

REVIEW ARTICLE

Synthesis of Wholly Aromatic Polyketones

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The structural design strategy and the synthetic approaches for the wholly aromatic polyketones and the monomers are described. Electrophilic aromatic arylation substitution polycondensation and aromatic coupling polycondensation have been investigated as synthetic routes for wholly aromatic polyketones by the author's group. Acyl-acceptant arene molecules as the electrophilic aromatic arylation substitution polycondensation type monomers and the aromatic nuclei for bis(chlorobenzoylated) compounds as the aromatic coupling polycondensation one were designed and synthesized employing 2,2'-dioxybiphenyl, 2,2'-dioxy-1,1'-binaphthyl, and *o*-terphenyl skeletons. Determining factors for monomers, which enable regioselective polycondensation, are also discussed. The properties of polyketones are also discussed briefly on the basis of polymer repeating unit structures.

KEY WORDS: Wholly Aromatic Polyketone / Electrophilic Aromatic Arylation / Acyl-Acceptant / Aromatic Ring Assembly / Regioselective Arylation / Consecutive Arylation / Aromatic Coupling / Self Complementary Monomer / Sequenced Polymer / Tandem Dual Arylation /

Aromatic polyketones are a group of aromatic polymers having ketonic carbonyl groups as the major linkage in the aromatic polymer main chain. Though there have been reported many examples of aromatic polyketones, almost all of them belong to the category of "aromatic poly(ether ketone)s."¹⁻⁵ In fact, the term "aromatic polyketone" is generally apt to be regarded identical to "aromatic poly(ether ketone)." As a representative material of this category of aromatic polymer, PEEK[®] (**1**), a poly(ether ether ketone), is well-known super engineering plastics showing superior thermal stability, mechanical strength, and chemical resistance. Figure 1 shows the structure of PEEK[®] (**1**). The repeating unit of the polymer is composed of three 1,4-phenylene moieties bonded with two ether linkages and one ketonic carbonyl group. The structure suggests that PEEK[®] (**1**) might have properties more attributable to aromatic ether rather than aromatic ketone.

On the other hand, aromatic polymers that have main chain structure composed of only aromatic rings and ketonic carbonyl groups are another type of aromatic polyketones (Figure 2).⁶ The authors' group has been investigating the synthesis of aromatic polyketones free from main chain hetero linkages, wholly aromatic polyketones, during recent one and a half decades. Contrary to aromatic poly(ether ketone)s, wholly aromatic polyketones were seldom reported before.

Prior to discussion of synthetic chemistry of wholly aromatic polyketones, the overview of aromatic polyketones including aromatic poly(ether ketone)s is briefly summarized to discriminate between aromatic poly(ether ketone)s and wholly aromatic polyketones.

Aromatic polyketones are obliged to have copolymer structure composed of aromatic rings and ketonic carbonyl groups. From this point, aromatic polyketones are regarded as

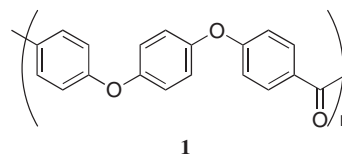
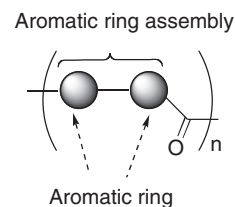
Figure 1. PEEK[®] (**1**).

Figure 2. Structure of wholly aromatic polyketone.

polyarylenes bearing inserted carbonyl groups. These polymers are classified into wholly aromatic polyketones or others according to the absence or presence of hetero linkages in the main chain. Aromatic poly(ether ketone) is the representative polymer of the latter type.

As a natural consequence of the structural characteristics, aromatic poly(ether ketone)s have possibility of wide variation of molecular structure. Moreover, introduction of ether linkage is required to overcome the limitations in synthetic practice and to achieve the satisfactory physical property.

