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First Synthesis of High Molecular Weight Poly(2,6-difluoro-1,4-phenylene oxide) by Oxidative Polymerization

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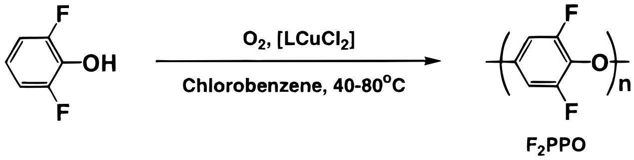
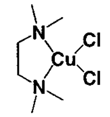
The polymerization of fluorinated phenols by the nucleophilic addition−elimination reaction via Meisenheimer complexes is a potential route to provide poly(aryl ether)s, when a strong electron-withdrawing group activates the fluorine atom.[1] On the other hand, oxidative C−O coupling of fluorophenols is expected to provide poly(fluorophenylene oxide)s whose surviving fluorine substituents can be used for the further modification of the polymer by the reaction with various nucleophiles. However, the oxidative coupling of fluorophenols has been impeded by their high oxidation potentials due to the electron-withdrawing nature of the fluorine substituents.[2,3] Indeed, poly(2,6-difluoro-1,4-phenylene oxide) (F_2PPO) has only been obtained by the polycondensation of 5,7-difluoro-1-oxaspiro[2,5]octa-4,7-dien-6-one,[4] but the monomer synthesis requires two further steps from 2,6-difluorophenol. The resulting polymer ($M_n = 5600$) has not been characterized.

We report herein the first synthesis and characterization of the high molecular weight F_2PPO by the oxidative polymerization of 2,6-difluorophenol using copper-catalyzed $4e^-$ transfer to O_2. This investigation has particular importance in that the O_2 splitting reactions by the $4e^-$ transfer has been found in many enzymatic oxidation processes, which pose a considerable challenge to modeling the biological processes for synthetic applications.[5] The typical example is the convenient synthesis of an engineering plastic poly(1,4-phenylene sulfide) by the vanadium-catalyzed oxidative polymerization of diphenyl disulfide,[6] which proceeds at the expense of O_2 that is predominantly reduced to H_2O.[7] It has been established that the breaking of the O−O bond in O_2 is fostered by the homolytic character of a μ-η^1:η^1-peroxovanadium(IV) that forms during the reaction of O_2 with an oxophilic vanadium(III).[8] On the other hand, recent studies on copper−O_2 chemistry have realized the prevalent formation of the $[(Cu^{III})_2(\mu\text{-}O)_2]^{2+}$ and $[(Cu^{II})_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)]^{2+}$ core with a variety of peralkylated diamine or triamine ligands at low temperatures, due to the inhibition of the typical subsequent reaction with additional Cu(I) to provide oxo- or hydroxocopper(II) products and overall 4:1 Cu:O_2 stoichiometry.[9] Recent work revealed not only the oxyhemocyanin-like reversible O_2-releasing ability of a Cu_2O_2 core[10] but also the oxytyrosinase-like reactivity with readily oxidized substrates such as 2,4-di-*tert*-butylphenol to yield the C−C coupled and/or oxygenated products.[11]

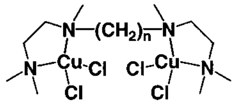
Our interest in the catalysis of the oxidation of 2,6-difluorophenol was stimulated by the indications that the 2:1 Cu:O_2 stoichiometry could induce a strong oxidizing power, which was demonstrated by the remarkable decomposition process of Cu_2O_2 complexes upon warming in the absence of external substrates by oxidizing the alkyl substituent of the ligand.[12] For a comparative study, copper(II) dichloride with peralkylated amine ligands, such as *N,N,N′,N′*-tetramethylethylenediamine (tmed) (**1**), *N,N′*-bis(2-(dimethylamino)ethyl methyl)alkylenediamine ($C_n$tmed$_2$) (**2**−**4**), and 1,4,7-triisopropyl-1,4,7-triazacyclononane (tacn) (**5**) were selected as the catalyst.

Scheme 1

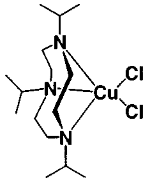




[Cu(tmed)Cl_2] (**1**)



[Cu($C_n$tmed$_2$)Cl_2]:
n = 4 (**2**), 5 (**3**), 6 (**4**)



[Cu(tacn)Cl_2] (**5**)

