

Precision Synthesis of Aromatic Polymers Controlled by Transition Metal Complex Catalyst

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Oxidative polymerization of phenolic monomers and cross coupling polymerization of asymmetrically functionalized monomers are described as the precision synthesis for aromatic polymers controlled by transition metal catalysts. New methodologies, namely radical-controlled oxidative polymerization of phenols with high regioselectivity and asymmetric oxidative coupling polymerization of naphthol derivatives with high stereoselectivity have been developed. For Kumada-Tamao type and Suzuki-Miyaura type cross coupling polymerization, not only the head-to-tail selectivity has been regulated, but also catalyst transfer polycondensation has converted the polymerization growth mechanism from stepwise growth into chain growth.

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Introduction

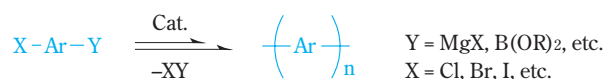
For polymer synthesis, impure structures cannot be eliminated from the polymer chain, so precision in several orders of magnitude more than that for organic synthesis is required. Heat resistance and mechanical strength are reduced remarkably by several percent of structural impurities, and conductivity and light emission are greatly affected by structural impurities in the order of ppm. In order to form ideal high-dimensional structures to achieve a maximum of performance and functionality, polymer synthesis techniques with precise control of one-dimensional structures such as regioselectivity, stereoselectivity, terminal end structures and molecular weight distribution are necessary.

In this paper, we discuss precision synthesis controlled by transition metal catalysts for aromatic polymers which have high performance and high functionality. Oxidative coupling reactions of radicals generated through one electron oxidation, and cross coupling reactions via oxidative addition and reductive elimination are representative of the types of polymerization reactions for aromatic monomers using transition metal catalysts. For the former, we introduce (i) oxidative polymerization of phenolic monomers, and for the latter, (ii) cross coupling polymerization of asymmetrically functionalized monomers (**Scheme 1**)¹⁾.

(i) Oxidative Polymerization of Phenolic Monomers



(ii) Cross-Coupling Polymerization of Asymmetric Monomers

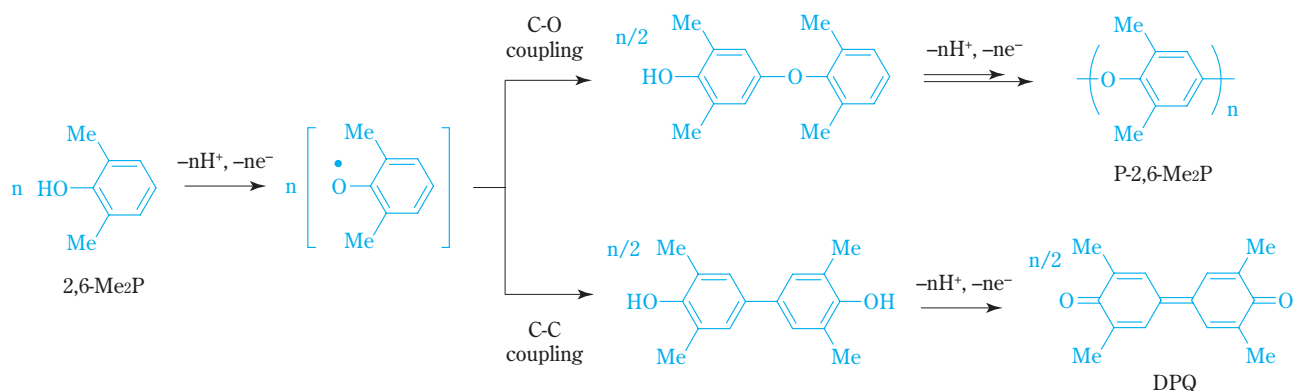


Scheme 1

Oxidative Polymerization of Phenolic Monomers

1. Regioselective oxidative polymerization of phenols

Oxidative polymerization of phenols was discovered by Hay et al. at GE in the latter half of the 1950s.^{2), 3)} By carrying out a reaction on 2,6-dimethylphenol (2,6-Me₂P) at room temperature in an oxygen atmosphere using a copper/amine catalyst, poly-(2,6-dimethyl-1,4-phenylene oxide) (P-2,6-Me₂P) was synthesized²⁾ (**Scheme 2**). P-2,6-Me₂P is known to be completely miscible with polystyrene, and this polymer alloy is widely used as an engineering plastic.³⁾ The reaction mechanism for this polymerization is one electron oxidation of 2,6-Me₂P by the catalyst, followed by C-O



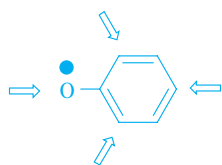
Scheme 2

coupling of the phenoxy radicals to produce P-2,6-Me₂P (if C-C coupling occurs, diphenoquinone (DPQ) is generated). The catalyst is reduced after the coupling, re-oxidized by oxygen, and yields water as a byproduct.

This oxidative polymerization is not only environmentally friendly but also economical, because (a) the reaction temperature is moderate, (b) the product eliminated is only water and (c) halogen compounds are not necessary for the monomers.⁵⁾

Numerous transition metal catalysts, of which copper/diamine catalysts are representative, have been developed as oxidative polymerization catalysts,³⁾ and horseradish peroxidase (HRP) and other enzymatic catalysts have also been reported on.⁴⁾

However, obtaining useful polymers using conventional oxidative polymerization catalysts has been limited to those with 2,6-position substituents for phenols. The reason is that the ortho positions of phenoxy radicals can also become reaction points, so if both ortho positions are open, branching and cross-linking occur, causing a substantial lowering of the polymer properties. In other words, oxidative polymerization of phenols is a low-loading and low-cost method for synthesizing aromatic polyethers, but the range of applications for conventional catalysts is limited.



The authors took a hint from organisms with the function of not generating free radicals and have developed regioselective oxidative polymerization of phenols

using an enzyme model catalyst,⁶⁾ which is described below. In addition, the mechanism for showing C-O/C-C coupling selectivity for 2,6-Me₂P, which has not been clarified, will be also discussed.^{1)a, 6)1}

(1) Design concept for enzyme model catalyst

Up until now, there have also been many reports of research into oxidative polymerization catalysts for phenols that are unsubstituted in the ortho position(s). For example, copper/pyridine catalysts,⁷⁾⁻⁹⁾ copper/diamine catalysts,¹⁰⁾ iron/Schiff base catalysts¹¹⁾ and other transition metal catalysts as well as enzymatic catalysts such as HRP have been examined,¹²⁾ but there are absolutely no examples of success in excluding ortho position coupling using these catalysts.

To solve the difficult problem of why it is impossible for conventional catalysts to control phenoxy radical coupling, we focused on an active oxygen species of oxidation catalyst. As a result, we arrived at the hypothesis that the active oxygen complexes for conventional catalysts are electrophilic or radical, and therefore they take hydrogen atoms from phenols, probably generating free radicals (**Fig. 1**).^{6)a, b} For example, a copper (I)/diamine complex reacts with dioxygen to form a bis (μ -oxo) dinuclear copper (III) complex,¹³⁾ and HRP forms an iron (IV) oxo complex as an active oxygen complex.¹⁴⁾ It has been reported that when these active oxygen species react with phenols, free phenoxy radicals are generated.^{13), 15)}

We considered that the utilization of biological functions might prevent the generation of free radicals that cause deterioration in tissue. From studying the reaction mechanisms of oxidation enzymes, it was reported that a μ - η^2 : η^2 -peroxo dinuclear copper complex (1)¹⁶⁾ (the active oxygen complex of tyrosinase which synthe-

