4$ (2 equiv to water) was added.

Table IV
Oxidation of Polymeric Terminal Diols with $Cu(NO_3)_2$ Mediated by 2[a]

polymer	yield, %	conv,[b] %	turnover	$\bar{M}_n$ [$\bar{M}_w/\bar{M}_n$][c] before	$\bar{M}_n$ [$\bar{M}_w/\bar{M}_n$][c] after
	90	84	4	9400 [1.7]	8400 [1.7]
	95	65	3	4500 [1.6]	6800 [2.0]
	96	23	1	4900 [1.9]	6400 [2.0]

[a] Solvent, dichloromethane; catalyst, 0.2 equiv; $Cu(NO_3)_2$, 4 equiv; $Cu(OH)_2$, 1 equiv; room temperature; 14 h. [b] Conversion of hydroxyl to carbonyl group in the obtained polymer was estimated by IR. [c] Estimated by GPC based on PSt standards.

Table V
Synthesis of Polymeric Nitroxyl Radical

solvent	TEMPO, equiv	NaH, equiv	temp	time, day	product x,[a] %	product y,[a] %	product form	product em[b]	catalyst
DMF	1.5	1.5	rt	4	21	61	powder	370.68	**P-1**
THF	1.0	1.0	50 °C	2	72	10	beads	1545.10	**P-2**

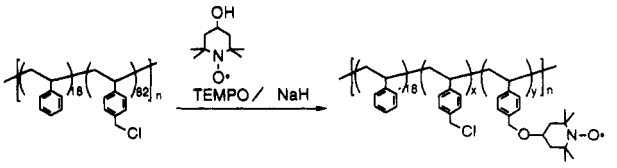
[a] Determined by elemental analysis. [b] Exchange mass.

the oxidation, the oxidized polymer was obtained in 92% yield with 100% OH conversion, but $\bar{M}_n$ slightly increased after the oxidation. When the amount of the oxidant was decreased to 2 equiv, $\bar{M}_n$ increased sharply after the oxidation and a bimodal GPC curve was observed. This is indicative of the formation of higher molecular weight polymer probably by some intermolecular reaction similar to that observed in the oxidation without $Cu(OH)_2$. These results suggest that some side reaction (e.g., acetalization) may compete with the oxidation. In order to enhance the oxidation rate, a larger amount of oxidant or the acid-trapping agent was used. In both cases 100% OH conversion was attained and $\bar{M}_n$ was not changed after the oxidation.

As shown above, these heterogeneous oxidations (2 and 4 were soluble but copper salts were insoluble) proceeded efficiently. Another heterogeneous system (2 and copper salts were soluble and 4 was insoluble) was examined; the oxidation of 4 was carried out with 0.1 equiv of 2 and 4 equiv of $Cu(NO_3)_2$ in a mixed solvent (CH_2Cl_2:*N*-methylpyrrolidone = 25:10 (v/v)) at room temperature for 35 h to recover 4 in 95% yield. It is suggested that the polymer chain may shield the hydroxyl groups from the oxidation.

Application of this catalytic system to the oxidation of other polymeric terminal diols was also examined. The oxidation of several polymers containing ether, ester, and olefin groups in their backbones was carried out with 0.2 equiv of 2, 4 equiv of $Cu(NO_3)_2$, and 1 equiv of $Cu(OH)_2$, in dichloromethane at room temperature for 14 h. The results are summarized in Table IV. In any case, the conversion of the hydroxy groups did not reach 100%. Now efficiency in the oxidation of these polymers may be explained by assuming the complexation of Cu(II) salt with the polymers which inhibits the oxidation of nitroxyl radicals to the oxoaminium salt.

Oxidation of Hydrogenated Polybutadiene Terminal Diols with $Cu(NO_3)_2$ Mediated by Polymeric Nitroxyl Radical. Copolymer beads of *p*-(chloromethyl)-styrene and styrene (=82:18 calculated by elemental analysis) cross-linked with divinylbenzene were used as base polymer for polymeric nitroxyl radical. Reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) with the cross-linked polymer beads was carried out in the presence of sodium hydride in *N*,*N*-dimethylformamide or tetrahydrofuran. Two types of polymeric nitroxyl radicals, **P-1** (x:y = 21:61) and **P-2** (x:y = 72:10) were prepared. Contents of nitroxyl radical groups in the



polymers are listed in Table V. The oxidation of 4 with $Cu(NO_3)_2$ and $Cu(OH)_2$ was carried out in the presence of **P-1** or **P-2** (0.2 equiv) in dichloromethane at room temperature for 24 h. Results are shown in Table VI. The

Table VI
Oxidation of Hydrogenated Polybutadiene Terminal Diol with $Cu(NO_3)_2$ Mediated by Polymeric Nitroxyl Radical[a]

catalyst	$Cu(NO_3)_2$,[b] equiv	yield, %	conv,[c] %	$\bar{M}_n$ [$\bar{M}_w/\bar{M}_n$][d] before	after
P-1	4	90	87	3600 [1.4]	5900 [2.2]
P-1	8	98	100[e]	3800 [1.4]	4100 [1.7]
P-1	4 (grained)	91	92	4500 [1.4]	4600 [1.6]
P-2	8	89	100[e]	3700 [1.4]	4100 [1.5]
P-2	4 (grained)	90	100[e]	3700 [1.4]	4300 [1.5]

[a] Solvent, dichloromethane; catalyst, 0.2 equiv; $Cu(OH)_2$, 1 equiv; room temperature and 24 h. [b] Trihydrate. [c] Conversion of hydroxyl to carbonyl group in the obtained polymer was estimated by IR. [d] Estimated by GPC based on PSt standars. [e] No OH absorption was observed in IR spectrum.

oxidation with 4 equiv of $Cu(NO_3)_2$ in the presence of **P-1** caused an increase in $\bar{M}_n$, although an absorption of C=O was observed in IR spectrum of the obtained polymer. When the amount of $Cu(NO_3)_2$ was increased to 8 equiv, 98% yield and 100% conversion of OH groups was achieved without change of $\bar{M}_n$. When $Cu(NO_3)_2$ was powdered to increase its surface area, $\bar{M}_n$ was not changed before and after the oxidation. Although the conversion did not reach 100%, the reaction was accelerated, indicating the reaction at surface of $Cu(NO_3)_2$. In contrast, when **P-2** was used instead of **P-1**, both oxidations with 8 equiv of $Cu(NO_3)_2$ and 4 equiv of powdered $Cu(NO_3)_2$, were also completed without any change of $\bar{M}_n$. This may suggest that only nitroxyl radicals supported on the surface of the polymer beads catalyze efficiently the oxidation of **4**.

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Registry No. **2**, 95407-69-5; **5**, 144375-62-2; $K_3Fe(CN)_6$, 13746-66-2; $Fe_2(SO_4)_3$, 10028-22-5; $FeCl_3$, 7705-08-0; $Fe(NO_3)_3$, 10421-48-4; $Cu(ClO_4)_2$, 13770-18-8; $CuCl_2$, 7447-39-4; $CuBr_2$, 11129-27-4; $Cu(NO_3)_2$, 3251-23-8; $Cu(OH)_2$, 20427-59-2; THF (homopolymer), 24979-97-3; THF (SRU), 25190-06-1; polybutylene adipate (copolymer), 25103-87-1; polybutylene adipate (SRU), 24936-97-8; 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, 2226-96-2; poly[styrene-*co*-*p*-(chloromethyl)styrene] (copolymer), 29464-22-0.