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### OXIDATIVE POLYMERIZATION OF 2,6-DISUBSTITUTED PHENOLS CATALYZED BY IRON-SALEN COMPLEX

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## OXIDATIVE POLYMERIZATION OF 2,6-DISUBSTITUTED PHENOLS CATALYZED BY IRON-SALEN COMPLEX

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### ABSTRACT

Oxidative polymerization of 2,6-disubstituted phenols has been performed by using iron(III)-salen complex and hydrogen peroxide as catalyst and oxidizing agent, respectively. The oxidative reaction of 2,6-dimethylphenol produced the polymer along with a byproduct dimer of 3,5,3',5'-tetramethyl-4,4'-diphenyl-quinone. The addition of pyridine suppressed the formation of the dimer to mainly give the polymer with molecular weight of more than  $1 \times 10^4$  in high yields. From NMR analysis, the polymer was found to consist of exclusively 1,4-oxyphenylene unit. Effects of the solvent composition, added amount and type of amine, and catalyst amount have been systematically investigated. 2-Allyl-

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6-methylphenol and 2,6-diphenylphenol produced the corresponding polymer under the similar polymerization conditions, whereas the formation of C-C coupling dimer was observed in using 2,6-diisopropylphenol and 2,6-dimethoxyphenol as monomer.

## INTRODUCTION

Oxidative polymerizations have afforded various functional polymers. Typical examples are polyaniline, polypyrrole, and polythiophene showing high conductivity [1-3]. These polymers are synthesized by electrolysis or chemical oxidation processes. Another example is poly(1,4-oxyphenylene) (poly(phenylene oxide), PPO), which was first synthesized from 2,6-dimethylphenol by using a copper/amine catalyst [4, 5]. PPO is widely used as high-performance engineering plastics in industrial fields, since the polymer has excellent chemical and physical properties, e.g., a high glass transition temperature (ca. 210°C) and mechanically tough property [6].

For the last decade, enzymatic syntheses of polyaromatics have been extensively developed [7-11]. Oxidative polymerization of phenol derivatives catalyzed by peroxidase produced a new class of polyphenols showing high thermal stability [12-18], in which hydrogen peroxide is used as an oxidizing agent. The enzymatic process is expected to be an alternative way for preparation of phenol polymers without use of toxic formaldehyde, which is a monomer for production of conventional phenolic resins (phenol-formaldehyde resins). Very recently, we have found that model complexes of tyrosinase induced the regioselective polymerization of 4-phenoxyphenol to give crystalline unsubstituted PPO [19].

Complexes of a metal with N,N'-ethylenebis(salicylideneamine) (salen) or its derivatives have been extensively studied as oxidation catalyst. In particular, Mn(III) and Co(II)-salens showed excellent catalytic ability toward enantioselective epoxidation of olefins and versatile synthesis of alkoxyamines [20-23]. Immobilization of these complexes onto the synthetic polymers was performed to develop a polymeric catalyst for the highly selective reactions [24, 25].

In most oxidative polymerizations of phenol derivatives, except those using peroxidase catalyst, oxygen molecules and metal oxides were used as an oxidizing agent; so far, there were few reports [26] on the oxidative polymerization using hydrogen peroxide. This study deals with the oxidative polymerization

of 2,6-disubstituted phenol derivatives (**1**) catalyzed by Fe(III)-salen complex (**2**) using hydrogen peroxide as oxidizing agent (Scheme 1). To our knowledge, this is the first example that a metal-salen complex showed high catalytic activity toward the oxidative polymerizations.

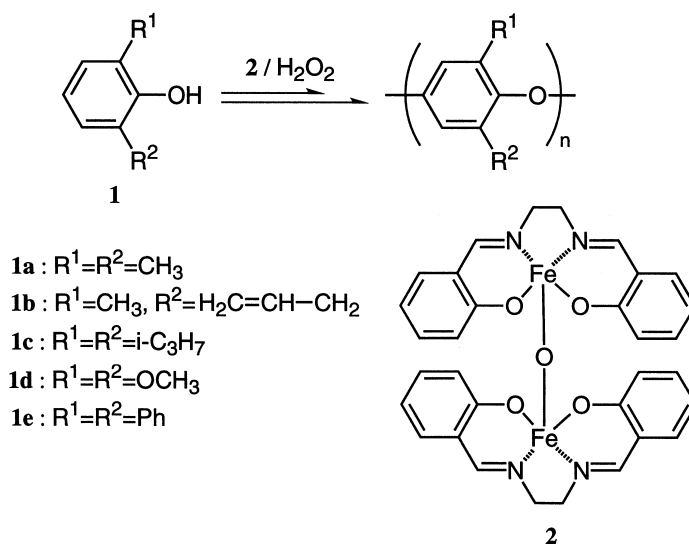
## EXPERIMENTAL

### Materials

Fe-salen complex (**2**) was synthesized according to the literature [27]. Other reagents and solvents were commercially available and used as received.