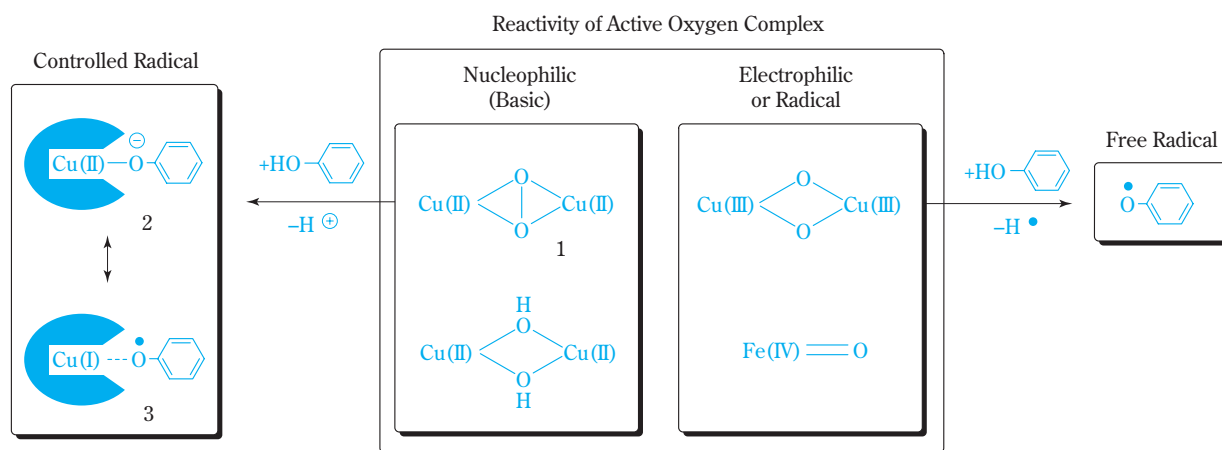


Fig. 1 Working hypothesis for regioselective oxidative polymerization catalyst

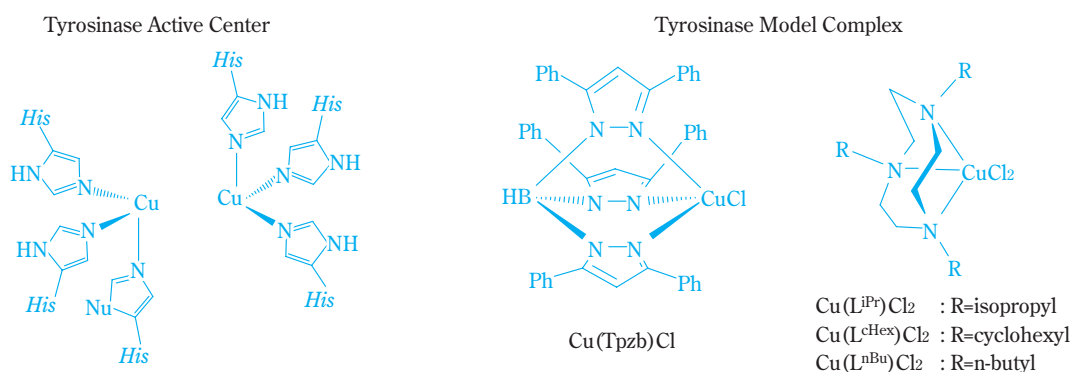


Fig. 2 Tyrosinase active site and its model complexes

sizes melanin pigment from phenol derivatives) is nucleophilic (strictly basic).^{17), 18)}

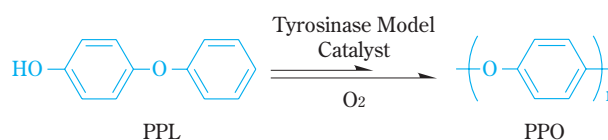
Complex 1 takes protons from phenols to give a phenoxy-copper (II) complex (2) via an acid-base reaction. Complex 2 is equivalent to a phenoxy radical-copper (I) complex (3), where 2 and/or 3 are not “free radicals” but “controlled radicals.” If coupling occurs from the controlled radicals, ortho position coupling should be inhibited by the steric hindrance of the catalyst.

We selected a tyrosinase model complex that forms active oxygen complex 1 for the regioselective oxidative polymerization catalyst. Specifically, this involved a hydro-trispyrazolborate copper complex (Cu (Tpzb) Cl) and a triazacyclononane copper complex (Cu (L^R) Cl₂ where R = isopropyl (iPr), cyclohexyl (cHex) and n-butyl (nBu)) (Fig. 2). A number of oxygen/dinuclear copper complexes have been reported in the field of bioinorganic chemistry,¹⁹⁾ and the present complex are attracting attention as examples of biologically inspired oxidation catalysis.²⁰⁾

(2) Regioselective oxidative polymerization of 4-phenoxyphenol

[1] Dimerization and polymerization of 4-phenoxyphenol

For our first target, we took on the challenge of synthesizing poly (1,4-phenylene oxide) (PPO) using the above oxidative polymerization catalyst.^{6)a-d} There have only been a few reports of synthesizing PPO such as Ullmann condensation of 4-bromophenol,²¹⁾ polymerization of spiro compounds,²²⁾ and electrochemical oxidative polymerization of phenol,²³⁾ and the synthesis has not been possible by oxidative polymerization with conventional catalysts. We first used 4-phenoxyphenol (PPL), which is a phenol dimer, as the starting monomer (Scheme 3).



Scheme 3

Oxidative polymerization of PPL was performed in oxygen (1atm) at 40°C in toluene or THF with Cu (Tpzb) Cl or Cu (L^R) Cl₂ for the catalyst (**Table 1**, entries 1–6). We carried out polymerization with the conventional copper (I) chloride/*N,N,N',N'*-tetraethyl ethylenediamine (CuCl/teed)¹⁰ (entry 7) and tyrosinase enzyme itself (entry 9) as the catalysts. In addition, we carried out a reaction using AIBN as an equivalent oxidant for a modeling system for the free radical coupling (entry 8). The coupling selectivity was evaluated by the ratio of dimer production at the first stage. We found from LC-MS analysis that there were four types of PPL coupling dimer, and the structures were determined by comparing with authentic samples of these dimers (**Fig. 3**). Dimers p-4 and o-4 are based on C-O coupling, and oo-22 and oo-13 are C-C coupling dimers.

The ratios for dimer production at the first stage in the oxidative polymerization of PPL are given in **Table**

1. It is characteristic of the free radical system in entry 8 that the C-C dimers oo-22 and oo-13 are produced in large amounts, and the p-4 selectivity was low (82%). The dimer ratios with the CuCl/teed catalyst in entry 7 are substantially the same as those for the free radical coupling system (entry 8).

Conversely, in the systems using the Cu (Tpzb) catalyst and Cu (L^R) catalyst (entries 1–6), C-C dimers were hardly detected at all except for the Cu (LiPr) catalyst/THF solvent system (entry 4). We found that they showed high p-4 selectivity (90 to 95%). If the free radical coupling occurs, C-C dimers must be generated, so the free radical coupling is almost completely excluded in the present catalysis because almost no C-C dimers were detected. In addition, as the bulkiness of substituent R in the Cu (L^R) catalysts increases from nBu to iPr and cHex, the o-4 dimer decreases to 9, 7 and 5 (%) (entries 6, 3 and 5). This suggests that there is steric inhibition of ortho position coupling by the

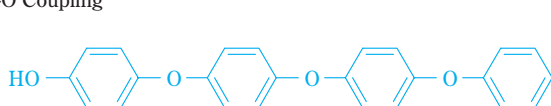
Table 1 Dimer formation of PPL

Entry	Catalyst	Oxidant	Solvent	Time (h)	Conv. (%)	Yield ^{a)} (%)	Dimer ratio (%)			
							p-4	o-4	oo-22	oo-13
1	Cu(Tpzb)Cl ^{b)}	O ₂ ^{e)}	Toluene	0.25	13	9	91	9	0	0
2	Cu(Tpzb)Cl ^{b)}	O ₂ ^{e)}	THF	1.7	11	7	91	9	0	0
3	Cu(L ^{iPr})Cl ₂ ^{b)}	O ₂ ^{e)}	Toluene	0.2	9	8	93	7	0	0
4	Cu(L ^{iPr})Cl ₂ ^{b)}	O ₂ ^{e)}	THF	7.5	12	9	89	7	1	3
5	Cu(L ^{cHex})Cl ₂ ^{b)}	O ₂ ^{e)}	Toluene	0.2	7	7	95	5	0	0
6	Cu(L ^{nBu})Cl ₂ ^{b)}	O ₂ ^{e)}	Toluene	0.2	12	12	90	9	0	1
7	CuCl / teed ^{c)}	O ₂ ^{e)}	Toluene	0.02	17	12	79	6	2	13
8	–	AIBN ^{f)}	Toluene	120	27	15	82	4	2	12
9	Tyrosinase ^{d)}	Air ^{g)}	Acetone/buffer(5/5)	1	14	<0.1	–	–	–	–

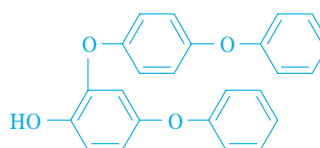
a) Total yield of dimmers. b) Cu complex (5mol%), 2,6-diphenylpyridine. c) CuCl (5mol%), teed. d) Enzyme (2wt%).

e) Under dioxygen at 40°C. f) Oxidized by AIBN under nitrogen at 40°C. g) Under air at 25°C.

C-O Coupling

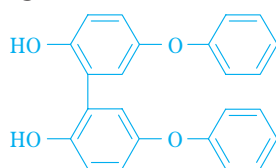


p-4

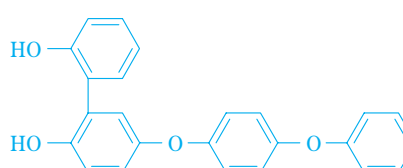


o-4

C-C Coupling



oo-22



oo-13

Fig. 3 Oxidative coupling dimers from PPL

substituent groups on the catalyst.

After completion of the reaction, a large excess of methanol was added, and the polymer was isolated as the methanol-insoluble part. When C-C dimers did not arise at the first stage (entries 1–3, 5 and 6), white polymers with molecular weights of 700 to 4700 were obtained, and we found from NMR and IR analysis that they mainly had 1, 4-phenylene oxide structures. Furthermore, we found from DSC analysis that the melting points (Tms) of the polymers were 171 to 194°C, showing crystallinity. This result was the first example that crystalline PPO can be synthesized by catalytic oxidative polymerization.

