DOI: 10.1002/chem.201001516

Modulation of the Aerobic Oxidative Polymerization in Phenylazomethine Dendrimers Assembling Copper Complexes

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Abstract: The aerobic oxidative polymerization of phenol derivatives can provide poly(phenylene oxide)s, which are known as engineering plastics. This oxidation can be carried out with atmospheric oxygen molecules as the oxidizing reagent in the presence of copper complexes as the catalyst; however, stoichiometric or excess amounts of bases are also generally required. By using a phenylazomethine dendrimer complexed with several equivalent amounts of copper chloride, the additive (base)-free polymerization of 2,6-difluorophenol was successful with a very small amount of the catalyst (0.7 mol% of copper for the monomer) because the dendrimer was composed of many Schiff base units, affording a base and catalyst (copper complex) condensed reaction field. The resulting polymer was nearly linear and the molecular weight was very high. When the equimolar amount of the copper complex in one dendrimer molecule was increased, the polymer obtained under this reaction condition was rather branched, resulting in a higher glass transition temperature.

Keywords: copper · dendrimers · oxidation · polymerization · poly(phenylene oxide)s

Introduction

Poly(phenylene oxide) (PPO) and the corresponding derivatives known as engineering plastics are industrially important materials, which have very high thermal and chemical stability.[1] The synthetic route has been developed over the past half a century.[2,3] In particular, the oxidative polymerization of phenols by using oxygen in the air as an abundant and clean reagent was initially proposed by Hay et al.,[4] and is the most effective way to synthesize the PPOs (also called polyphenylene ethers: PPEs). Although this process does not involve any toxic oxidizing reagent and byproduct (molecular oxygen is directly reduced to water through a 4e$^-$ reduction process), there are some issues restricting their industrial applications: 1) This catalytic system requires excess amounts of base to facilitate the deprotonation reaction despite being a chemically green process. To reduce the total waste, the base should be reduced or removed from the catalytic system. 2) The resulting linear polymer often has a very high crystallinity and melting point. Although this is a feature of the linear PPOs, the polymer product is difficult to process. For the purpose of improving the productivity, alloying with other polymers is a common practice.[2] However, this alloying process may cause a loss in the advantage regarding the PPOs thermal and chemical stabilities. It is desired to improve the system with respect to the atom economy and the productivity.

The fluorinated derivative of PPOs synthesized from 2,6-difluorophenol (F_2PhOH) as a monomer may provide a new avenue to reduce the total waste.[5] Oyaizu et al. reported that the excess base could be removed by using the fluorinated monomer because it has a higher acidity than other phenol derivatives, such as 2,6-dimethylphenol.[6] However, F_2PhOH is difficult to oxidize due to the electron-withdrawing substituents, thus very large amounts of the catalyst (copper complex) are still required to polymerize F_2PhOH.[5,6]

In a previous communication, we reported that a minimum amount of the copper complex with a dendritic phenylazomethine (DPA) ligand effectively oxidized F_2PhOH to afford poly(2,6-difluorophenylene oxide) (F_2PPO).[7] Dendrimer architecture has attracted much attention as a platform for catalysts[8] and catalyst preparations[9] because it allows the flexible design of a microenvironment around the

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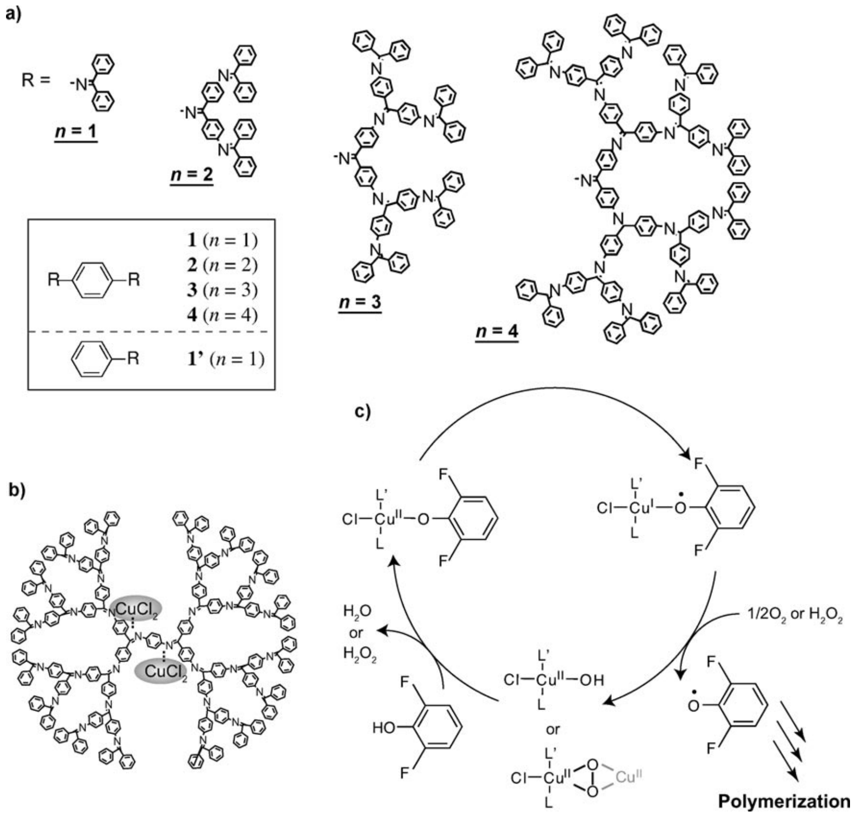
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001516.