An admixture of 2,6-difluorophenol and a small amount of the catalyst ([monomer]/[Cu] = 20) in chlorobenzene afforded F_2PPO after stirring under O_2 (Scheme 1).[13] The polymer was obtained as an off-white powder after precipitation from methanol. *o*-Dichlorobenzene, fluorobenzene, benzotrifluoride, nitrobenzene, 1,2-dichloroethane, and 1,1,2,2-tetrachloroethane can also be used as the solvent, but no polymer was obtained with DMF, THF, or alcohols. The polymerization results are summarized in Table 1. The conventional Cu−pyridine catalyst did not afford F_2PPO (runs 1 and 2) so that with catalysts **1**−**5** the less coordinating 2,6-diphenylpyridine was employed as a base in order to depress the ligand-exchange reaction. Indeed, polymerization did not proceed with only $CuCl_2$ and 2,6-diphenylpyridine. Interestingly, a base is not essential for the polymerization (run 9), in contrast to the polymerization of 2,6-dimethylphenol, which proceeds only under basic conditions via phenolate stems from the reduced basicity of the 2,6-difluorophenolate.[3] The amount of O_2 uptake with respect to the polymer yield was in accordance with the $4e^-$ reduction of O_2. The polymer was almost quantitatively obtained but only with a prolonged polymerization time (>72 h). With readily reoxidized catalysts,[11] the slow rate of polymerization indicates that the phenol oxidation step rate determines the overall reaction. The molecular weight of F_2PPO increased during the last stage of the polymerization, indicating a step growth mechanism. In particular, polymerization with **5** at 80 °C gave high molecular-weight F_2PPO (M_w = 66 000, run 10). Side reactions are initiated at temperatures higher than 80 °C, resulting in defects such as the C−C coupled quinoid structure.

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Table 1. Oxidative Polymerization of 2,6-Difluorophenol[a]

run	catalyst[b]	base[c]	solvent[d]	T [°C]	t [h]	polymer yield [%]	$M_n^e \times 10^{-3}$	$M_w^e \times 10^{-3}$
1	CuCl	Py	ClBz[h]	40	72	0		
2	CuCl	Py	ClBz	80	96	8		
3	**1**	2,6-Ph_2Py[f]	ClBz	40	72	43		
4	**2**	2,6-Ph_2Py	ClBz	40	72	63		
5	**3**	2,6-Ph_2Py	ClBz	40	72	75	2.3	4.8
6	**4**	2,6-Ph_2Py	ClBz	40	72	42		
7	**5**	2,6-Ph_2Py	ClBz	40	72	78	3.1	6.4
8	**5**	2,6-Ph_2Py	ClBz	40	96	90	2.7	8.4
9	**5**	*g*	ClBz	40	96	83	1.9	7.4
10	**5**	2,6-Ph_2Py	ClBz	80	96	100	13.0	66.0
11	**5**	2,6-Ph_2Py	*o*-Cl_2Bz[i]	40	96	88	4.5	17.0

[a] 0.5 mol/L. [b] [Cu] = 0.025 mol/L. [c] 0.25 mol/L. [d] Continuously saturated with O_2. [e] Determined by GPC with PS standard. [f] 2,6-Diphenylpyridine. [g] Without base. [h] Chlorobenzene. [i] *o*-Dichlorobenzene.

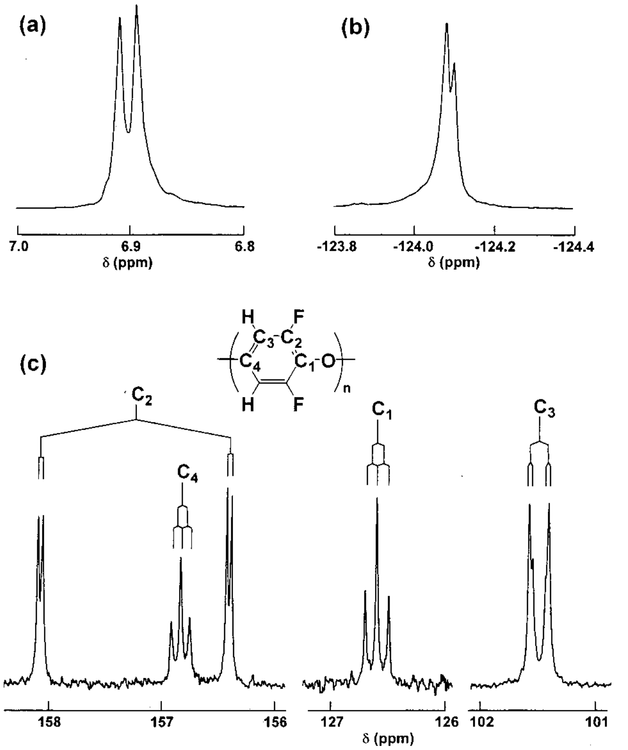

Figure 1. The 600 MHz ^{1}H (a), 470 MHz ^{19}F (b), and 151 MHz ^{13}C NMR (c) of the soluble part of F_2PPO in [D_8]THF. Trifluoroacetic acid ($\delta = -76.5$ ppm) was used as the external standard for ^{19}F NMR.