On the other hand, when C-C dimers were generated (entries 4, 7 and 8), we did not observe any melting points in the polymers obtained. The C-C coupling structures reduced the polymer crystallinity remarkably. Moreover, in the tyrosinase catalyst system (entry 9), almost no products of oxidative coupling were detected, and only a blackish brown insoluble material was obtained.

It is known that if the molecular weight of PPO is sufficiently extended, it has a Tm of 298°C,²¹⁾ and we can expect that it would be a super engineering plastic that can compete with poly (1, 4-phenylene sulfide) (PPS), which has a Tm of 285°C.

The reason why the molecular weight of PPO synthesized in this oxidative polymerization is low is that PPO precipitates from the reaction solvent during polymerization owing to the high crystallinity. As a result of investigations into the reaction temperature and reac-

tion solvent, we were able to increase the molecular weight to a maximum of 8100.^{6)c}

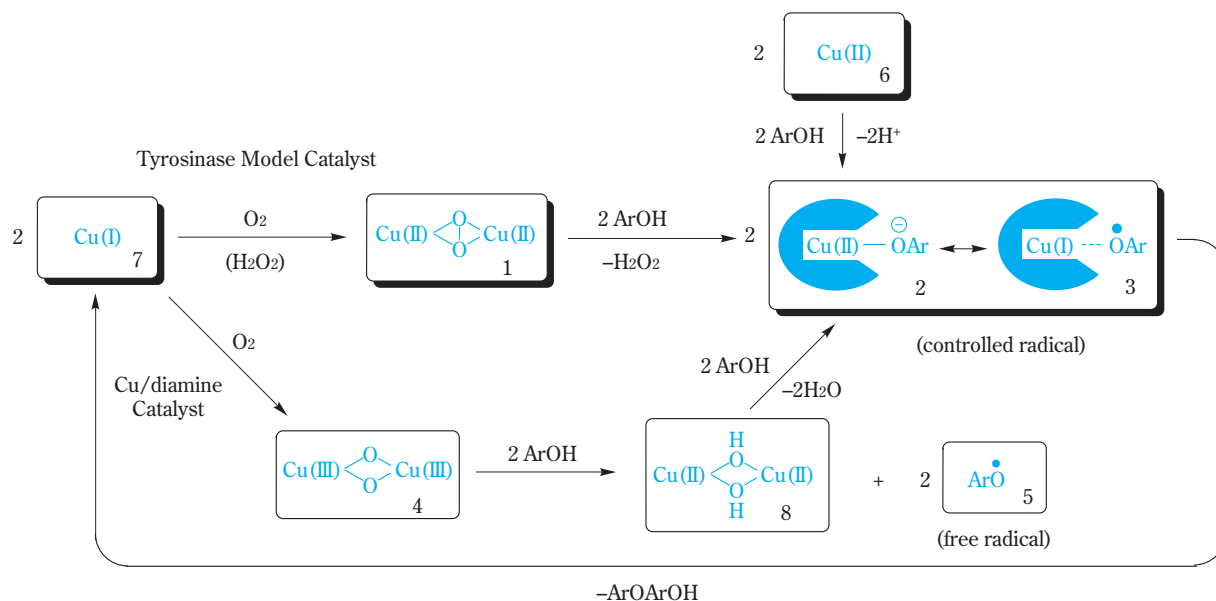
However, study into further increasing the molecular weight is necessary for achieving a sufficient mechanical strength.

[2] Reaction mechanisms for catalytic cycle and chain extension

The presumed reaction mechanism for the catalytic cycle (**Table 1**, entries 1–3, 5 and 6) is shown in **Scheme 4**. First, Cu (II) Cl reacts with PPL to form a phenoxo-copper (II) complex (2) via ligand exchange. This is equivalent to a phenoxo radical-copper (I) complex (3) (controlled radical). In the static state, the contribution of 2 is dominant, but in the reaction, the contribution of 3 appears dynamically, leading to radical coupling. (The reaction mechanism for coupling of controlled radicals is discussed later.)

A copper (I) complex (7) is generated after coupling, but the most important feature of this catalyst is that if 7 reacts with oxygen, only basic $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$ dinuclear copper (II) complex (1) is formed.^{16), 24)} Complex 1 reacts with 4-fluorophenol and gives rise to the phenoxo-copper (II) complex,^{17), 18)} and it is known that if it then reacts with an acid, hydrogen peroxide is produced.²⁴⁾ It can be assumed that the controlled radical is reproduced along with the hydrogen peroxide by the reaction of 1 and PPL. Moreover, it has been confirmed that if hydrogen peroxide is reacted with 7, 1 is formed.^{6)a, b}

Since all of the coupling occurs through the con-



Scheme 4

trolled radical in this catalytic system, the catalyst can control the coupling exclusively. We referred to this as “radical-controlled oxidative polymerization” to indicate oxidative polymerization where phenoxy radicals can be completely controlled by the catalyst.

When we carried out ESR analysis with the PPL oxidative polymerization in a steady state,^{6g} a mononuclear copper (II) complex that was different from the starting Cu (II) Cl was detected, and it was almost the same as the complex obtained by the reaction with 4-fluorophenol. The complex detected in the steady state was presumed to be a phenoxo-copper (II) complex, and along with this structure being supported, it can be assumed that the rate-determining step is coupling by the controlled radical.

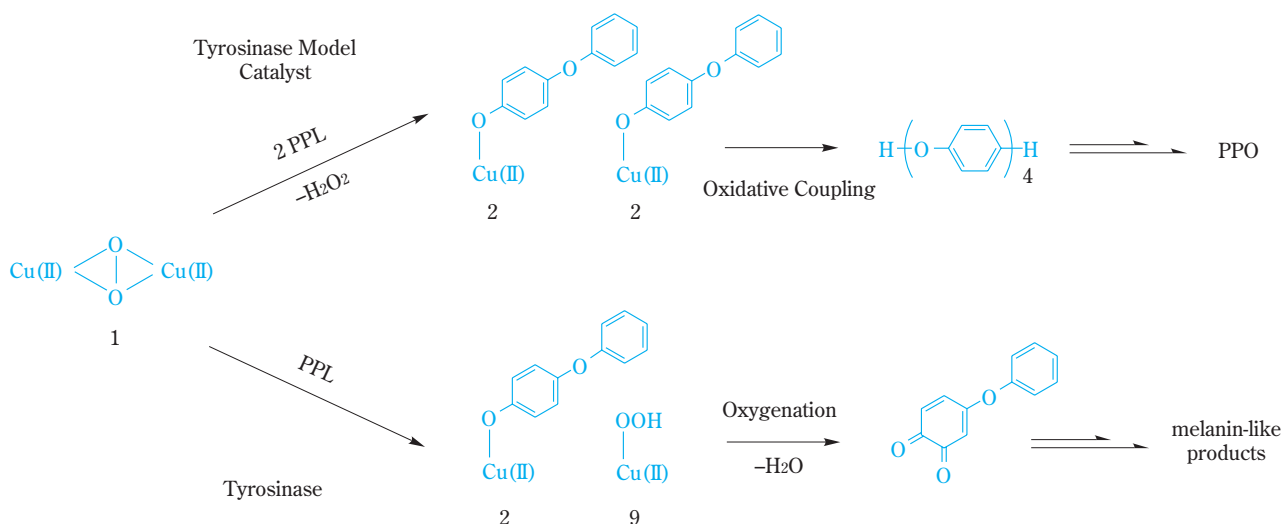
In computational analysis of the catalytic cycle mechanism, there has been another mechanism proposed by another group,²⁵ but their results could not explain the experimental data sufficiently. When the energy of the optimized structure for various reaction intermediates was calculated and the validity of the reaction route was evaluated, we obtained the results that supported the above mechanism.^{6e}

On the other hand, with the Cu/teed catalyst (entry 7), it has been reported that 7 reacts with oxygen to give a bis (μ -oxo) dinuclear copper (III) complex (4).¹³ In addition, it is also known that the Cu (L^{Pr}) catalyst gives rise to 4 in a THF solvent (entry 4).²⁶ If 4 is reacted with a phenol, hydrogen atoms are removed, and free radicals (5) and a bis (μ -hydroxo) dinuclear copper (II) complex (8) are formed.²⁴ Although the reaction of 8 with phenol gives the controlled radicals, the catalytic cycle always includes a process that gen-