From the viewpoint of isomerism of molecules, when the molar ratio of the oxygen atoms and the carbonyl groups is in some common value for aromatic poly(ether ketone)s, such aromatic poly(ether ketone)s are regarded as the structural isomers of polyarylates or polycarbonates. The difference

between poly(ether ketone)s and polyarylates or polycarbonates is whether oxygen atoms are bonded directly to carbonyl groups or not. As described above, presence of ether oxygen and carbonyl groups separately by distance of aromatic ring affords the characteristic property of the polymer. The separately situated ethereal oxygen atoms and carbonyl groups are considered to bring about far more flexible unit structure than that of polyarylates. Polyarylates have rather planar and rigid ester linkages. This also explains characteristic polymorphism property of the aromatic poly(ether ketone)s. It is quite reasonably concluded that the presence of ether linkage in aromatic poly(ether ketone)s should affect the property substantially. On the contrary, wholly aromatic polyketones, *i.e.*, copolymer solely comprised of pure aromatic ring and ketonic carbonyl group, are expected to show distinct polymer properties against those of aromatic poly(ether ketone)s.

On the basis of above consideration on the fundamental molecular structure, the structure, the property, and the synthesis of aromatic poly(ether ketone)s are roughly surveyed.

Some of the aromatic poly(ether ketone)s show superior physical properties and chemical resistance as super engineering plastics.¹⁻³ Among the super engineering plastics having comparable properties such as aromatic polyimides, polyarylates (LCP), and aramide polymers, characteristics of aromatic polyketones are distinctively different from these polymers in some points.

Essentially, aromatic polyketones are composed of only three elements, *i.e.*, carbon, hydrogen, and oxygen. Namely, these polymers are regarded as non-hetero element aromatic high-performed polymers. From this point, poly(phenylene ether), polyarylates (LCP), and phenol resins are considered to belong to the same category. Achievement of highly performed property without hetero atoms is of great value as organic polymer materials of low environmental load. In a natural course, the potential of these polymers as practical polymeric materials is of great significance to be evaluated.

From the point of solid aggregation propensity of polymer molecules, most aromatic poly(ether ketone)s are essentially semi-crystalline with high melting temperature. At the same time, the aromatic poly(ether ketone)s tend to show polymorphism. Especially, the complex phase transitions behaviors between the glass transition temperature (T_g) and the melting temperature are characteristically observed in several aromatic poly(ether ketone)s. This thermal property obviously disturbs the practical use of this type of polymer. This characteristic phenomenon is attributed to the ability of the rotation around the ether linkage in the polymer main chain. Quantitative elucidation of the determining factors has been an important subject for understanding the aromatic polyketones from both scientific and practical stand points. The structural analysis in relation with polymorphism of aromatic poly(ether ketone)s was intensely investigated during the period from late 1980's to early 1990's by many researchers.⁷⁻²¹

One of the driving forces for the polymorphism of aromatic poly(ether ketone)s elucidated *via* these investigations is specific alternation property of the main chain conformation.

In addition to the flexibilization brought about by ethereal linkage, aromatic poly(ether ketone)s have another perturbation factor promoting conformation alteration.

As the long conjugated system of ester linkage and aromatic ring tends to maintain planar well-aligned conformation, the polymer main chain of polyarylates apparently affords high-performed physical properties through regular alignments by long extended π -plane of aromatic rings and ester moieties, carbonyl group attached to hetero atoms.

On the contrary, aromatic ketone moiety of aromatic poly(ether ketone)s gives characteristic conjugation structure, which distinctly differs from ester linkage in polyarylates. The conjugation around ketonic carbonyl group in diaryl ketone has a rather short conjugation length and the extension of orbital in the two aromatic rings is linked indirectly. That is, one ketonic carbonyl group conjugates with two adjacent aromatic rings. However, the two aromatic rings themselves have no direct linkage. It is unambiguous that the two aromatic rings conjugate *via* a ketonic carbonyl group but the conjugation between them is doubtlessly indirect. Such switchback-like conjugation is distinguished from typical long-straight conjugation as cross-conjugation. The cross conjugation is supposed to allow rather easy rotation around the bond between ketonic carbonyl carbon atom and aromatic *ipso* carbon. This is presumed to be one of the major driving forces for polymorphism of aromatic poly(ether ketone)s.

In addition to this, the coexistence of ether linkage and ketonic carbonyl group in the main chain probably makes the polymer chain highly flexible, which leads the polymer thermal behavior much complex along with the easy rotation of aryl-ketonic carbonyl bond.

The electronic structural feature in aromatic ether linkage has essentially common with aryl aryl ketone. The two aromatic rings of diaryl ether conjugate with ethereal oxygen *via* super cross-conjugation of allene like molecular orbital structure. In each of two cases, the conjugation of two arenes is indirect. Thus, the polymer chain of aromatic poly(ether ketone)s forms flexible and weakly fixed segment composed of aromatic rings, ether oxygen, and ketonic carbonyl group to afford complex thermal behavior.