Polymer with **5** (run 10) was 89 wt % soluble in THF. The NMR spectra of the soluble part of F_2PPO corroborated the 1,4-phenylene structure (Figure 1). The ^{1}H NMR spectrum exhibited a single ^{19}F-coupled doublet peak at 6.90 ppm assigned to the aromatic protons. No peak assignable to the terminal phenolic protons[4] (ca. 8.7 ppm) was prominent. The ^{19}F NMR spectrum exhibited a doublet peak at −124.09 ppm.[14] The ^{13}C NMR spectrum showed four ^{19}F-coupled absorptions with which the coupling constants up to ^4J were determined. The IR spectrum of the THF insoluble part of F_2PPO coincided with that of the soluble part, which exhibited no peak assignable to the carbonyl or epoxy moiety,[4] but a peak due to an ether bond was observed at 1107 cm^{-1}. The elemental analysis of both the THF soluble and insoluble part was in accordance with the empirical formula.[13]

The explicit linear structure prompted us to investigate the properties of F_2PPO. It is known that poly(2,6-disubstituted phenylene oxide)s show diverse properties depending on the nature of the substituents.[15] The polymer with methyl groups is an engineering plastic with excellent processability and mechanical strength based on its low crystallinity and unique blending properties.[15] The completely aromatic polymers such as poly(2,6-diphenyl-1,4-phenylene oxide)[16] and poly(1,4-phenylene oxide)[17] show improved thermal stabilities, but the concomitant high crystallinity degrades their processability and blending properties.[15] The fluorine substituents in the para position of the pendant phenyl group in 2,6-diphenyl(phenylene oxide)s lowers the crystallinity,[18] so that it is anticipated that the introduction of fluorine substituents onto the phenylene oxide chain should lead to both higher thermal stability and lower crystallinity.

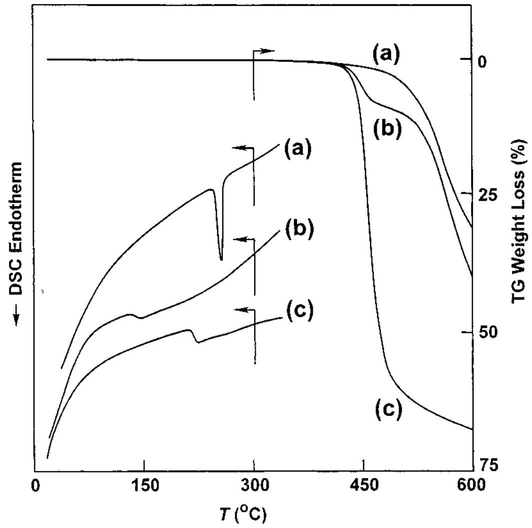

Figure 2. TGA and DSC thermograms for (a) F_2PPO (THF insoluble part), (b) F_2PPO (THF soluble part), and (c) poly(2,6-dimethylphenylene oxide) under N_2. The temperature was scanned from room temperature at a rate of 10 °C/min.

The THF soluble part of F_2PPO has a glass transition temperature T_g of 137 °C demonstrated by an endothermic shift in the initial baseline of the DSC thermogram (DSC curve b in Figure 2). The lack of both the crystallization exotherm above the T_g and the melting endotherm indicates that the polymer is amorphous.[19] On the other hand, the THF insoluble part was crystalline with a melting point T_m of 255 °C and a heat of fusion of 21 J/g (curve a), but it had little measurable crystallinity when cooled from the melt. These properties are reminiscent of those of poly(2,6-dimethylphenylene oxide) isolated by methanol precipitation which is only 5−15% crystalline ($T_m = 267$ °C) but tends to be amorphous ($T_g = 205{-}220$ °C) upon annealing.[20]

The stability against thermolysis is indeed enhanced by the replacement of the methyl group with fluorine

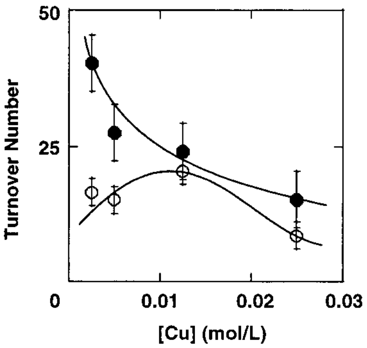

Figure 3. Turnover of complexes **1** (○) and **3** (●) during the catalysis of the oxidative polymerization of 2,6-difluorophenol (0.5 mol/L) in the presence of 2,6-diphenylpyridine (0.25 mol/L) in chlorobenzene for 72 h at 40 °C. Turnover number = [polymer yield (%)] × [monomer]/100[Cu].

due to the strength of the C−F bond compared with that of the aliphatic C−H bond. In the absence of oxygen, poly(2,6-dimethylphenylene oxide) ($M_n = 17\,000$) shows the onset of decomposition near 420 °C[20] followed by a strong exothermic reaction accompanied by a rapid drop in weight of ca. 70% (TGA curve c in Figure 2). In contrast, F_2PPO (amorphous, THF soluble, $M_n = 13\,000$) shows the onset of decomposition near 430 °C followed by only a slight weight loss (7%) (curve b).[21] The crystalline part is even more stable with a weight loss beginning at 480 °C (curve a).