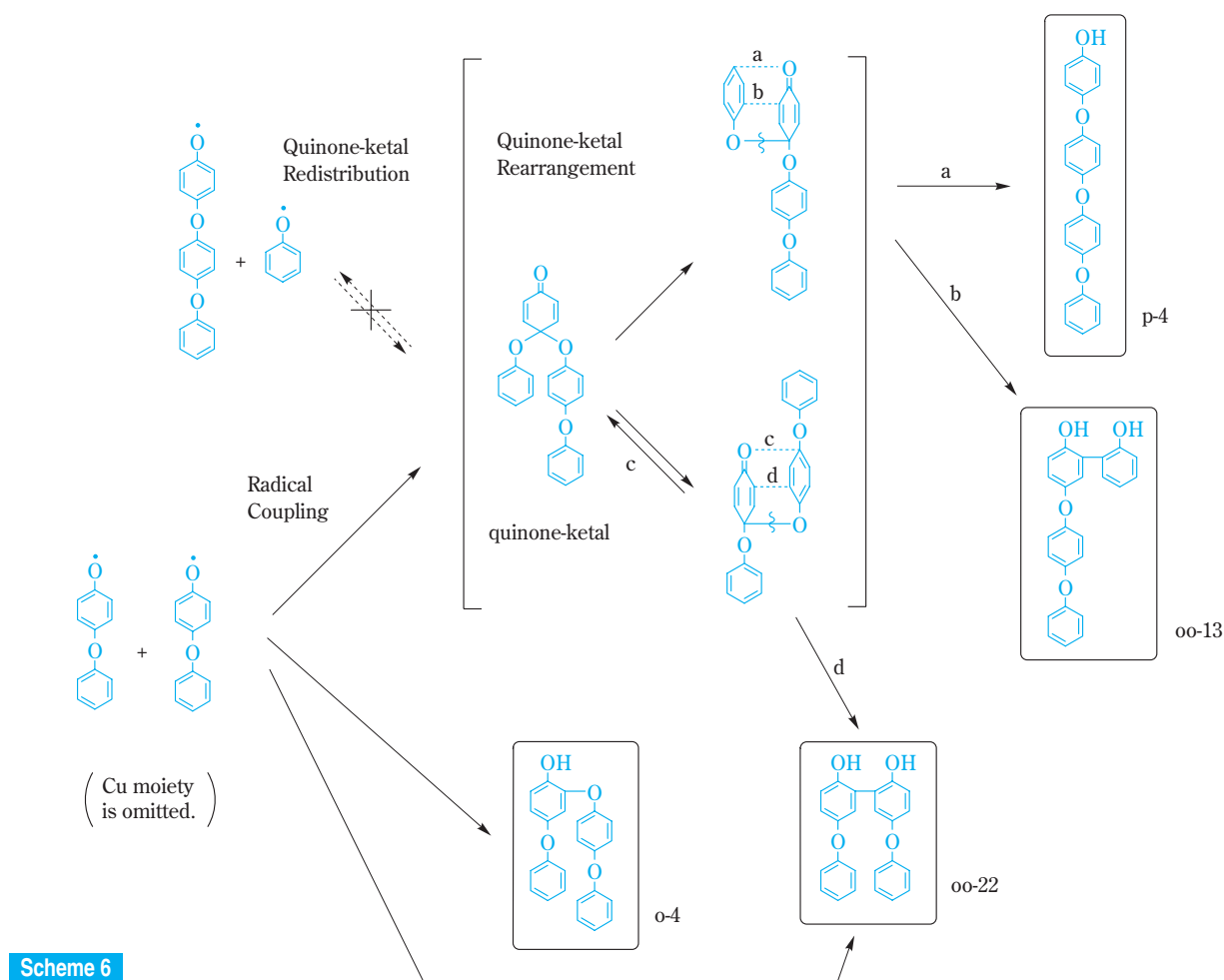
erates free radicals.

The difference between the tyrosinase enzyme (entry 9) and its model complex can be explained as follows (**Scheme 5**). We presume that only one molecule of PPL can come into proximity with the tyrosinase enzyme because of the restriction of its reaction pocket, so 2 and a hydroperoxo-copper (II) complex (9) are generated, followed by an oxygenation reaction.¹⁷ However, the model complex does not have this restriction, so two molecules of PPL can react with 1 to give two molecules of 2, leading to oxidative coupling reaction. In other words, for the highly selective oxidative coupling catalyst, it is necessary only to have the function of forming μ - η^2 : η^2 -peroxo complex, and it can be said that use of its model complex where that function alone is extracted is the main point.

The polymerization growth mechanism for PPL is shown in **Scheme 6**. The copper complex interacts with the controlled radical, but the copper complex part is omitted here for simplicity. First, two molecules of the phenoxy radical are coupled (the reaction mechanism to be described later), but since the contribution of the radicals is only at the phenol unit (conjugation by ether bonding being cut off, and there being no contribution by the radicals to the 4-phenoxy unit), quinone ketal, o-4 or oo-22 are generated. With this catalyst, quinone ketal is selectively generated because of the inhibitory effect on ortho position reactions. Next, two types of mechanism have been proposed for the reaction from quinone ketal, namely a rearrangement mechanism and a redistribution mechanism, but for PPL, absolutely no trimers are detected, so the reaction follows the former mechanism.⁸ There



Scheme 5



is a possibility that p-4 (a), oo-13 (c) or oo-22 (d) will arise from the rearrangement reaction of quinone ketal, but this catalyst specifically produces only p-4. It can be assumed that this catalyst not only works in the radical coupling process but also in the quinone ketal rearrangement process.^{6)c} From the above fact, it is possible to control the regioselectivity in the polymer by the interaction of this catalyst only with the reaction sites for the radical coupling and the quinone ketal rearrangement.

(3) Regioselective oxidative polymerization of other phenols

[1] Substituent effects of phenols

With this polymerization, we should also be able to synthesize polyphenylene oxides with high selectivity from phenols that do not have substituents in ortho positions, so we investigated applications to other phenols.^{6)f-k} We used phenol (PL), 3-methylphenol (3-MeP), 2-methylphenol (2-MeP), 2,5-dimethylphenol (2,5-Me₂P), and 2,6-Me₂P as the monomers and used Cu (LⁱPr) Cl₂ as the catalyst.^{6)f} For comparison, we used

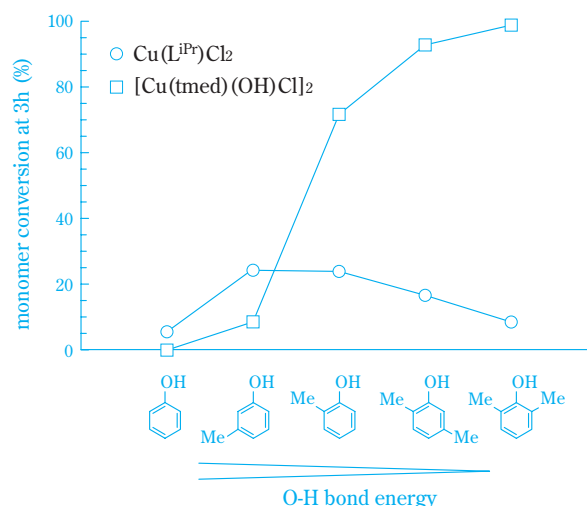


Fig. 4 Initial reaction rates in oxidative polymerization of phenols by the Cu(LⁱPr) or Cu(tmed) catalyst

the representative conventional catalyst [Cu (N,N,N',N'-tetramethyl ethylenediamine) (OH) Cl]₂ ([Cu (TMED) (OH) Cl]₂). The results of examining the initial reaction rates are shown in Fig. 4.

For the Cu (tmed) catalyst, the reaction rate increased as the O-H bond energy for the phenols became smaller. This catalyst gives rise to bis (μ -oxo)-dinuclear copper (III) complex 4 for the oxygen activated species; the process by which 4 abstracts hydrogen atoms from phenols is thought to be rate-determining.

On the other hand, with a Cu (LiPr) catalyst, we found that when the number of methyl groups in the ortho positions increases, the reaction rate decreases, even if the O-H bond energy of the phenols becomes lower. For this catalyst, $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$ dinuclear copper (II) complex 1 reacts with phenols to give controlled radicals, and then, ortho position substituents would prevent the formation of controlled radicals. These results also support the catalyst cycle mechanism described previously.

[2] Regioselective oxidative polymerization of phenol

PPL is an expensive monomer, and to achieve cost competitiveness with PPS, it is desirable to use inexpensive PL as the starting material. When we carried out oxidative polymerization of PL using this catalyst^{6g} (Table 2), we confirmed that high selectivity for para and C-O coupling (PPL selectivity) was obtained. However, a large amount of C-C coupling occurred (the reason to be described later), and the obtained polymer did not show crystallinity. We are considering a two-step process, oxidative coupling of PL^{6m} to PPL and subsequent oxidative polymerization of PPL to PPO.

[3] Regioselective oxidative polymerization of monomethylphenol

If Cu (L^{Pr}) is used in the oxidative polymerization of 2-MeP, a white polymer with a molecular number of 3800 is obtained, and it mainly has a 2-methyl-1,4-phenylene oxide structure.^{6)h} With a Cu (TMED) catalyst, a brown polymer with a molecular number of 4100 is obtained, and this polymer contains ortho branches.