As described above, many works were undertaken to clarify the relation of the structure and the thermal behavior of aromatic poly(ether ketone)s in 1980's to early 1990's. For example, X-ray crystallographical analyses have also revealed the presence of two or more crystal forms of some of these aromatic poly(ether ketone)s.²²⁻²⁷ One of the successful works on this theme is that of Blundell and the co-workers, where polymorphism of PK99 (**2**, Figure 3) is explained on the basis of step-wise elongation of rigid-planar segments with rise of temperature. The rather flexible conjugated unit comprised of aromatic ring, ether bonding, and ketonic carbonyl group is assumed to make some short-length unit of regular structure. The units are postulated to undergo thermal transition giving further structured units having extended length. At the same time, the polymer mass is considered to show the corresponding phase transition. The step-by-step growth of the length of

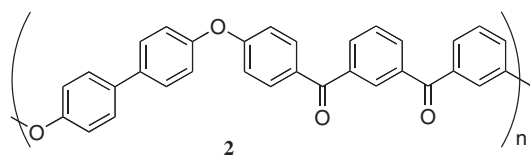


Figure 3. PK99.

the regularly structured units is supposed to proceed with phase transition until the melting of the polymer occurs.

This schematic explanation is one of the plausible interpretations for complex thermal transition behavior between T_g and melting point for some kinds of aromatic poly(ether ketone)s.²⁸ Crystal structure and its transition behavior were also investigated by DSC, WAX, specific heat, heat of melting, far infrared spectroscopy.^{29,30}

To explain the characteristic thermal behavior of aromatic poly(ether ketone)s commonly on the basis of the length of the aromatic assembly moieties in polymer main chain, the PRCL (partial rigid chain length) theory has been also applied to assess the length of the possible formation of the straightly extended unit in the polymer molecules.³¹

The mode of the linkage of phenylene moiety, *i.e.*, which type of phenylene moiety is involved in the ring assembly unit of the main chain of the polyketone is supposed to determine the aggregation behavior of the polymer. The aggregation state is supposed to determine directly the solid structure and the property of the polymer. Especially, because of the absence of hetero bonding except for ether linkage in the aromatic poly(ether ketone)s, the structure and the property are considered to depend largely on the linkage position in the arylene moiety. For the extended aromatic polymers, whether *m*-phenylene moiety or *p*-type one is included as the main chain component should participate in determination of the structure as a major factor.

The *m*-linkage in aromatic poly(ether ketone)s causes low temperature transition and makes many undistinguished thermal transitions resulting in more complex thermal transitions.^{32–34} Low temperature transition temperature practically facilitates the dealing of the polymer but complex thermal transition is unfavorable for size stabilization and high physical property. The effect of introduction of *m*-phenylene moiety into aromatic poly(ether ketone) skeleton on the polymer thermal property was roughly summarized as a short account.³⁵

As described above, some of the characteristic thermal properties of aromatic poly(ether ketone)s are attributed to perturbation of the molecular chain arrangement accompanying with the restructuring of the regularity in conformation of the repeating units. Probably, the phase transition is mainly due to the flexibility of the ether bondings in the polymer chain. In a similar fashion, the heat resisting property is probably due to the piling of the aromatic rings. In this course, the highly performed thermal properties of aromatic poly(ether ketone)s are achieved in a quite different manner from that of polyarylates.

In the last decade, however, the trend of the investigation on aromatic poly(ether ketone)s sifted from fundamental analysis

of structure-property relationship to practical utilization such as solubilization of aromatic poly(ether ketone),^{36,37} preparation of high-porous material,^{38–41} application to fuel-cell membranes,^{42–45} and so on. Along with this trend, the synthetic approach also shifted to the preparation of substituted aromatic poly(ether ketone)s, especially those bearing perfluoroalkyl groups,^{46–49} and aromatic copoly(ether ketone)s having naphthylene moieties^{50,51} or additional functional groups.⁵² Application of aromatic poly(ether ketone)s as high-performed coating material is one of the main usages of this type of polymer.^{53,54} Aromatic copoly(ether ketone)s showing LCP property were also reported.^{55,56} Several synthetic approaches with the aid of direct condensation agent⁵⁷ or superacid-mediated reaction^{58,59} and those by utilization of specially structured compounds^{60–62} were also reported.