catalytic center. The dendrimer catalysts usually decrease the catalytic activity in compensation for high selectivity of substrates. However, there are a few examples demonstrating a significant positive catalytic effect of dendrimers due to the hydrophobic microenvironment, high density of the catalytic center, or a large steric effect.[10] Our dendrimer is composed of phenylazomethine monomers, which can act as a Schiff base complexing with various metal ions and as a Brønsted base playing the role of proton storage (Scheme 1).[11–14] In the interior of the dendrimer, the local concentration of the bases reaches 2.7 $\mathrm{mol\,L^{-1}}$ when it is in the free-base form. In the case of the metal complex, the concentration of the metal complex can be increased up to 2.7 $\mathrm{mol\,L^{-1}}$, providing unexpected reactivity as a catalyst.[14,15] An integrated catalyst, in which the copper complexes and the bases are densely packed, enables complete removal of the additive bases with very low catalyst concentration because all the components required for the polymerization are provided in close vicinity to the catalytic center in the dendrimer reactor. In addition, the interior conditions are precisely controlled by the stoichiometry between the dendrimer ligand and the copper complexes due to the fine metal assembling character of the dendrimer minimizing the statistical distribution of the number of metal complexes and the position in the dendrimer molecule. The changes in the local concentration of the copper and the bases may cause changes in the polymerization mechanisms resulting in a different regioselectivity of the product polymer. Here we show that the aerobic polymerization of F_2PhOH under an additive-free condition with different metal assembling structures is demonstrated. These polymerization afforded F_2PPOs with different degrees of branching, which vary in the character of the hydrodynamic and thermal properties. Each F_2PPO polymer obtained by using these catalysts had a superior thermostability than conventional PPE (polyphenylene ether).

Results and Discussion

Preparation of copper–dendrimer catalysts: As reported elsewhere, the phenylazomethine dendrimers (**1**–**4**: Scheme 1) act as macromolecular ligands allowing precise metal assembling in the nanoscopic structure.[11,12] Into the layer-by-layer architecture, metal salts (Lewis acid) are accumulated from the layer closest to the core through a stepwise process. Anhydrous copper(II) chloride can be accumulated in the dendrimer ligands (**1**–**4**) as previously reported.[7] Upon the complexation of **4** (four generations) with $CuCl_2$ in chloroform/acetonitrile (1:1), typical UV/Vis absorption attributed to the π–π* transition (ca. $\lambda_{max} = 300$ nm) of the phenylazomethine structure was shifted to a longer wavelength ($\lambda_{max} = 400$ nm) as reported for other metals. Although the preferred metal ($CuCl_2$) binding to the inner layer was indicated by several characterization methods (UV/Vis, NMR, and X-ray absorption fine structure spectroscopy), the metal assembly on the outer layer (3rd and 4th layers) may dissociate under dilute conditions due to the weak binding constant ($K_d \approx 10^3\,\mathrm{M^{-1}}$). However, the binding scheme of the phenylazomethine dendrimer is different from that of polyamidoamine (PAMAM)-type dendrimers in which many coordination modes could be observed.[16–18] The UV/Vis titration suggested that the binding constant to the inner layer (1st and 2nd layers) was estimated to be higher than $10^5\,\mathrm{M^{-1}}$ based on the linear increase in the absorption attributed to the complex with the concentration of total $CuCl_2$ added to the solution. This precise complexation with the phenylazomethine dendrimer was explained as a result of internal electrostatic gradient along the layer-by-layer structure.[12] The rigid and



Scheme 1. a) Chemical structure of phenylazomethine dendrimer ligands. b) Stepwise complexation of the dendrimer ligand (**4**) with $CuCl_2$. c) Assumed catalytic cycle of the oxidative polymerization.

shape-persistent architecture of the phenylazomethine dendrimer,[19] as well as that of known shape-persistent dendrimers,[20] is also an important factor to retain their precise nanostructure[21] and coordination. Under catalytic conditions ([Cu] > 3 mM), quantitative complexation is expected for the inner layers.

For the preparation of the catalysts, copper complexes were formed under the same conditions of the UV/Vis measurement (in chloroform/acetonitrile at room temperature) and evaporated to dryness. During the complexation process, the concentration of **4** was 0.89 mM using the proper amount of chloroform/acetonitrile solvent. The stoichiometry between the dendrimer ligand (**4**) and $CuCl_2$ was adjusted during this complexation treatment. Finally, the catalyst in the solid state was redissolved in chlorobenzene, and used as the catalyst. The formation of the complex in chlorobenzene was also determined by the UV/Vis absorption spectra, which were similar to that in chloroform/acetonitrile. The amount of these reagents ($CuCl_2$, **4**) was set according to the stoichiometry defined for each entry (Table 1) based on the amount of F_2PhOH (1 mmol).

Table 1. Yields of F_2PPO obtained by aerobic oxidative polymerization of F_2PhOH by using different catalysts.

Entry	Ligand	[Cu]/[L][a]	Base (conc. [M])	[cat.] [mol %][b]	Yield [%]
1	**4**	2	–	0.71	71
2	**4**	4	–	0.71	82
3	PAMAM G2[c]	4	Ph_2Py[d] (0.25)	5.0	0
4	Py[e]	–[e]	Py (4.3)	0.71	0
5	Py[e]	–[e]	Py (4.3)	5.0	46
6	TMED[f]	1	Ph_2Py[d] (0.25)	5.0	71
7	TMED[f]	1	Ph_2Py[d] (0.25)	0.71	0
8	TMED[f]	1	–	5.0	36
9	TMED[f]	1	–	0.71	0

[a] Equimolar amount of $CuCl_2$ for the ligand. [b] Molar amount of the catalyst (copper) for the monomer. [c] Poly(amidoamine) dendrimer. [d] 2,6-Diphenylpyridine. [e] Pyridine was employed as both the ligand and base. Thus, the stoichiometry for [Cu]/[L] cannot be defined. [f] Tetramethyl ethylenediamine.