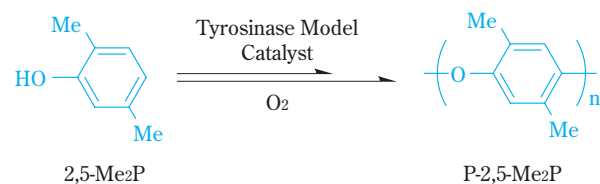
As with PL, 3-MeP has a comparatively high oxida-

tion potential, and up until now almost no polymers have been obtained with oxygen-oxidative polymerization. From oxidative polymerization of 3-MeP using the Cu (L^{iPr}) catalyst, we obtained a pale yellow poly (phenylene oxide) which had a high molecular weight of Mn=40,000.⁶ⁱ The Cu (L^R) complex has a triangular pyramid structure, and because of the Jahn-Teller effect, the Cu (II) species that favors the planar structure is made unstable, so the oxidation-reduction potential for Cu (I)/Cu (II) becomes high. In other words, the Cu (II) species for the Cu (L^R) complex has a high level oxidation ability, so it can be assumed that this species is capable of oxidative polymerization of phenols with high oxidation potential such as PL and 3-MeP.

The polymers obtained from 2-MeP and 3-MeP exhibited absolutely no crystallinity.

[4] Regioselective oxidative polymerization of dimethylphenol

Among these other phenols, one that deserves special mention is 2,5-Me₂P. From oxidative polymerization of 2,5-Me₂P using this catalyst, we found a new crystalline poly (2,5-dimethyl-1,4-phenylene oxide) (P-2,5 Me₂P)^{6j} (**Scheme 7**). When we polymerized 2,5-Me₂P in the presence of Cu (LⁱPr) (monomer to 5 mol%) in toluene at 40°C under oxygen (1 atm), we obtained a white polymer as the methanol-insoluble part. This polymer barely dissolved in normal organic solvents, but at 150°C, it completely dissolved in *o*-dichlorobenzene. From GPC analysis, the polymer had a molecular



Scheme 7

Table 2 Dimer formation of PL

Entry	Oxidation system	Time (h)	Conv. (%)	Yield ^{a)} (%)	Dimer ratio				
					PPL	o-2	pp-2	po-2	oo-2
1	Cu(tacn)Cl / O ₂ ^{b)}	1	2.8	0.14	62	3	5	21	8
2	AIBN ^{c)}	71	3.8	0.35	15	14	2	48	21

a) Total yield of dimers: 4-phenoxyphenol (PPL), 2-phenoxyphenol (o-2), 4,4'-diphenol (pp-2), 4,2'-diphenol (po-2), 2,2'-diphenol (oo-2).

b) Oxidative coupling of phenol catalyzed by Cu(tacn)Cl₂ (0.5 mol%) and 2,6-diphenylpyridine in toluene under dioxygen at 40°C.

c) Oxidative coupling of phenol oxidized with AIBN in toluene under nitrogen at 40°C.

weight of 19,300, and from NMR analysis, it had a 1,4-phenylene oxide structure. In addition, from DSC analysis, the melting point of the polymer was observed to be 300°C or more in both the first scan and the second scan (T_m up to 305°C).

A melting point of approximately 240°C after methanol-precipitation of P-2,6-Me₂P is observed, but once P-2,6-Me₂P is melted, even after being slowly cooled and annealed, it does not crystallize again.²⁷⁾ Whether or not thermoplastic polymers show crystallinity after melting and molding is important in terms of practicality, so P-2,6-Me₂P is classified as a noncrystalline polymer. In this sense, P-2,5-Me₂P is a crystalline polymer with completely different characteristics from the conventional P-2,6-Me₂P.

For a thermoplastic polymer with a T_m that exceeds 300°C, poly (1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylene carbonyl) (PEEK) has a T_m of 334°C, and even though it is extremely expensive, it has almost exclusive possession of the market for this class of polymers. Compared to PEEK, the T_m of P-2,5-Me₂P is slightly lower but is still at almost the same level. If we consider the fact that the production costs will be much lower, we can expect a high level of cost performance for this polymer.

However, since the crystallinity of P-2,5-Me₂P is high in the same way as for PPO and since the polymer precipitates from the reaction solvent during polymerization, it prevents increases in molecular weight, needing some methods of further increasing the molecular.

Recently it has been found that crystalline P-2,5-Me₂P is obtained even if a copper/amine catalyst attached into mesoporous material²⁸⁾ or copper/2-arylpyridine catalyst²⁹⁾ is used.

By the way, if 2,6-Me₂P is used for this catalysis, it mainly yields C-C coupled DPQ (with the reason described below).^{1)a}

[5] Controlled radical coupling mechanism

The differences in the coupling selectivities for various phenol monomers can be explained in terms of the presumed mechanism for the controlled radical coupling reactions as follows (Fig. 5).^{1)a} When two molecules of the controlled radicals come into proximity with each other, their highly bulky copper complex parts separated as far as possible. If the reaction first occurs at location A, C-C coupling arises in the para positions. When it approaches location B, C-O coupling occurs in the para positions. At the more proximate

location C, C-O and C-C coupling arises at the ortho positions, but because of the steric hindrance of the copper complex parts, coupling at location C tends to be depressed.

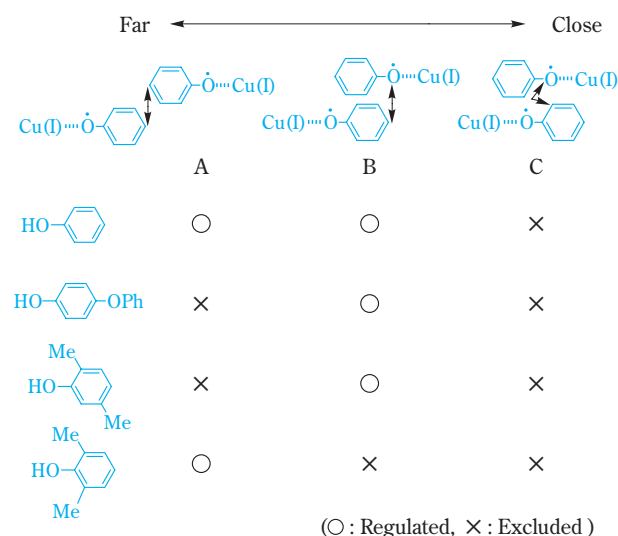


Fig. 5 Reaction mechanism of coupling from controlled radicals of PL, PPL, 2,5-Me₂P, and 2,6-Me₂P

In the case of PL, locations A and B are possible, and in addition to C-O coupling occurring at para positions, C-C coupling also occurs at para positions. With PPL and 2,5-Me₂P, location A is excluded because of the steric repulsion of the 4-phenoxy group and 5-methyl group respectively, so the coupling arises from location B with C-O type at the para positions. With 2,6-Me₂P, location B becomes unstable because of the steric constraints of the 2,6-dimethyl group, and the C-C coupling at the para positions from location A becomes the main reaction.

As per the above, this catalyst has the function of inhibiting ortho position coupling, but it does not have the function of distinguishing between C-O and C-C for para positions. We are currently designing catalysts that can not only show para/ortho selectivity, but which can also show C-O/C-C selectivity.

(4) Mechanism for coupling selectivity of 2,6-dimethylphenol

As has been described up to this point, conventional oxidative polymerization catalysts appear to generate free radicals, but with oxidative polymerization of 2,6-Me₂P, P-2,6-Me₂P is obtained selectively (Scheme 2). The mechanism for the selectivity of C-O (P-2,6-

Me₂P)/C-C (DPQ) selectivity has not yet become clear during the approximately half century since Hay's discovery, and we are also working on elucidating this problem.^{1)a, 6)l}

[1] Controlled radical coupling mechanism

As a result of experiments where DPQ was the principal product obtained from oxidation reactions of 2,6-Me₂P using ferricyanide salts³⁰⁾ and benzoyl peroxide,³¹⁾ many researchers presumed that the free radical coupling is C-C selective and that coupling from the controlled radicals must be what is needed to make it C-O selective (Scheme 8 (b)).^{6)l}

However, products which seemed to be P-2,6-Me₂P were also obtained with ferricyanide salt systems,³⁰⁾ and with benzoyl peroxide systems, a different mechanism where benzoyl perester intermediates are formed has been proposed.³²⁾ In other words, one might think that there was a misunderstanding in the experimental results described above. As is discussed previously, the coupling from controlled radicals would be C-C selective.