### Oxidative Polymerization of 2,6-Disubstituted Phenols

A typical run was as follows (entry 4 in Table 1). 2,6-Dimethylphenol (0.61 g, 5.0 mmol), **2** (3.3 mg, 5.0  $\mu$ mol) and pyridine (0.10 mL) in 10 mL of 1,4-dioxane were placed in a 50 mL of flask. 5% Hydrogen peroxide (3.4 mL, 5.0 mmol) was added dropwise for 1 hour at room temperature. The mixture was stirred under air. After 3 hours, the reaction mixture was poured into a large amount of methanol. The precipitates were separated by centrifugation and washed with methanol, following by drying *in vacuo* to give the polymer (0.56 g, 91% yield).



Scheme 1.

## Measurements

Size exclusion chromatographic (SEC) analysis was carried out using a Tosoh SC8010 apparatus with a refractive index (RI) detector under the following conditions: TSKgel G3000H<sub>HR</sub> column and tetrahydrofuran (THF) eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained using polystyrene standards. NMR spectra were recorded on a 270 MHz JEOL JNM-EX270J or a 400MHz Bruker DPX-400 spectrometer. IR spectra were recorded on a Horiba FT720 spectrometer. DSC measurement was made at a 10°C/min heating rate under nitrogen using a Seiko SSC/5200 differential scanning calorimeter calibrated with an indium reference standard. TG analysis was performed using a Seiko SSC/5200 apparatus for thermogravimetry/differential thermal analysis at a heating rate of 10°C/min in a gas flow rate of 300 mL/min.

## RESULTS AND DISCUSSION

### Oxidative Polymerization of 2,6-Dimethylphenol Catalyzed by Fe(III)-Salen Complex

The oxidative polymerization of 2,6-dimethylphenol (**1a**) was performed by using Fe(III)-salen (**2**) and hydrogen peroxide as catalyst and oxidizing agent, respectively, at room temperature under air. As a polymerization solvent, 1,4-dioxane was used since it shows high solubility toward PPO and is miscible with a aqueous hydrogen peroxide solution. Hydrogen peroxide was added dropwise to the reaction mixture for 1 hour. By the addition of hydrogen peroxide, the reaction solution turned dark-red, afterwards the precipitates were formed. After 3 hours, the products were isolated by pouring the reaction mixture into a large amount of methanol (yield 78%). In the chart of size exclusion chromatography (SEC), two peaks were observed and their peak areas were almost the same. The number-average molecular weight and its index of the peak in lower elution volume were  $1.6 \times 10^4$  and 1.5, respectively. <sup>1</sup>H NMR chart of the product shows two singlet peaks at  $\delta$  6.6 and 7.7 in the aromatic region, which were attributed to methyl protons of poly(2,6-dimethyl-1,4-oxyphenylene) and a dimer of **1a**, 3,5,3',5'-tetramethyl-4,4'-diphenoquinone (DPQ), respectively [28]. The ratio of integrated areas of these peaks was 52:48, which was very close to that determined by SEC. Thus, the peak of higher elution volume in the SEC chart was ascribed to DPQ. The DPQ formation is explained by the para-para coupling of radical species from **1a**.

In the oxidative polymerization of **1a** using a copper catalyst, the addition of amine suppressed the DPQ formation, yielding PPO [29, 30]. Here, the polymerization of **1a** by using **2** as catalyst was performed in the presence of pyridine with a different amount (Table 1). A small amount of pyridine was effective for the suppression of the DPQ formation (entry 2). As the added amount of pyridine, the content of the polymer in the methanol-insoluble part increased. DPQ was not formed in using 1.0 mL of pyridine (entry 5). These results indicate that the addition of pyridine effectively suppressed the DPQ formation. In the subsequent experiment, the amine amount is fixed as 0.1 mL. The molecular weight of the polymer scarcely changed by the added amount of pyridine.