Polymerization: By using the prepared dendrimer–copper catalysts, F_2PhOH was polymerized under saturated oxygen conditions. F_2PhOH (1 mmol) and the catalyst (the amounts are shown in Table 1) were dissolved in chlorobenzene (2 mL) under an oxygen atmosphere at ambient pressure, and heated to 80 °C. As shown in Table 1, the dendrimer–copper catalyst (entries 1 and 2) can afford F_2PPO by using very small catalyst concentrations (0.71 mol % of copper for the monomer) after polymerization for 72 h. More noteworthy is the catalytic oxidative polymerization without any additive bases, which are generally required in a typical catalyst system. Compared with the conventional catalyst system, the total amount of the waste (ligand, copper and additive) to obtain 1 g of F_2PPO are drastically reduced. Copper–pyridine complexes and copper–tetramethylethylene diamine (TMED) were known as catalysts for the polymerization of PPOs.[6] Application of these catalysts for the F_2PPO synthesis is possible; however, no polymerized product (F_2PPO) was obtained when the amount of catalyst was less than 0.71 mol %, or no bases (pyridine or 2,6-diphenylpyridine) were added to the reaction system. As shown in entries 4 and 5 in Table 1, the copper–pyridine catalyst was activated only when a large amount of catalyst (5 mol %) was used with excess base (4.32 M of pyridine). In this case, 11.5 g of additives, which include the catalyst and base, should be employed to produce 1 g of F_2PPO. No product was afforded when the catalyst was reduced to 0.71 mol % for the monomers. Copper–TMED acts as a more efficient catalyst for the polymerization relative to copper–pyridine. When a large amount of the catalyst (5 mol %) was used (Table 1, entry 6), a considerable amount of F_2PPO was obtained in the presence of an excess amount (0.25 M) of the base (2,6-diphenylpyridine). Although the total waste was reduced by using the copper–TMED catalyst, the amount of the additive used to produce 1 g F_2PPO was 1.40 g because excess base was still required. It should be noted that a small amount of F_2PPO was obtained in the catalytic system without base (Table 1, entry 8). However, this catalyst did not work when the catalyst was reduced to 0.71 mol % regardless of the presence or absence of the base (Table 1, entries 7 and 9). No catalytic activity was observed when the dendritic ligand was replaced by the PAMAM, which has been widely used as a dendrimer ligand for the catalysis or metal nanoparticle synthesis (Table 1, entry 3). The coordination structure of the copper complex in PAMAM has been revealed to contain multiple coordination sites[17,18] of the copper that are used for the ligation by the dendrimer due to the local flexibility.[22] Compared with these reference catalysts, the $4CuCl_2$@**4** and $2CuCl_2$@**4** catalysts do not require any additive base, and are workable under very diluted conditions. [Herein, the catalyst of the dendrimer complex containing n equimolar amount(s) of $CuCl_2$ is expressed as $nCuCl_2$@**4**.] The total waste required to produce 1 g F_2PPO with $4CuCl_2$@**4** is only 0.11 g, which is about 1/100 the amount of that for the copper–pyridine complex.

The generation number of the dendrimer strongly affects the catalytic performance. Under the same conditions employing a minimal amount of the catalyst (0.71 mol %) without any bases, $2CuCl_2$@**1**, $2CuCl_2$@**2**, and $2CuCl_2$@**3** did not afford the PPO products (Figure 1 a). In addition, the yields under the various stoichiometric conditions ([$CuCl_2$]/[**4**]) decreased by increasing $CuCl_2$ amount in the dendrimer. This result demonstrates that the peripheral base capsule around the catalytic center is also indispensable for its efficient catalysis (Figure 1 b). A rough estimation of the nanoenvironment inside the dendrimer based on its hydrodynamic volume suggested a very high local concentration of the copper complex (180 mM) and base (2.7 $mol L^{-1}$), which is about 10 times greater than the typical conditions for conventional catalysis (0.25 $mol L^{-1}$). The results of these experiments demonstrated the necessity of the base and catalyst condensed reaction field for the additive (base)-free oxi-

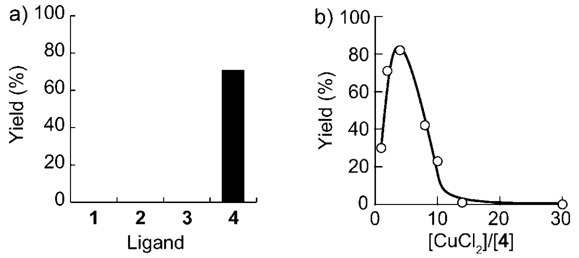


Figure 1. a) Generation number dependence of the dendrimer ligand on the yield of F_2PPO. b) Variation in the yield when the stoichiometry between $CuCl_2$ and the dendrimer ligand (**4**) was changed. All batches were treated with a catalyst concentration ([Cu]) of 0.71 mol% at 80°C for 72 h. The polymerization conditions used were similar to that of entry 1 in Table 1.

dative polymerization of F_2PhOH under diluted catalyst conditions.

The polymer product (F_2PPO) was characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy measurements in which the head (OH terminal), intermediate, and tail (Ph terminal) monomers were individually recognized (Figure 2). The weight-average molecular weight (M_w) of the obtained polymer was estimated to be 32000 by a triple-detection analysis based on size exclusion chromatography (TriSEC). We isolated the relatively low-molecular-weight polymers by using preparative SEC and analyzed by ^{19}F NMR spectroscopy. The ratio of the integrals between each ^{19}F signal (F_1, head; F_2, intermediate; F_3, tail) provided information about the averaged molecular weight of the polymer. The calculated value of the molecular weight ($M_n = 4000$) from the NMR spectroscopy result was in good agreement with that estimated from the TriSEC analysis ($M_n = 4500$, $M_w = 4600$).