[2] Ion coupling mechanism

Reedijk has proposed an ion coupling mechanism where phenol undergoes nucleophilic coupling to two-electron oxidized phenoxonium cations as the mecha-

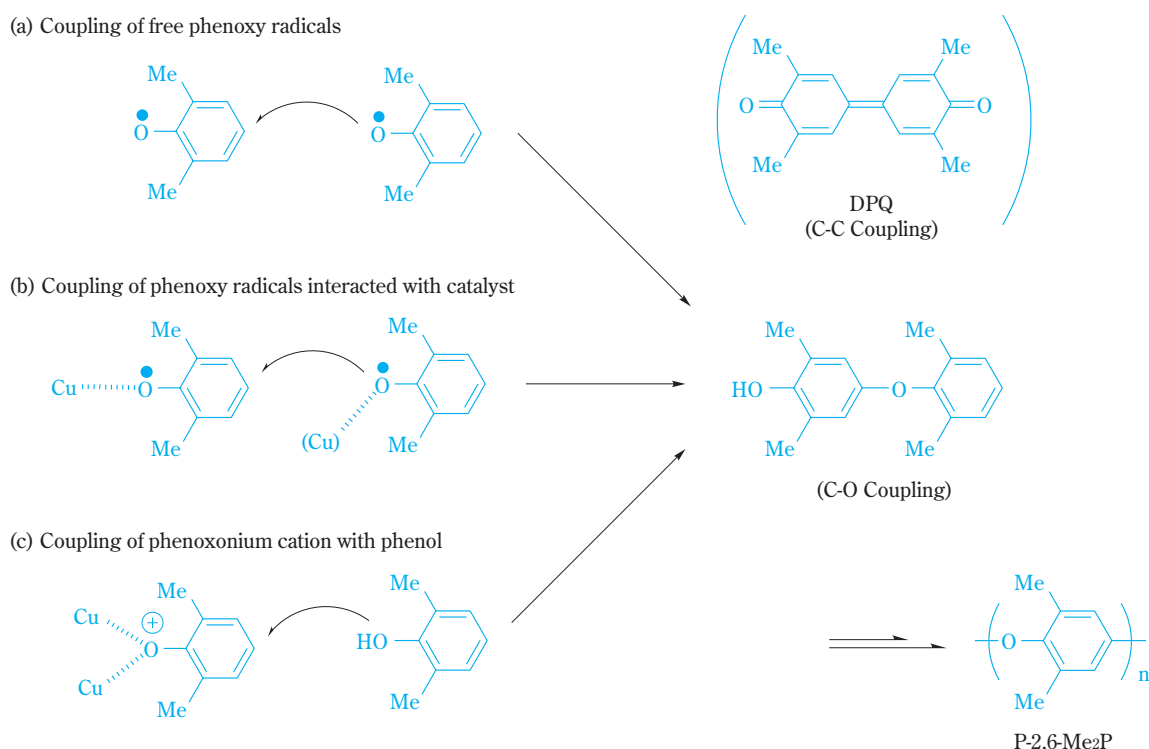
nism for the C-O selectivity of 2,6-Me₂P (Scheme 8 (c)).³³⁾

However, even if primary amines, which are more highly nucleophilic than 2,6-Me₂P, were present in excessive quantities, the production of P-2,6-Me₂P was not inhibited, so we can assume that the ion coupling mechanism can be eliminated.^{6)l}

[3] Free radical coupling mechanism

We established the hypothesis that if either an acid is present or a base is present during the free radical coupling of 2,6-Me₂P (Scheme 8 (a)), C-O/C-C selectivity may be controlled. We carried out the test using the free radical coupling model, and the following results were found; the system with no additive produced DPQ and P-2,6-Me₂P at a ratio of 1:1, but if an acid was added, only DPQ was yielded, and with an amine additive, only P-2,6-Me₂P was obtained.^{6)l} From these results, we can assume that for the free radical coupling of 2,6-Me₂P, P-2,6-Me₂P via C-O coupling is produced in the presence of a base and DPQ via C-C coupling is produced in the presence of an acid.

With respect to the 2,6-Me₂P radical coupling mechanism, we carried out analysis using computational chemical methods, and made estimates as follows (Fig. 6).^{1)a} First of all, we can consider coupling occurring in a "completely free" radical state under basic conditions



Scheme 8

(Fig. 6 (a)). Since the interaction of the σ orbital of the oxygen atom with the π orbit of the carbon atom is bent at the location of the C-O coupling, the benzene rings are separated from each other, showing almost no steric repulsion. However, if the π orbitals of the two carbon atoms interact with each other at the C-C coupling location, steric repulsion arises between the benzene ring and the hydrogen atom in the para position. Therefore, C-O coupling is dominant under basic conditions. On the other hand, under acidic conditions, we can consider the coupling of radicals interacting with acid or phenol (Fig. 6 (b)). The phenol that interacts with the radical causes large steric repulsion at the C-O coupling location, but there is almost no effect at the C-C coupling location. Therefore, conversely, C-C coupling has the advantage under acidic conditions.

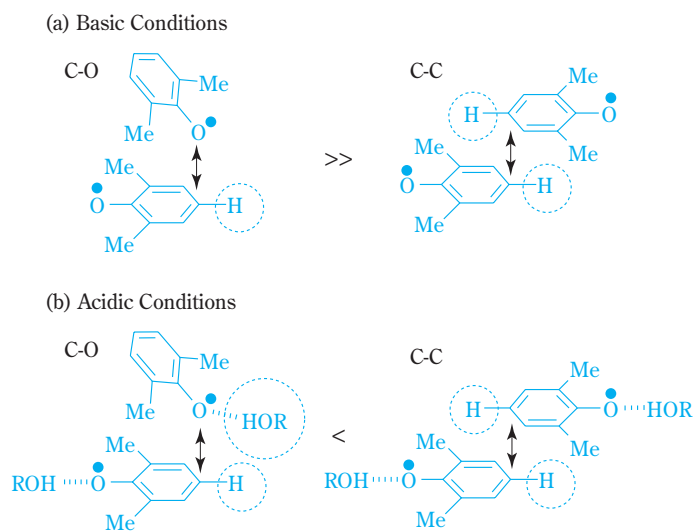
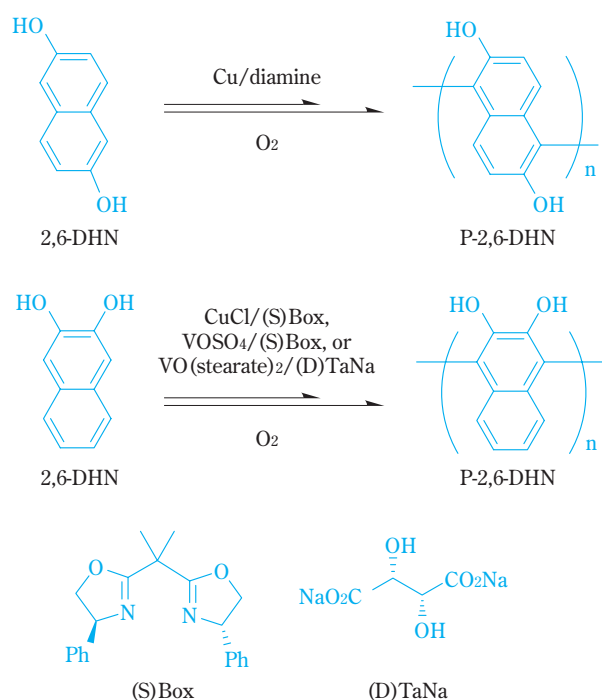


Fig. 6 Reaction mechanism of coupling from free radicals of 2,6-Me₂P in (a) basic and (b) acidic conditions

We can assume that the C-O selectivity of 2,6-Me₂P, which has been discussed for over a half century, is determined by a simple mechanism that is based on completely free radical coupling in basic conditions.

2. Oxidative polymerization of naphthols

In oxidative polymerization (Scheme 9) of β -naphthol monomers, the C-C coupling at the α -position arises selectively for reasons based on the monomer structures. Ueda et al. and Suzuki et al. have reported regioselective polymerization using a copper/diamine catalyst,^{34)–36)} and poly (2,6-dihydroxy-1,5-naphthalene) (P-2,6-DHN) has been synthesized from 2,6-dihydroxynaphthalene (2,6-DHN).



Scheme 9

In addition, axial asymmetry arises in naphthalene polymers where the α positions are C-C coupled because of a rotational barrier in the main chain.

Habaue et al. have discovered “asymmetric oxidative coupling polymerization” of a naphthol derivative using an optically active catalyst.^{37), 38)} When oxidative polymerization of 2,3-dihydroxy naphthalene (2,3-DHN) was carried out using CuCl/(S) box catalyst, poly (2,3-dihydroxy-1,4-naphthalene) (P-2,3-DHN) with a molecular weight of 27,000 and a specific optical rotation of -40 was obtained. From the results of dimer model reactions, optical selectivity is estimated to be approximately 40% ee, and we can understand this selectivity if we assume that approximately half of the reaction mechanism for the copper/diamine catalyst gives rise to free radicals described previously.