The oxidative polymerization of **1a** catalyzed by a copper/amine is known to involve several side reactions, resulting in Mannish-base- and DPQ-incorporations into the polymer [31]. The polymer structure was confirmed by using NMR spectroscopy. Before the measurement, the polymer was further purified by washing with acetone for the complete removal of DPQ. In the  $^1\text{H}$  NMR spectrum, there are two main peaks at  $\delta$  2.1 and 6.6, which are due to the methyl and aromatic protons of 2,6-dimethyl-1,4-oxyphenylene unit [31, 32]. Beside these peaks, a multiplet peak at  $\delta$  7.1 ascribed to the terminal phenyl pro-

TABLE 1. Effect of Pyridine Amount in Oxidative Polymerization of 2,6-Dimethylphenol (**1a**) Catalyzed by Fe(III)-Salen Complex (**2**)<sup>a</sup>

Entry	Amount of Pyridine (mL)	Yield <sup>b</sup> (%)	Polymer Content <sup>c</sup> (%)	Mn <sup>d</sup> ( $\times 10^{-3}$ )	Mw/Mn <sup>d</sup>
1	0	78	50	16	1.5
2	0.001	100	93	15	1.6
3	0.01	88	97	16	1.5
4	0.10	91	99	11	1.4
5	1.0	89	100	12	1.4

<sup>a</sup> Polymerization of **1a** (5.0 mmol) using **2** (5.0  $\mu\text{mol}$ ) as catalyst in the presence of pyridine in 1,4-dioxane (10 mL) at room temperature for 3 h under air.

<sup>b</sup> Methanol-insoluble part.

<sup>c</sup> Polymer ratio in methanol-insoluble part, determined by SEC.

<sup>d</sup> Determined by SEC.

tons was observed. No additional peaks were detected both in  $^1\text{H}$  NMR spectrum. These data indicate that the present polymer was composed of exclusively 1,4-oxyphenylene unit.  $^{13}\text{C}$  NMR analysis supports the polymer structure.

The effect of amine structure has been examined by using 2,6-lutidine, N,N,N',N'-tetraethylethylenediamine (TEED) and triethylamine (Table 2). The yield of the methanol-insoluble part and the molecular weight of the polymer were not so different from those using pyridine. In all cases, the polymer content in the methanol-insoluble part was more than 96%. These data suggest that the polymerization behavior was not much affected by the amine structure.

The polymerization has been performed in various organic solvents in the presence of pyridine (Table 3). In good solvents for PPO, i.e., 1,4-dioxane, THF, and dimethoxyethane, the polymer with molecular weight of more than  $1 \times 10^4$  was obtained in high yields (entries 2, 3, and 6). In these solvents, the polymer content in the methanol-insoluble part was very high ( $\geq 98\%$ ). The highest molecular weight was achieved by using dimethoxyethane as solvent (entry 2). Acetonitrile, N, N-dimethylformamide (DMF), and 2-propanol afforded the oligomer (entry 1, 4, and 5). This is probably due to the low solubility of PPO

TABLE 2. Effect of Amine Structure in Oxidative Polymerization of 2,6-Dimethylphenol (**1a**) Catalyzed by Fe(III)-Salen Complex (**2**)<sup>a</sup>

Entry	Amine	Yield <sup>b</sup> (%)	Polymer Content <sup>c</sup> (%)	Mn <sup>d</sup> ( $\times 10^{-3}$ )	Mw/Mn <sup>d</sup>
1	2,6-Lutidine	91	96	14	1.6
2	Pyridine	91	99	11	1.4
3	TEED <sup>e</sup>	91	100	9.4	1.3
4	Triethylamine	91	100	9.6	1.3

<sup>a</sup> Polymerization of **1a** (5.0 mmol) using **2** (5.0  $\mu\text{mol}$ ) as catalyst in the presence of amine (0.1 mL) in 1,4-dioxane (10 mL) at room temperature for 3 h under air.

<sup>b</sup> Methanol-insoluble part.

<sup>c</sup> Polymer ratio in methanol-insoluble part, determined by SEC.

<sup>d</sup> Determined by SEC.

<sup>e</sup> N,N,N',N'-tetraethylethylenediamine.