Kinetic study: As can be observed from the yields of the F_2PPO product, the difference in the catalytic activities of the catalysts is significant. More detailed analyses were carried out by monitoring the monomer conversion, turnover number (TON), and redox reaction of the copper complex.

The monomer (F_2PhOH) conversion was quantitatively determined by gas chromatography by monitoring the residual peak of the monomer (Figure 3a). When the catalyst concentration was high (5 mol%), the monomer was consumed just after the reaction started. In both catalyst systems employing $4CuCl_2$@**4** and Cu–TMED, the monomer conversion reached almost 100% at 5 h. When the catalyst concentration was decreased to 1.3 and 0.71 mol%, the conversion rate clearly decreased. It is notable that the dendrimer catalyst ($4CuCl_2$@**4**) constantly converts more of the monomers than the Cu–TMED catalyst. The dendrimer catalyst retained high catalytic activity under diluted conditions, whereas Cu–TMED had lost activity.

Further analyses were carried out by monitoring the number of reactive points (monomer, −OH terminal of the polymer) based on the ^{19}F NMR signals. During the initial stage of polymerization, four independent ^{19}F signals were observed. The turnover number (TON) of the catalyst was calculated by using Equation (1) by applying the values of the integrations (I_{mono}, I_1, I_2, and I_3) for each ^{19}F signal corresponding to the fluorine atom on the monomer ($\delta = -135.96$ ppm), −OH terminal unit ($\delta = -131.39$ ppm), repeating unit ($\delta = -124.09$ ppm), and Ph terminal unit ($\delta = -126.50$ ppm), respectively.[5,6]

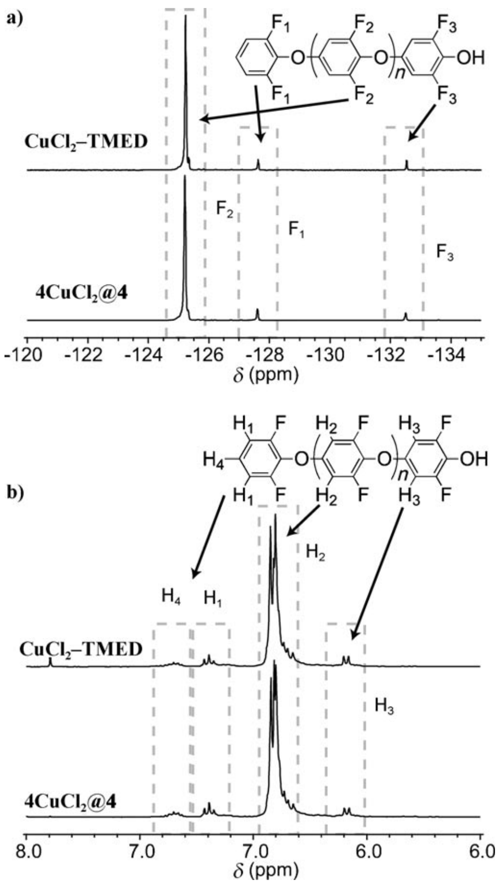


Figure 2. ^{19}F (a) and ^{1}H NMR (b) spectra of F_2PPO synthesized with $CuCl_2$–TMED and $4CuCl_2$@**4** as the catalysts. The polymerization conditions used were the same as those of entries 6 and 2 in Table 1. For each sample, a part of the polymer was isolated by preparative HPLC with GPC columns at the same elution volume. The molecular weight of the isolated polymer was 3500 and 4500, respectively.

$$[\mathrm{TON}] = \frac{C^0_{\mathrm{mono}}}{C^0_{\mathrm{Cu}}} \times \frac{I_1 + I_2}{I_1 + I_2 + I_3 + I_{\mathrm{mono}}} \tag{1}$$

in which C^0_{mono} and C^0_{Cu} are the initial concentration of the fed monomer (F_2PhOH) and the copper atom. For the copper–TMED catalyst, the integrated TON (Figure 3b) increased with the reaction time within the monitoring time (0–6 h).

The turnover frequency (TOF) was obtained as the slope of the plot between TON and the reaction time for each amount of the catalyst (5.0, 1.3, and 0.71 mol%). The TOF was clearly dependent on the catalyst amount. When the amount of catalyst was lower, the TOF value was deter-