As a result of collaboration research with Habaue into asymmetric oxidative polymerization catalysts for 2,6-DHN,³⁹⁾ P-2,3-DHN where the specific optical rotation of 2,6-DHN was +140 was obtained using a VOSO₄/(S) box catalyst, and from dimer analysis at the initial stages of polymerization, it was found that the optical selectivity was 80% ee.^{39)a} This is the same (S) box ligand, but the P-2,3-DHN obtained with the copper catalyst and vanadyl catalyst have opposite optical rotation signs, and therefore, the reaction mechanisms would be different. Furthermore, it has been found that when a VO (stearate)₂/(D)TaNa catalyst is used, the

initial optical selectivity reaches 88% ee.^{39)b} The reaction solvent for VOSO₄/(S) box catalysis was preferably a solvent that contains an alcohol, which is not preferable for VO (stearate)₂/(D)TaNa catalysis. Because for the latter catalysis, the optical selectivity disappeared in alcohol-containing solvents, so hydrogen bonding would play an role in showing the selectivity. We have nearly come to understand the mechanism with copper catalysts, but we do not understand it with vanadyl catalysts yet.

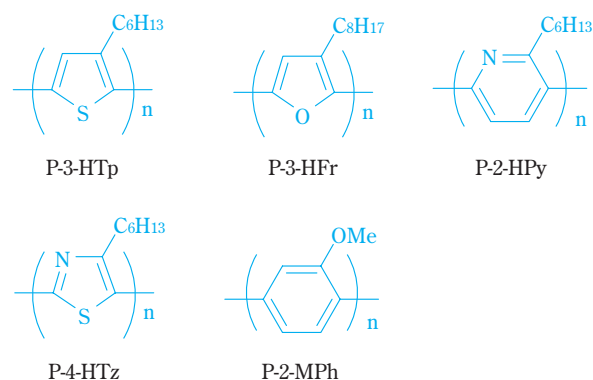


Fig. 7 Head-to-tail regulated polymers

Cross Coupling Polymerization

1. Cross coupling polymerization of asymmetric monomers

Cross coupling reactions using transition metal complex catalysts, and in particular reactions that form C-C bonds, are technology that could be called a Japanese specialty. In the latter half of the 1970s, Yamamoto et al. first synthesized polymers from Mg-containing monomers using Kumata-Tamao coupling,⁴⁰⁾ and in the latter half of the 1980s, Suzuki-Miyaura coupling polymerization of boronate-containing monomers was reported.⁴¹⁾ In terms of cross coupling polymerization, the method of using at least two monomers that have been symmetrically functionalized ($M-Ar^1-M + X-Ar^2-X \rightarrow -(Ar^1-Ar^2)_n-$) is in wide general use because of the easiness for monomer synthesis. On the other hand, the method of using asymmetrically functionalized monomers ($M-Ar-X \rightarrow -(Ar)_n-$), although the monomer synthesis is somewhat difficult, can regulate the orientation for polymerization extension, so it is possible to control the one-dimensional structures more precisely.

The research on cross coupling polymerization of asymmetric monomers that first attracted attention was the improvement by more than 100 times in the mobility of poly (3-hexyl-2,5-thiophene) (P-3-HTp, **Fig. 7**) that underwent head-to-tail (HT) regulation over random forms.⁴²⁾ In 1992, HT-regulated P-3-HTp was obtained by Kumata-Tamao⁴³⁾ cross coupling polymerization using Mg-containing monomers and Negishi⁴⁴⁾ cross coupling polymerization using Zn-containing monomers, which were 3-alkylthiophene monomers halogenated and metalated at the 2- and 5- positions, respectively. Taking this research as an opportunity, HT-regulated polymers having furan (P-3-HFr)⁴⁵⁾ and pyridine (P-2-HPy)⁴⁶⁾ structures were synthesized.

In recent years, the conjugated aromatic polymers

obtained by cross coupling polymerization have been applied to photoelectric functional materials. Specifically, the polymers show characteristics such as (a) printability, (b) flexibility, (c) intramolecular charge mobility, and (d) self-assembly of higher dimensional structures, prompting applications in areas such as organic electroluminescent materials, organic transistor materials and organic photovoltaic materials.

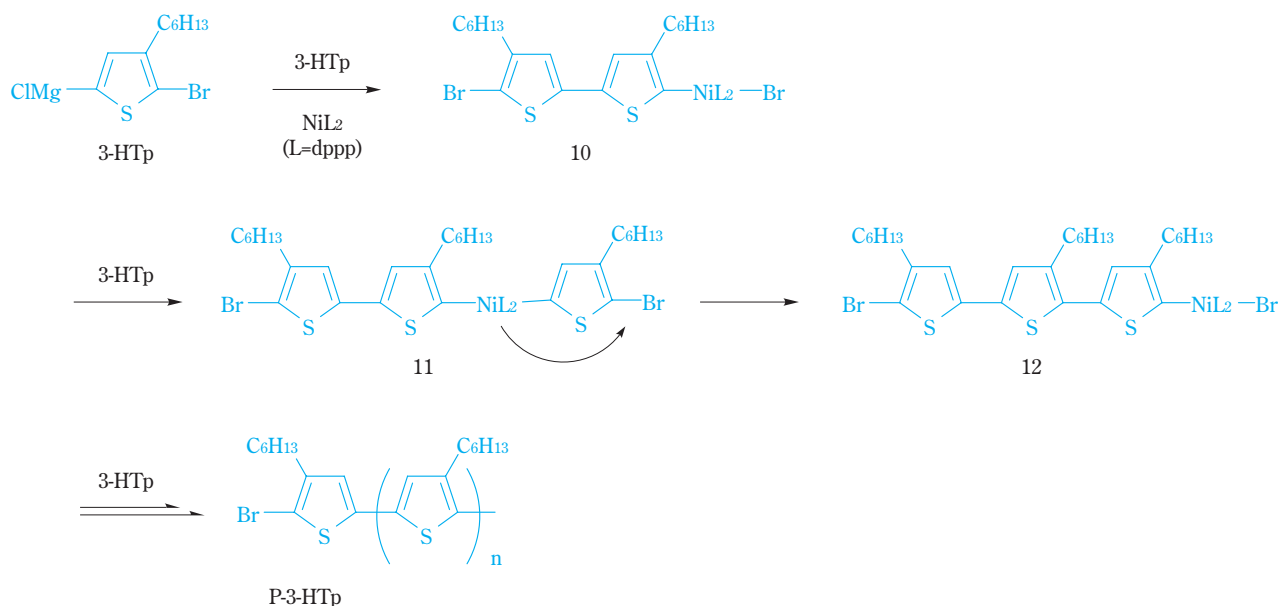
The authors have also focused on cross coupling polymerization of asymmetric monomers from the standpoint of precise regulation of the one-dimensional structures for photoelectric materials.⁴⁷⁾ In Kumata-Tamao coupling polymerization, the functional groups of the monomer were preferentially selected, and hence, poly (4-hexyl-2,5-thiazole) (P-4-HTz) was obtained from 2-chloro-4-hexyl-5-iodothiazole.^{47)a} Asymmetric monomers were also used in Suzuki-Miyaura coupling polymerization, and HT-regulated poly (2-methoxy-1,4-phenylene) (P-2-MPh) was synthesized.^{47)b} In addition, functional groups may be left only on one terminal end in the polymerization of an asymmetric monomer, followed by that of another asymmetric one, leading to the production of an aromatic diblock polymer.^{47)c} Furthermore, after a partial halogenation of the main chain of an aromatic polymer, an aromatic graft polymer can be synthesized without cross-linking by the graft-polymerization of another asymmetric monomer.^{47)d}

2. Chain-growth polycondensation by cross coupling polymerization

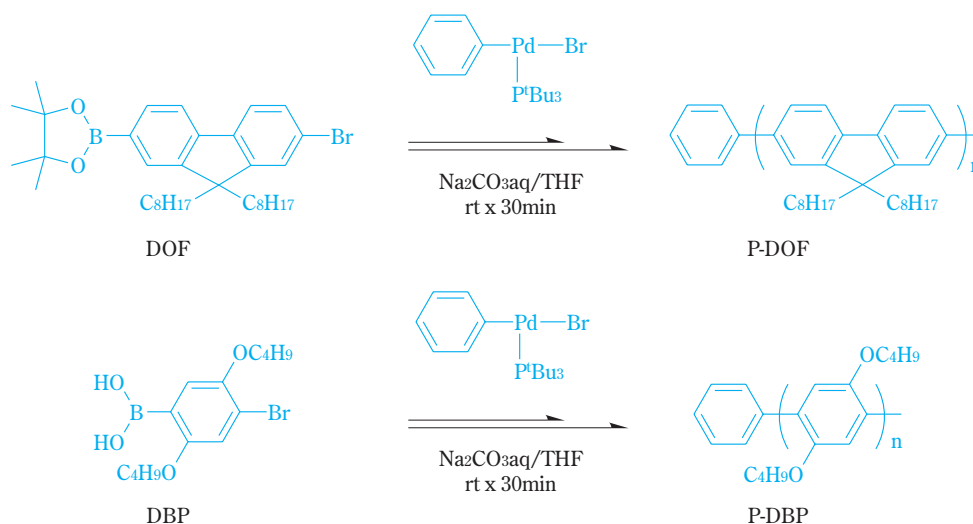
Recently, Yokozawa et al.⁴⁸⁾ have discovered that Kumata-Tamao coupling polymerization of asymmetric monomers can be converted from stepwise growth types to chain-growth types. This reaction mechanism⁴⁹⁾ (**Scheme 10**) first involves 10, which is an ini-

tiator, from the reaction of two molecules of thiophene monomer (3-HTp) with NiL_2 ($\text{L} = 1,3\text{-bis (diphenylphosphino) propane (dppp)}$) catalyst. Ni-aryl complexes are generally unstable, so the initiator cannot be externally introduced from the outside, although it can be formed within the reaction system. After the 3-HTp reacts with 10 to generate 11, the Ni complex migrates intramolecularly to produce 12, followed by chain extension reactions. This polymerization method is called “catalyst transfer polycondensation,” and it behaves like living chain growth polymerization. Similar polymers with substituents containing ethers⁵⁰⁾ and phenylene units⁵¹⁾ can be obtained. In addition, polymers regulated on one terminal end⁵²⁾ and diblock polymers⁵³⁾ can also be synthesized.