TABLE 3. Effect of Organic Solvent in Oxidative Polymerization of 2,6-Dimethylphenol (**1a**) Catalyzed by Fe(III)-Salen Complex (**2**)<sup>a</sup>

Entry	Solvent	Yield <sup>b</sup> (%)	Polymer Content <sup>c</sup> (%)	Mn <sup>d</sup> (x10 <sup>-3</sup> )	Mw/Mn <sup>d</sup>
1	Acetonitrile	91	91 <sup>e</sup>	2.3	1.6
2	Dimethoxyethane	91	99	19	1.4
3	1,4-Dioxane	91	99	11	1.4
4	DMF	98	93 <sup>e</sup>	1.9	1.4
5	2-Propanol	70	92 <sup>e</sup>	2.2	1.4
6	THF	91	98	16	1.4

<sup>a</sup> Polymerization of **1a** (5.0 mmol) using **2** (5.0 μmol) as catalyst in the presence of pyridine (0.1 mL) in organic solvent (10 mL) at room temperature for 3 h under air.

<sup>b</sup> Methanol-insoluble part.

<sup>c</sup> Polymer ratio in methanol-insoluble part, determined by SEC.

<sup>d</sup> Determined by SEC.

<sup>e</sup> Determined by <sup>1</sup>H NMR.

toward these solvents. <sup>1</sup>H NMR analysis showed that the DPQ content in the product was low (less than 10%).

The synthesis of phenylene oxide oligomer from **1a** was reported: peroxidase catalyst in an aqueous organic solvent [32] and copper/amine catalyst in a mixture of good and poor solvents for PPO [31]. Next, a mixed solvent of 1,4-dioxane and water was used in order to control the molecular weight (Table 4). By the addition of water, the molecular weight greatly decreased. The decrease of the polymer yield was observed in the aqueous 1,4-dioxane, probably due to the loss of the oligomer during the purification procedure.

In this study, a very small amount of the catalyst (0.10 mol% for the monomer) produced the polymer in high yields, showing the very efficient catalysis of **2**. Further, we decreased the catalyst amount (0.01 mol% for **1a**) in the polymerization in 1,4-dioxane in the presence of 0.001 mL of pyridine, resulting in the very low yield of the polymer (5%). In the above experiments, hydrogen peroxide was added dropwise for 1 hour. Next, hydrogen peroxide was added all



TABLE 4. Oxidative Polymerization of 2,6-Dimethylphenol (**1a**) Catalyzed by Fe(III)-Salen Complex (**2**) in an Aqueous 1,4-Dioxane<sup>a</sup>

Entry	Water Content (vol %)	Yield <sup>b</sup> (%)	Mn <sup>c</sup> (x10 <sup>-3</sup> )	Mw/Mn <sup>c</sup>
1	0	91	11.0	1.4
2	20	74	3.8	1.6
3	40	56	2.3	1.5
4	60	56	1.5	2.1
5	80	50	1.6	2.0

<sup>a</sup> Polymerization of **1a** (5.0 mmol) using **2** (5.0 μmol) as catalyst in the presence of pyridine (0.1 mL) in a mixture of 1,4-dioxane and water (10 mL) at room temperature for 3 h under air.

<sup>b</sup> Methanol-insoluble part.

<sup>c</sup> Determined by SEC.

at once in the monomer solution to give the polymer with molecular weight of 2500 in 15% yield, suggesting that the dropwise addition of hydrogen peroxide was required for the efficient synthesis of PPO.

Thermal properties of the polymer were evaluated by using differential scanning calorimetry (DSC) and thermogravimetry (TG). In the DSC measurement under nitrogen, glass transition temperature (T<sub>g</sub>) was observed at 187°C, which is lower than that of the commercially available PPO [6]. This is probably due to the lower molecular weight of the present polymer. In the TG measurement under nitrogen, the weight loss was barely observed below 400°C (the temperature at 5 wt% loss = 397°C). These data indicate the polymer obtained by using **2** as catalyst showed excellent thermal stability.

#### Oxidative Polymerization of Other 2,6-Disubstituted Phenols Catalyzed by Fe(III)-Salen Complex

Besides **1a**, other 2,6-disubstituted phenols, 2-allyl-6-methylphenol (**1b**), 2,6-diisopropylphenol (**1c**), 2,6-dimethoxyphenol (**1d**), and 2,6-diphenyl-phenol (**1e**) were used as monomer. In the polymerization of **1b** in 1,4-dioxane under the similar reaction conditions of **1a** (entry 4 in Table 1), the polymer with molecu-