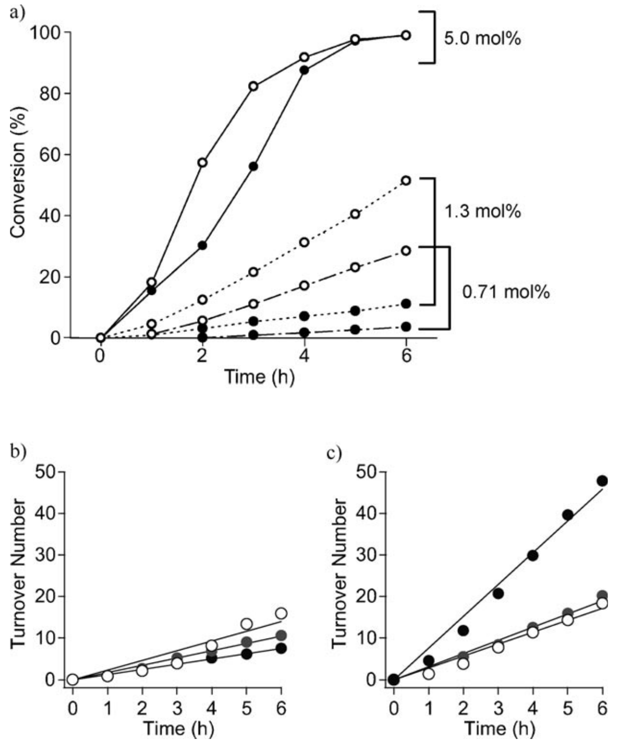


Figure 3. a) Conversion of F_2PhOH monomers in the reaction mixture. ○: Cu–dendrimer, ●: Cu–TMED. Turnover number of the catalytic oxidation of F_2PhOH by Cu–TMED (b) and $4CuCl_2$@**4** (c). The concentrations of the catalysts were 5.0 (○), 1.3 (●), and 0.71 mol % (●). TOF values of 2.33 (5.0), 1.74 (1.3), and 1.25 h^{-1} (0.71 mol %) for Cu–TMED (b) and 2.85 (5.0), 3.17 (1.3), 7.63 h^{-1} (0.71 mol %) for $4CuCl_2$@**4** (c) were obtained.

mined to be much lower. To facilitate the oxidative polymerization, it is reported that the formation of the binuclear $[(Cu^{III})_2(\mu\text{-}O)_2]^{2+}$ and $[(Cu^{II})_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)]^{2+}$ complexes is important for the efficient oxidation of the substrates.[23] The present dependence on the catalyst concentration is also explained by the formation of the dicopper complex. In a relatively high concentration of the copper catalyst, the formation of the dicopper complex is facilitated due to statistical factors. While conventional catalysts decreased their activity, the copper–dendrimer catalyst ($4CuCl_2$@**4**) retained a very high activity under the diluted conditions (Figure 3c). Contrary to our expectations, the TOF for the minimum amount of the catalyst (0.71 mol %) showed the highest value. The reason why the TOF increased has not yet been elucidated. The Michaelis–Menten kinetics predicts that the product-formation rate should be proportional to the concentration of the catalyst (enzyme); therefore, the TOF (reaction rate divided by the catalyst concentration) should be constant for every catalyst concentration. The relatively low TOF for the higher catalyst concentration (5 mol %) of the copper–dendrimer system suggests that unfavorable side reaction would prevent the growth of the product polymer when the catalyst concentration was relatively high. Similar dependence on the catalyst concentration was also observed in the other catalytic system employing a dicopper complex. Trace amounts of the C–C coupled quinonoid structure was indeed observed as that reported by Oyaizu et al.[6]

To determine the redox properties for each copper–ligand complex, cyclic voltammetry measurements were carried out. All measurements were performed in nitrobenzene (5 mL) in the presence of tetra-*n*-butylammonium perchlorate (0.2 mol L^{-1})[24] as the supporting electrolyte. Before the measurements, all of the sample solutions were deaerated by N_2 bubbling for 5 min. The details for each sample are shown in Table 2. Although a quasi-reversible wave attributed to the Cu^I/Cu^{II} redox couple was observed around 0 V versus Ag/Ag^+ for all of the copper complexes, the redox potential was significantly different (Table 2). The copper complexes with the phenylazomethine dendrimer (**4**) and its model compound composed of only one phenylazomethine unit (**1′**) displayed relatively higher redox potentials than the other complexes with TMED and pyridine. These redox potentials suggest that the phenylazomethine complex is more difficult to oxidize to the Cu^{II} valence state than the TMED or pyridine complexes.

Table 2. Electrochemical and electron-transfer properties of copper complexes with different ligands.

Ligand	[Cu]/[L]	E^0 [V vs. Ag/Ag^+][a]	k_e [min^{-1}][b]
4	4	0.35	1.0×10^{-2}
1′ (model)	1/2	0.34	9.4×10^{-3}
pyridine	1	−0.10	9.7×10^{-4}
TMED	1/250	−0.18	6.8×10^{-3}

[a] Redox potential of the Cu^I/Cu^{II} redox couple in nitrobenzene with $[Bu_4N][ClO_4]$ (0.2 M). [b] Quasi-first-order rate constant for the reduction of the Cu^{II} complex by F_2PhOH (0.2 M) in nitrobenzene under an N_2 atmosphere.

On the contrary, electron transfer from the phenol monomers to the phenylazomethine complex is faster than with conventional catalysts. The kinetic trace for the electron-transfer reaction between the copper complex and phenols was monitored by the UV/Vis absorption change, as reported by Tsuchida et al.[25] The monitoring wavelength was 800 nm at which the characteristic d–d transition absorption band of Cu^{II}–L was observed. The results summarized in Table 2 indicate that the phenylazomethine compounds (including the model complex and the dendrimer complex) have a relatively strong oxidizing power for F_2PhOH. This would be an advantage for the oxidation of F_2PhOH, which requires a relatively strong oxidizing reagent, due to the higher oxidation potential of F_2PhOH.[26] However, they do not explain the high catalytic activity of $4CuCl_2$@**4**. Indeed, $4CuCl_2$@**4** shows a much higher activity than the model complex (**1′**), even though both the electron-transfer and redox potentials are almost identical. The answer to the question is provided from the concentration dependence of the TOF. Whereas the TOF of the mononuclear complex, such as TMED, significantly dropped with decreasing concentration, the dendrimer complex retained the TOF even at a very low concentration (0.71 mol %). This could be explained by the concentration effect of the copper complexes in the dendritic nanocapsule. In addition, the concentration effect of the bases should be indispensable for efficient catalysis because the generation-number dependence (Figure 1) shows a drastic enhancement in the activity for the 4th generation dendrimer (**4**).