Contrary to the aromatic poly(ether ketone)s described above, there have been scarcely reported synthesis and characterization of wholly aromatic polyketones.

The absence of the hetero linkage in the main chain largely restricts the option of the synthetic methods for wholly aromatic polyketones. Practically, electrophilic aromatic arylation condensation acts important roles in monomer synthesis and polymerization.

Such circumstance has prompted the authors' group to investigate the synthesis of aromatic polymers free from main chain hetero linkage except for ketonic carbonyl groups, *i.e.*, wholly aromatic polyketones.

To perform construction of aromatic ring assembly and ketonic carbonyl group copolymer structure, fine design of the molecules and the choice of the reagent are critical. In this consequence, the authors' group has employed aromatic ring assembly compounds such as 2,2'-dioxybiphenyl and its related molecules with electronically equivalent structures or sterical analogy as activated and tolerable acyl-acceptant molecule.

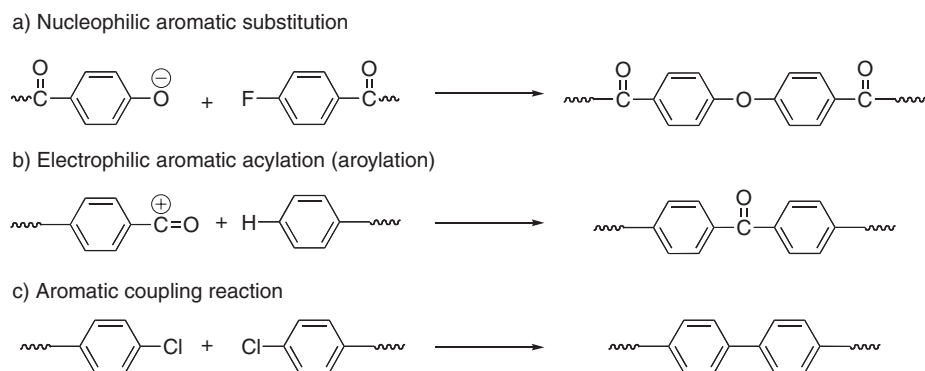
In this article, the syntheses of wholly aromatic polyketones by both electrophilic aromatic arylation substitution polycondensation and aromatic coupling polycondensation *via* utilization of several acyl-acceptant molecules of potential chain elongation ability are discussed. In a natural consequence, the study largely depends on development of homologous and analogous acyl-acceptant molecules affording enhanced polymerizability or characteristic polymer structures. Furthermore, synthetic protocols for wholly aromatic polyketones having characteristic sequence structure are also described.

SYNTHETIC METHODS FOR AROMATIC POLYKETONES

Before discussion of the synthetic approaches for wholly aromatic polyketones, the general synthetic methods for aromatic polyketones are briefly surveyed.

Bond Formation Reactions for Aromatic Polyketone Synthesis

There are several possible bonds to be formed in the chain elongation for aromatic polyketone synthesis such as



Scheme 1.

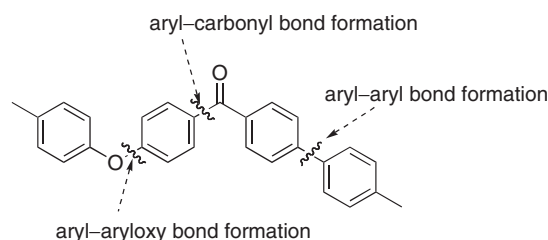


Figure 4. Bond formations of aromatic polyketone synthesis.

aryl–aryl bond, aryl–carbonyl bond, and aryl–aryloxy bond (Figure 4).

In addition, plausible approaches *via* aromatic ring formation or CO insertion into aryl–aryl moiety have also attractive possibility. These approaches are essentially divided into two kinds. One is a bond-forming reaction to make aromatic ketonic moiety and the other is formation of aromatic ring assembly.

Among the possible bond-forming routes classified above, the practical choices are limited to three methods, *i.e.*, bond formations between aryl–aryl, aryl–aroyl, and aryl–aryloxy moieties (Figure 4). In order to perform the formation of linkage in aromatic polyketone synthesis, the following condensation reactions have been concrete methods, *i.e.*, nucleophilic aromatic substitution, electrophilic aromatic arylation, and aryl–aryl coupling (Scheme 1).