lar weight of 8700 was obtained in 88% yield. In the  $^1\text{H}$  NMR spectrum of the polymer, five main peaks were observed: a singlet peak at  $\delta$  2.1 due to the methyl protons, peaks at  $\delta$  3.2, 5.0, and 5.8 ascribed to the protons of allyl group, and a singlet peak at  $\delta$  6.5 due to the aromatic protons. It is to be noted that the dimeric byproduct (DPQ derivative) was not detected in the methanol-insoluble part from **1b**. FT-IR spectrum showed peaks at 1205 and 1028  $\text{cm}^{-1}$  due to the C-O-C vibration. These data indicate that the polymer from **1b** was of 1,4-oxyphenylene unit structure. From **1e**, an oligomer with molecular weight of 1500 was obtained in 59% yield.  $^1\text{H}$  NMR analysis of the product showed that the characteristic peak of the DPQ derivative from **1e** at  $\delta$  8.1 was much smaller than that due to the aromatic protons of the oxyphenylene unit, indicating that the catalysis of **2** afforded the PPO derivative from **1e**.

In the reaction of **1c**, the yield of the methanol-insoluble part was low (17%). In the  $^1\text{H}$  NMR spectrum of the product, observed was a characteristic singlet peak at  $\delta$  7.6 ascribed to the aromatic protons of the DPQ derivative from **1c**. From the integrated ratio between this peak and peaks of the isopropyl group, the DPQ content in the product mixture was 80%. IR spectrum showed a characteristic sharp peak at 1663  $\text{cm}^{-1}$  due to the carbonyl moiety of DPQ. These data indicate that the main product by the oxidative coupling of **1c** by the Fe-salen complex was the DPQ derivative. This may be since the bulky substituent of **1c** prevented the polymer formation. A similar behavior was observed in using copper/amine catalyst [5]. From **1d**, an insoluble product was formed in 69% yield. In the IR spectrum of the product, there was a characteristic strong peak at 1628  $\text{cm}^{-1}$  ascribed to the carbonyl vibration, assuming the formation of the DPQ derivatives from the oxidative coupling of **1d** catalyzed by **2**.

Recently, we developed another approach to synthesize PPO derivatives by the polymerization of 3,5-dimethoxy-4-hydroxybenzoic acid (syringic acid) and 3,5-dimethyl-4-hydroxybenzoic acid by using peroxidase or laccase as catalyst [33, 34], which is a new type of oxidative polymerization involving elimination of not only hydrogen but also carbon dioxide from the monomer. However, **2** did not induce the oxidative polymerization of syringic acid under similar reaction conditions.

## CONCLUSION

Fe(III)-salen complex (**2**) was used as new catalyst for oxidative polymerization of phenol derivatives. We regard **2** as a model complex of peroxidase

having a heme as catalytic active site. The polymerization of 2,6-dimethylphenol catalyzed by **2** in the presence of an amine proceeded under mild reaction conditions to give the polymer exclusively consisting of 1,4-oxyphenylene unit. **2** showed a very high catalytic activity for the oxidative polymerization. The molecular weight could be controlled by the solvent composition. 2-Allyl-6-methylphenol and 2,6-diphenylphenol were also polymerized by **2** to give PPO derivatives.

We have preliminarily found that **2** catalyzed the polymerization of other phenols such as bisphenol-A and p-t-butylphenol to give soluble polymers. Further investigations on the oxidative polymerizations of various phenol derivatives by using **2** as catalyst and the evaluation of catalytic ability of metal-salen complexes for the oxidative polymerizations are under way in our laboratory.

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### REFERENCES

- [1] E. M. Genies, A. Boyle, M. Lapkowski, and C. Tsintavis, *Synth. Met.*, **36**, 139 (1990).
- [2] A. G. MacDiarmid and A. J. Epstein, *Faraday Discuss. Chem. Soc.*, **88**, 315 (1989).
- [3] S. Jasne, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed, John Wiley & Sons, New York, Vol. 13, 1986, pp. 42-55.
- [4] A. S. Hay, *J. Polym. Sci.*, **58**, 581 (1962).
- [5] A. S. Hay, *J. Polym. Sci., Polym. Chem. Ed.*, **36**, 505 (1998).
- [6] D. Aycock, V. Abolins, and D. M. White, in *Encyclopedia of Polymer Science and Engineering*, 2nd Ed, John Wiley & Sons, New York, Vol. 11, 1986, pp. 45-95.
- [7] S. Kobayashi, S. Shoda, and H. Uyama, *Adv. Polym. Sci.*, **121**, 1 (1995).
- [8] S. Kobayashi, S. Shoda, and H. Uyama, in *The Polymeric Materials*