Complete removal of the additives (bases) in the present catalytic system employing the dendrimer ligand can be understood as the result of extreme condensation of the basic component. However, the stronger acidity of F_2PhOH due to the electron-withdrawing group (fluorine) may also assist the additive-free polymerization. An advantage of the dendrimer catalyst is rather an efficient oxidizing power under very dilute conditions. When the conventional catalysts (pyridine or TMED ligand) do not work well for the polymerization of F_2PhOH when they were employed under very dilute conditions (0.71 mol%). The dendrimer catalyst assembling copper complexes contains both Lewis acids and bases with redox properties. Based on this standpoint, the catalyst is similar to the "frustrated Lewis pairs"[27] enabling a cooperative function on catalysis. The all-in-one composite based on the dendrimer architecture is currently the only catalyst allowing the additive-free polymerization under very dilute conditions.

Structural analyses on the polymer product: As mentioned above, the F_2PPO product synthesized with the copper–dendrimer catalyst was almost the same as the product with the copper–TMED catalyst. However, detailed properties of these products (molecular weight and degree of branching) were quite different based on the catalyst composition (nCuCl$_2$@**4**: $n=2$, 4, 12, 28, 60). The examined catalytic systems are shown in Table 3 with the properties of the corresponding products. Because of the low activity of the catalyst producing many $CuCl_2$ molecules ($n>12$), the catalyst concentration in this examination is normalized by the concentration of the dendrimer.

The copper–dendrimer complex assembling four $CuCl_2$ molecules in one dendrimer (4CuCl$_2$@**4**) exhibits the highest catalytic activity. The optimal catalyst can afford an almost linear F_2PPO, which is determined by ^{19}F NMR spectroscopic analysis. In the NMR spectrum, three different part of the monomer units (OH terminal, repeating, and Ph terminal units) were individually observed. The integrations of each of the OH and Ph terminal units should be identical if linear polymer products are assumed. This was true when the stoichiometric amount of the copper/dendrimer was small ($n=2$ or 4). However, the ratio between the OH and Ph terminal units decreased when the amount of copper (n) increased (Figure 4). The difference in the number of each terminal unit should be due to branching of the polymer.

One possible explanation for the production of a branching part is an Ullmann-type nucleophilic substitution reaction. In this case, the branching unit is a monofluorinated monomer, as shown in Figure 4.[28] Several experimental data supported the nucleophilic substitution, as mentioned below. The chemical shift of a fluorine atom (F_4) on the branching unit was indeed observed in ^{19}F NMR spectra of the polymers at $\delta=-97$ ppm. It is quite surprising that the nucleophilic substitution was observed for the C–F bonding, which is generally activated only by a very strong electron-withdrawing group, such as CF_3, CN, and NO_2. However, in this case, the activated phenol partially oxidized by the copper complex is one of the possible reactants for substitution. The variation of the branching degree should be due to the difference of the reaction conditions around the catalytic center. When the stoichiometric amount of the copper complex was smaller, basic conditions should have been maintained in the dendrimer. This condition might lead to preferable deprotonation, accelerating the oxidative polymerization into the linear polymer. On the contrary, a larger amount of the copper complexes led to branching, which suppressed polymerization.

Quantitative analysis of branching was carried out by using ^{19}F NMR spectroscopy. Although the ^{19}F signal at the branching unit was too small to determine an accurate integral, the number of branching units could be calculated as the difference in the number of each terminal unit, as expressed by Equation (2):

$$2I_{br} = I_3 - I_1 \tag{2}$$

in which I_{br} is the integral of the fluorine signal on the branching unit, I_3 is that on the Ph terminal units, and I_1 is that on the OH terminal units. Based on an assumption of the polymer structure shown in Figure 4, the number of OH terminal units should be one.

Table 3. Results of the polymerization of F_2PhOH by using the copper–dendrimer catalysts under different stoichiometric conditions.

[CuCl$_2$]/[**4**]	CuCl$_2$ [mg^{-1}][a]	**4** [mg][b]	t [h][c]	Yield [%]	Soluble [%][d]	M_w (SEC)[e]	M_n (SEC)[f]	a[g]	M_n (NMR)[h]
2	1.92	40	24	trace	–[i]				
2	1.92	40	72	75	23	15100	5750	0.441	3750
4	2.02	20	24	21	89				
4	2.02	20	72	82	57	48400	7400	0.403	8840
12	5.82	20	24	47	92				
12	5.82	20	72	48	88	28800	6310	0.398	8660
28	13.7	20	24	22	76				
28	13.7	20	72	32	89	17900	4630	0.362	7480
60	28.8	20	24	2	–[i]				
60	28.8	20	72	21	79	20800	6910	0.299	7060

[a] Weight of $CuCl_2$ used for the polymerization. [b] Weight of dendrimer ligand used for the polymerization. [c] Polymerization time. [d] Percentage of the THF soluble part in the product. [e] Weight-averaged molecular weight of the product measured by SEC experiments. [f] Number-averaged molecular weight of the product measured by SEC experiments. [g] Mark–Houwink–Sakurada constant. [h] Number-averaged molecular weight of the product measured by ^{19}F NMR spectroscopy experiments. [i] This value could not be obtained due to the very small amount of the product.