In collaboration with Yokozawa, the authors examined the application of this polymerization method to Suzuki-Miyaura cross coupling, and consequently, we were successful in achieving living chain-growth polycondensation using a Pd catalyst as the external initiator.⁵⁴⁾ When we polymerized asymmetric fluorene monomer (DOF) in the presence of a $\text{Ph-Pd (Br) -P}^t\text{Bu}_3$ catalyst (5 mol%)⁵⁵⁾ in $\text{THF}/\text{Na}_2\text{CO}_3$ aq. and under argon atmosphere at room temperature, a monodispersed polyfluorene (P-DOF) with $M_n = 17,700$ and $M_w/M_n = 1.33$ was synthesized (**Scheme 11**).^{54)a, b} In addition, when phenylene monomer (DBP) was polymerized in the same manner, a polyphenylene (P-DBP) was obtained. The points in this polymerization are that P^tBu_3 is used as



Scheme 10



Scheme 11

the Pd complex ligand for showing intramolecular migration and that the Pd complex initiator is so stable that it can be externally introduced.

It was confirmed with MALLDI-TOF-MS of P-DOF that the phenyl group from the initiator bonded to one terminal end (Fig. 8).

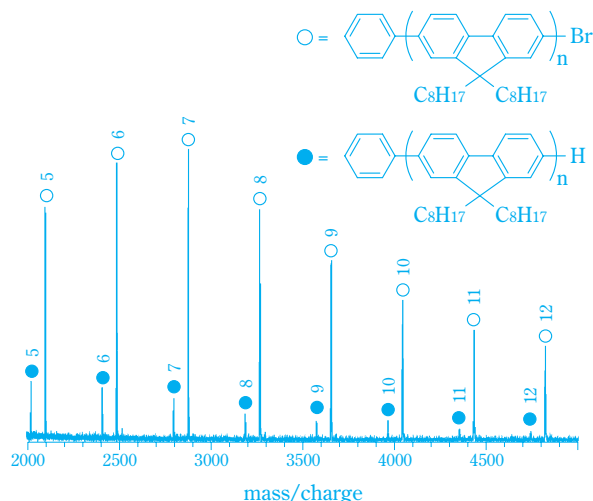


Fig. 8 MALLDI-TOF-MS spectrum of P-DOF^{54)a}

The reaction mechanism (Scheme 12) of this polymerization is that the Pd complex initiator reacts with the fluorene monomer DOF, followed by transmetalation to generate 13. From 13 to 14, the Pd complex migrates in an intramolecular manner with reductive elimination and oxidative addition. Furthermore, the transmetalation of DOF and the subsequent intramole-

cular migration are repeated, leading to chain-growth polycondensation. Although it is surprising that the Pd complex interacts with a length of one fluorene unit in intramolecular migration, this reaction mechanism was confirmed since 15 did not react at all even when 15 was present in this polymerization system.

We examined the relationship between the monomer conversion rate and the M_n (Fig. 9 (a)) and that between the monomer/initiator molar ratio and the M_n (Fig. 9 (b)) for this polymerization behavior. Both relationships were proportional, and therefore it

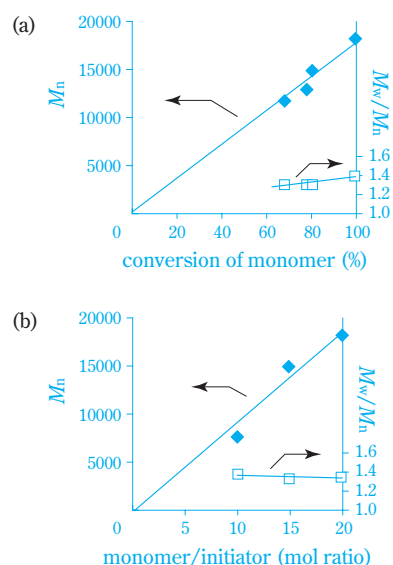
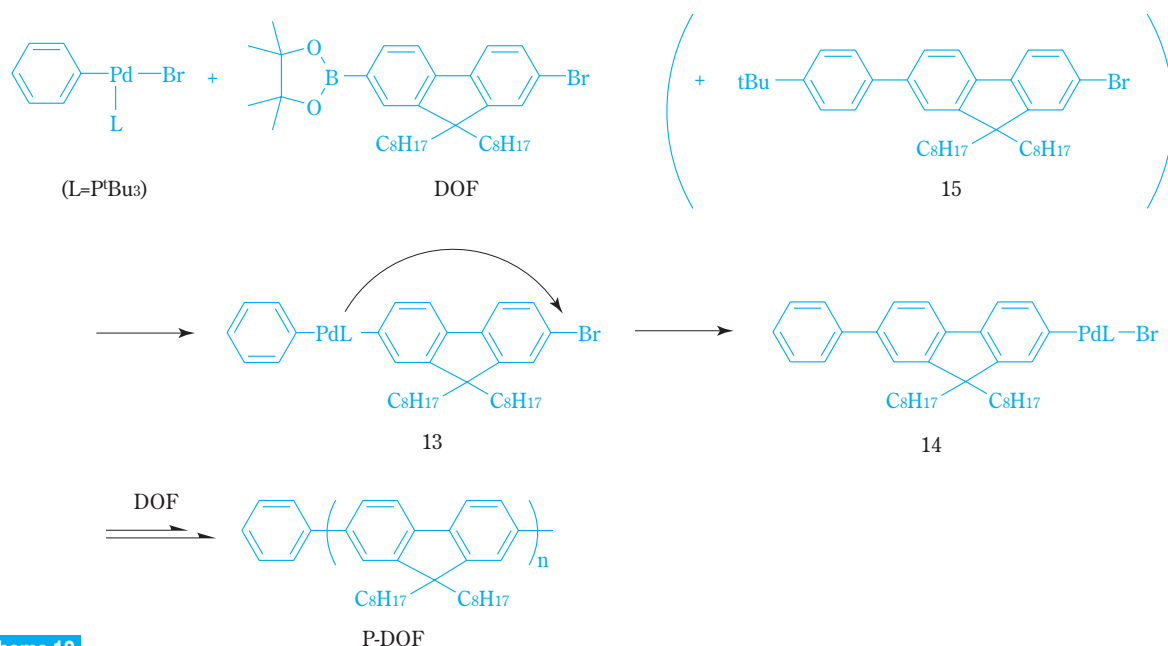


Fig. 9 Relationship of M_n with (a) monomer conversion and (b) mol ratio of monomer/initiator^{54)a}



Scheme 12

was clear that this polymerization showed a living polymerization nature.

In addition, we carried out co-polymerization with another asymmetric monomer after the polymerization of DOF, and hence, a monodispersed diblock polymer was obtained.^{54)c} It is important to carry out the polymerization in order starting from the monomer with lower electron density, because if this is reversed, the intramolecular migration of the Pd complex is disturbed, resulting in an increase in the molecular weight distribution. Furthermore, we have found that the polymerization of DOF occurs from the Pd complex initiator fixed on the metal surface. The present polymerization of aromatic monomers from the material surface has been achieved for the first time, because it is possible to use an external Pd complex initiator.

Conclusion

As described above, the control of regioselectivity and stereoselectivity in oxidative polymerization, which was not possible up to now, is possible by using transition metal complex catalysts, and the cross coupling polycondensation can be converted from a step-wise-growth type to a chain-growth type. Using these precision polymerization techniques, we would like to synthesize one-dimensional structures of aromatic polymers more precisely, and also form higher-dimensional structures such as chain packing and phase separation more sophisticatedly, in order to achieve the ideal levels of performance and functions for materials. However, the solubility of aromatic polymers is generally low, requiring trade-offs with the packing which determines performance and function, so a breakthrough on this difficult problem would be desirable.

We believe that creative techniques are not discovered overnight and are born of an unbroken line of continuous fundamental research. In company research, which requires speed, we think that joint research with outside institutions and utilization of national projects⁵⁶⁾ can provide an opening. Our dream is to contribute to human society through creative techniques, and we are tenaciously working to achieve this dream as soon as possible.

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