- Encyclopedia*, J. C. Salamone, Ed., CRC Press, Boca Raton, FL., 1996, pp. 2102-2107).
- [9] M. Ayyagari, J. A. Akkara, and D. L. Kaplan, *Acta Polymerica*, *47*, 193 (1996).
- [10] S. Kobayashi, S. Shoda, and H. Uyama, in *Catalysis in Precision Polymerization*, S. Kobayashi, Ed., John Wiley & Sons, Chichester, Chapter 8 (1997).
- [11] R. A. Gross, D. L. Kaplan, and G. Swift, (Ed.), *ACS Symp. Ser.*, *684* (1998).
- [12] J. S. Dordick, M. A. Marletta, and A. M. Klivanov, *Biotechnol. Bioeng.*, *30*, 31 (1987).
- [13] J. A. Akkara, K. J. Senecal, and D. L. Kaplan, *J. Polym. Sci., Polym. Chem. Ed.*, *29*, 1561 (1991).
- [14] H. Uyama, H. Kurioka, I. Kaneko, and S. Kobayashi, *Chem. Lett.*, 423 (1994).
- [15] P. Wang, B. D. Martin, S. Parida, D. G. Rethwisch, and J. S. Dordick, *J. Am. Chem. Soc.*, *117*, 12885 (1995).
- [16] H. Uyama, H. Kurioka, J. Sugihara, and S. Kobayashi, *Bull. Chem. Soc. Jpn.*, *69*, 189 (1996).
- [17] S. Kobayashi, H. Kurioka, and H. Uyama, *Macromol. Rapid Commun.*, *17*, 503 (1996).
- [18] H. Uyama, C. Lohavisavapanich, R. Ikeda, and S. Kobayashi, *Macromolecules*, *31*, 554 (1998).
- [19] H. Higashimura, K. Fujisawa, Y. Moro-oka, M. Kubota, A. Shiga, A. Terahara, H. Uyama, and S. Kobayashi, *J. Am. Chem. Soc.*, *120*, 8529 (1998).
- [20] W. Zhang, J. L. Loebach, S. R. Wilson, and E. N. Jacobson, *J. Am. Chem. Soc.*, *112*, 2801 (1990).
- [21] N. S. Finney, P. J. Pospisil, S. Chang, M. Palucki, R. G. Konsler, K. B. Hansen, and E. N. Jacobson, *Angew. Chem. Int. Ed. Engl.*, *36*, 1720 (1997).
- [22] H. Sasaki, R. Irie, and T. Katsuki, *Synlett.*, 300 (1993).
- [23] J. Dao, D. Benoit, and C. J. Hawker, *J. Polym. Sci., Polym. Chem. Ed.*, *36*, 2161 (1998).
- [24] B. B. De, B. B. Lohray, S. Sivaram, and P. K. Dhal, *Tetrahedron Asymm.*, *6*, 2105 (1995).

- [25] B. B. De, B. B. Lohray, S. Sivaram, and P. K. Dhal, *J. Polym. Sci., Polym. Chem. Ed.*, **35**, 1809 (1997).
- [26] E. Tsuchida, H. Nishide, and T. Nishiyama, *Makromol. Chem.*, **176**, 1349 (1975).
- [27] P. Pfeiffer, E. Breith, E. Lübbe, and T. Tumaki, *Ann.*, **503**, 84 (1933).
- [28] H. A. M. van Aert, M. H. P. van Genderen, G. J. M. L. van Steenpaal, L. Nelissen, E. W. Meijer, and J. Liska, *Macromolecules*, **30**, 6056 (1997).
- [29] H. Finkbeiner, A. S. Hay, H. S. Blanchard, and G. F. Endres, *J. Org. Chem.*, **31**, 549 (1966).
- [30] C. C. Price, *ACS Symp. Ser.*, **6**, 1 (1975).
- [31] H. A. M. van Aert, R. W. Venderbosch, M. H. P. van Genderen, P. J. Lemstra, and E. W. Meijer, *J. Mac. Sci.-Pure & Appl. Chem.*, **A32**, 515 (1995).
- [32] R. Ikeda, J. Sugihara, H. Uyama, and S. Kobayashi, *Macromolecules*, **29**, 8702 (1996).
- [33] R. Ikeda, H. Uyama, and S. Kobayashi, *Macromolecules*, **29**, 3053 (1996).
- [34] R. Ikeda, J. Sugihara, H. Uyama, and S. Kobayashi, *Polym. International*, in press.

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