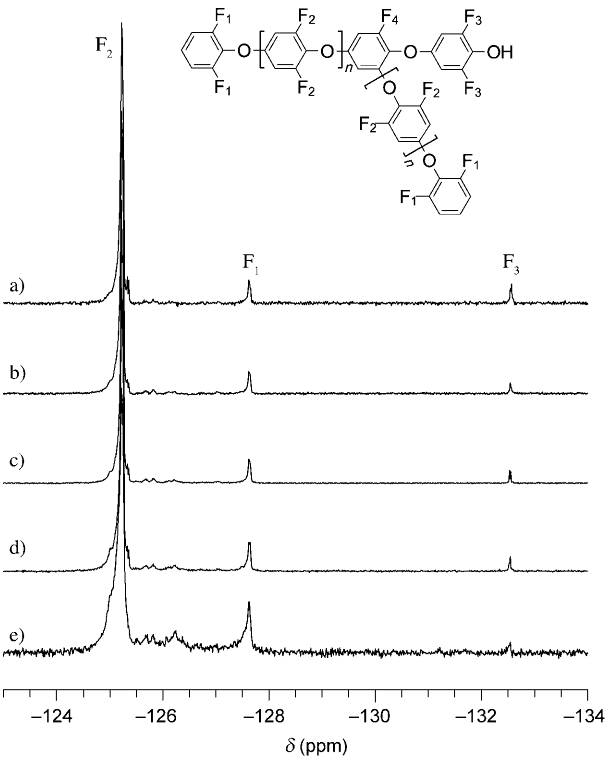


Figure 4. ^{19}F NMR spectra of F_2PPO synthesized with $2CuCl_2$@**4** (a), $4CuCl_2$@**4** (b), $12CuCl_2$@**4** (c), $28CuCl_2$@**4** (d), and $60CuCl_2$@**4** (e).

Therefore, the integral of these fluorine signals was normalized to the signal of the OH terminal unit. With the integral of the repeating unit (I_2), the number-averaged molecular weight (M_n) was determined by using Equation (3):

$$\begin{aligned} M_n &= 129N_1 + 128N_2 + 129N_3 + 109N_{br} \\ &= 129I_1 + 128I_2 + 129I_3 + 109(I_3 - I_1) \qquad (3) \\ &= 20I_1 + 128I_2 + 238I_3 \end{aligned}$$

in which N_1, N_2, N_3, and N_{br} are the number of the OH terminal units, repeating units, Ph terminal units, and the branching units, respectively. The estimated M_n for each entry agreed with that obtained by the SEC analyses described below. It should be noted that the percentage of the branching units for the entire polymer structure increased with the number of copper atoms assembled in the dendrimer. In particular, nearly 10 % of the branching was introduced when excess $CuCl_2$ to the ligand sites in the dendrimer was added ($60CuCl_2$@**4**). The degree of branching for $60CuCl_2$@**4** was determined to be 0.21, whereas the degree for $4CuCl_2$@**4** was 0.11.

The SEC analyses were carried out by using a standard polystyrene SEC column with a dual detector (viscometer and refractometer) to determine the absolute molecular weight by using a universal calibration method.[29] The size-separated chromatograms were analyzed with the detector and the molecular-weight distribution, and the relationship between the molecular weight and the intrinsic viscosity was determined. The M_n and M_w values were calculated for each entry, and the molecular-weight distribution (M_w/M_n) is shown. In addition, the Mark–Houwink–Sakurada constant (a)[30] was determined from the slope of the plot between the molecular weight and ln[η] ([η] is the intrinsic viscosity). The constant a is known to be around 0.7 for polymers with cylinder-like morphology, whereas it approaches 0 for polymers with globular-like morphology. Decreasing the constant a from 0.44 ($2CuCl_2$@**4**) to 0.30 ($60CuCl_2$@**4**) is interpreted as a result of the morphology change due to the variation in these branching degrees. This idea completely agrees with the results from the NMR spectroscopic analyses.

Although the branching degree obtained as a soluble part of the entire product might be slightly overestimated, the branching was clearly facilitated by changing the catalyst composition, which could be easily controlled based on the stoichiometry between the copper and the dendritic ligand. This fact was also supported by a percentage of the soluble part for $2CuCl_2$@**4**, which was much lower than those for the other compositions due to the higher crystallinity.

Thermostability: The polymers (F_2PPO) obtained by using the copper–dendrimer catalyst have a very high thermostability that is superior to conventional poly(phenylene ether) (PPE). While the 10 % weight-decreasing temperature ($T_{d10\%}$) of PPE was 463 °C, the F_2PPO synthesized with the dendrimer catalyst has a $T_{d10\%}$ of 526 °C. This stability is equivalent to poly(phenylenesulfide) (PPS),[31] which is a super engineering plastic with a $T_{d10\%}$ value of 525 °C. There was no dependence of the thermostability on the branching degree controlled by the stoichiometry of $CuCl_2$ and the dendrimer ligand. However, the glass transition temperature (T_g) was different due to the branching degree. The THF soluble part of the polymer was measured by differential scanning calorimetry (DSC). While the polymer synthesized by the copper–TMED catalyst exhibited a glass transition at 113 °C with a small endothermic peak corresponding to the melting point at 230 °C, the T_g for polymers synthesized with the dendrimer catalyst was about 130 °C, which is higher than that of copper–TMED (see the Supporting Information). In addition, the polymer exhibited no melting point, suggesting that the polymer phase is amorphous.

Conclusion

The aerobic oxidative polymerization of F_2PhOH was demonstrated by using copper–dendrimer complexes as the catalysts. Whereas the conventional catalysts, such as copper–TMED complexes, require a large amount of catalyst with excess bases as additives, the copper–dendrimer complex was active as the catalyst in a very small amount (0.71 mol %) even in the absence of additive bases. When several equivalent amounts (2–4 equiv) of copper chloride were complexed with the dendrimer ligand, the highest catalytic performance was observed. Under these reaction conditions, the polymer product, which has almost linear topology, was the same as that produced when using the copper–TMED catalyst. The branching degree was controlled by the stoichiometry between the dendrimer and copper chloride assembled within. It is important that the hybrid structure should be designed with a rigid architecture so as not to deactivate the catalytic center. Due to the rigid π-conjugating structure of the phenylazomethine dendrimer, the metal center can retain its fine conformation. Additive-free aerobic oxidation using the dendrimer catalysts decreased the total waste required to produce the PPO derivatives. Furthermore, the precise assembly of metal complexes can provide a new cooperative catalyst that exhibits unique catalytic activity and selectivity.