The question arises as to the origin of the catalytic activity. It is considered that the copper(II) atoms in the μ-η^2:η^2 Cu_2O_2 complexes that result from the reaction of Cu(I) and O_2 could be further oxidized according to the resonance, $[Cu^{II}(O_2{}^{2-})Cu^{II}]^{2+} = [Cu^{III}(O^{2-})_2Cu^{III}]^{2+}$.[22] Considering that F_2PPO is obtained only with copper complexes that are able to form the Cu_2O_2 core, the resulting dicopper complexes are likely to provide the oxidizing ability.[23] Although the Cu_2O_2 complexes with peralkylated amine ligands have been isolated only at low temperatures, their intervention in the catalysis was indicated not only by the room-temperature reactions of relevant complexes[11,17] but also by the marked increase in the turnover for **1** capable of forming an intramolecular Cu_2O_2 core even at a low concentration, in contrast to the decrease observed for the mononuclear **3** (Figure 3).

The thermodynamics of blending with other polymers such as polystyrene and further mechanistic studies on the catalysis are the focus of our continuing research.

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(13) ^{1}H NMR (600 MHz, [D_8]THF, TMS): $\delta = 6.90$ (d, $^{3}J(^{19}F, ^{1}H) = 8.65$ Hz). ^{19}F NMR (470 MHz, [D_8]THF, CF_3COOH ($\delta = -76.5$)): $\delta = -124.1$ (d, $^{3}J(^{1}H, ^{19}F) = 8.65$ Hz). ^{13}C NMR (151 MHz, [D_8]THF, TMS): $\delta = 101.5$ (dd, phenyl C3, $^{2}J(^{19}F, ^{13}C) = 21.6$ Hz, $^{4}J(^{19}F, ^{13}C) = 4.41$ Hz), 126.6 (dd, phenyl C1, $^{2}J(^{19}F, ^{13}C) = 15.7$ Hz), 156.8 (dd, phenyl C4, $^{3}J(^{19}F, ^{13}C) = 12.3$ Hz), 157.2 (dd, phenyl C2, $^{1}J(^{19}F, ^{13}C) = 251$ Hz, $^{3}J(^{19}F, ^{13}C) = 6.08$ Hz). IR (KBr): $\nu_{COC} = 1107$ cm^{-1}, $\nu_{CF} = 1219$ cm^{-1}, $\delta_{CH} = 847$ cm^{-1}. Anal. Calcd for $C_6H_2F_2O_2$: C, 56.3; H, 1.57%. Found for THF soluble part: C, 55.4; H, 1.34%. Found for THF insoluble part: C, 55.7; H, 1.44%.

(14) ^{19}F NMR can be used to probe the electron density at the C_2 atom (Figure 1). The low chemical shift indicates that the fluorine substituents would not be amenable to substitution with nucleophiles and that additional electron-withdrawing groups may be necessary to activate them by lowering the electron density at the site of nucleophilic reaction. Carter, K. R. *Macromolecules* **1995**, *28*, 6462.

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(21) The high thermal stability is achieved only with high molecular weight polymers. The lower molecular weight F_2PPO (run 11, $M_n = 4500$) comparable with that of the previous study[4a] showed the onset of decomposition near 380 °C followed by a significant weight loss (15%).

(22) A bis(μ-oxo)dicopper(III) complex has been isolated with 1,4,7-tribenzyl-1,4,7-triazacyclononane as a ligand. Mahapatra, S.; Halfen, J. A.; Wilkinson, E. C.; Pan, G.; Wang,

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(23) The diversity of reaction conditions that may reflect the resonance state of the Cu_2O_2 core makes it difficult to determine the active species. However, in view of the fact that 4-fluorophenol reacts with a $[Cu^{II}(O_2{}^{2-})Cu^{II}]$ complex to give a 4-fluorophenoxocopper(II) complex,[9b] the $[Cu^{II}(O_2{}^{2-})Cu^{II}]$ state is most likely to oxidize 2,6-difluorophenol. This is in consistent with the marked deactivation of the catalyst in THF where generation of a $[Cu^{III}(O^{2-})_2Cu^{III}]$ complex prevails.[9a]

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