Experimental Section

Chemicals: F_2PhOH used as the monomer compound and anhydrous $CuCl_2$ were purchased from Sigma–Aldrich. *N,N,N′,N′*-Tetramethylethylenediamine was acquired from Merck. All other chemicals (solvents, HCl, pyridine) were purchased from Kanto Kagaku and were used as received. The phenylazomethine dendrimer ligands (**1**–**4**) and the monomer model (**1′**) were prepared as previously reported.[7]

Polymerization of F_2PhOH: The polymerization of F_2PhOH using the dendrimer catalyst was carried out by using the modified procedures of the following protocol: Dendrimer **4** (19.48 mg, 1/280 mmol) and $CuCl_2$ (0.96 mg, 1/140 mmol, 2 equimolar amounts for **4**) were dissolved in chloroform/acetonitrile (4 mL, v/v = 1/1) to form the complex ($2CuCl_2@$**4**). After a few minutes of stirring at room temperature, the solution was concentrated to dryness to give a solid catalyst. Polymerization of F_2PhOH (130 mg, 1 mmol) was carried out in chlorobenzene (2 mL) at 80 °C in the presence of the catalyst (dendrimer complex prepared through the protocol) under an O_2 atmosphere (1 atm). After 72 h, the mixture was cooled and poured into methanol (400 mL) containing 5 % HCl. The precipitate was filtered and dried under vacuum at 60 °C for 24 h. For the modification of the protocol, the amounts of F_2PhOH and chlorobenzene were not changed, instead the amounts of **4**, $CuCl_2$, and chloroform/acetonitrile solvent were varied. Details of the protocols are shown in the Supporting Information. The total moles of **4** and $CuCl_2$ were determined according to the stoichiometries ([Cu]/[F_2PhOH] and [Cu]/[**4**]) defined for the reaction entries. The concentration of **4** in chloroform/acetonitrile (during the complexation reaction) was controlled at 0.89 mM for all entries with the proper amount of the solvent. For example, an experiment employing 1/140 mol % of copper in the $4CuCl_2@$**4** catalyst, 1/560 mmol of **4** and 1/140 mmol of $CuCl_2$ were dissolved in 2 mL of the chloroform/acetonitrile solvent for the catalyst preparation.

The control experiment displaying the polymerization of F_2PhOH by using the conventional catalyst was carried out under the following conditions: *N,N,N′,N′*-Tetramethylethylenediamine (0.83 mg, 1/140 mmol) and $CuCl_2$ (0.96 mg, 1/140 mmol) were dissolved in chlorobenzene (2 mL). The polymerization of F_2PhOH (130 mg, 1 mmol) was carried out in the solution at 80 °C in the presence of excess 2,6-diphenylpyridine (115 mg, 1/2 mmol) under an O_2 atmosphere. After 72 h, the mixture was cooled and poured into methanol (400 mL) containing 5 wt % HCl. The precipitate was filtered and dried under vacuum at 60 °C for 24 h. The procedure was modified according to the intended reaction conditions.

Analysis of the product by NMR spectroscopy: The polymer product (F_2PPO) obtained by reprecipitation was then analyzed by ^1H (400 MHz), ^{13}C (100 MHz), and ^{19}F (313 MHz) NMR spectroscopy by using an NMR spectrometer (JEOL, JMN-400GX alpha). The NMR sample solution was prepared with [D$_8$]THF as the solvent, and the insoluble part was removed by filtration prior to the measurement. The chemical shift of the ^1H and ^{13}C NMR spectra was referenced to tetramethylsilane (TMS: $\delta = 0$ ppm) and the residual solvent peak (THF) as the internal standards, respectively. The chemical shift of the ^{19}F NMR spectra was referenced to trifluoroacetic acid ($\delta = -76.5$ ppm) measured as an external standard. Before the measurements, the samples were dissolved in [D$_8$]THF, and the insoluble part was removed by filtration.

Analysis of the product by SEC: Analytical SEC was performed by using an HPLC instrument (Shimadzu, LC-10AP) equipped with two tandem SEC columns (Tosoh, TSK-GEL CMHXL and G3000HXL) at 40 °C. THF was used as the eluent at the flow rate of 1 mL min^{-1}. The insoluble part was removed by filtration prior to the measurement. The detection line was connected to a triple detector (Viscotek, TriSEC Model 302) operated at 30 °C. The molecular weights of the dendrimers were calculated by using the universal calibration method from the SEC data, which contains the refractive index (RI) and intrinsic viscosity (IV) charts.[29] Based on the relationship between the molecular weight and the hydrophobic radius, the Mark–Houwink–Sakurada constant was derived from the slope of the plot.[30]

Acknowledgements

This work was supported in part by Grant-in-Aids for Scientific Research on Innovative Areas (“Coordination Programming” Area 2107, No. 21108009) and Grant-in-aid for Scientific Research (No. 19205020) from the Ministry of Education, Culture, Science and Technology (MEXT) of Japan.

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[24] ***Caution!*** The perchlorate salt is explosive. Handle with care avoiding mechanical pressure and static electrical sparks. Hexafluorophosphate (PF_6^-) salts are safer electrolytes and are also available for these kinds of experiments.

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Received: June 1, 2010