The three methods have generality as bond formation reaction in polymer synthesis for some extent. As easily realized, the third method to aryl–aryloxy bond formation inevitably affords hetero linkage in the polymer main chain, it is not applicable for wholly aromatic polyketone synthesis.⁶³

Nucleophilic Aromatic Substitution. Nucleophilic aromatic substitution generally shows good chemoselectivity. By this method, regular structure is assured on condition that rather expensive fluorinated arene substrate monomers are provided and drastic reaction conditions are maintained. Though this method is strictly prohibited for the purpose of the synthesis of wholly aromatic polyketones as mentioned above, the nucleophilic aromatic substitution by strong carbanion nucleophile followed by conversion to carbonyl group is applicable.⁵

Electrophilic Aromatic Arylation. The most representative electrophilic aromatic substitution giving C–C bond is Friedel–Crafts alkylation and acylation. Usually, the reaction is undertaken by use of alkyl halide or acyl halide with the aid of Lewis acid such as AlCl₃. Compared to nucleophilic aromatic substitution, this method suffers from low reactivity and poor selectivity. In a natural sequence of this, the method is regarded difficult to be applied as enchainment reaction of polyketone synthesis.

Aromatic Coupling Reaction. Transition metal-catalyzed aromatic coupling is one of the most useful synthetic topics for recent decades. There have been reported various approaches for homo aryl coupling and cross aryl coupling.

Intramolecular^{63,64} or intermolecular aromatic ring formation^{65–70} is a plausible protocol for this polymer synthesis. Functional group interconversion of a substituent attached to the main chain of the precursor polymer to carbonyl group is also one of the possible approaches.⁵ Furthermore, ternary coupling of aryl–carbonyl–aryl moieties are expected as transition metal complex catalyzed carbonyl group insertion^{71–74} or double acylation of two arene rings with phosgene or equivalents.⁷⁵

About aryl–aroyl bond formation, Friedel–Crafts type C–C bond formation is one of the most reliable methods. However, the specific reasons for aromatic polyketone synthesis described later, various modifications are needed to accomplish this type of bond formation. Furthermore, contrary to aryl–aryl cross-coupling of aryl halide and areneboric acid derivatives catalyzed by palladium-complex,⁷⁶ nickel-complex catalyzed aryl–aryl homo-coupling^{77–80} possesses still place to be developed and is consequently attractive as practical and economical polycondensation method.

From the point of generality and economic preference, the authors' group has adapted electrophilic aromatic substitution and nickel-complex-mediated aryl–aryl homo-coupling as enchainment reaction of the polycondensation.

In this course, the investigation on the synthesis of aromatic polyketones has been focused to the routes by the aid of the electrophilic aromatic arylation or the combination of nickel-complex-mediated aryl–aryl coupling with it.

Background for Electrophilic Aromatic Aroylation Polycondensation and Aryl–Aryl Coupling Polycondensation

Electrophilic aromatic aroylation is apparently the choice of the preparation method for diaryl ketones. However, this method is particularly limited to be applied.

Compared to Friedel–Crafts alkylation, Friedel–Crafts acylation requires far higher enhancement of the reactivity of the acyl-acceptant substrate arenes. The arenes are required to bear at least one electron-donating group.

The reactive species generated in the course of the reaction is supposed to be acylium ion or its equivalent. Acylium ions are stabilized far highly compared to alkyl cations. The higher stabilized the electrophile is, the weaker the electrophilicity is. Consequently, electrophilic attack of acylium ion to arene ring generally needs the large enhancement of the electron density of the substrate arenes.

Acylium ion approaches the π -electron clouds of the substrate arene ring from the direction perpendicular to the aromatic plane to afford stable π -complex between the acylium ion and the π -electrons. After the formation of the complex, the transformation of the π -complex to the σ -complex gradually proceeds. In this consequence, the transition states are rather high energy ones unless special enhancements of the reactivity are absent. Furthermore, conjugated carbon electrophiles tend to have rather larger molecular size than hard cationic electrophiles such as alkyl cations. It means that the steric effect around the reaction center of electrophilic aromatic aroylation is significant. Generally, the achievement of high regioselectivity is rather difficult when the reaction proceed *via* such high energy process.

In other words, high stability of the acylium ion or equivalent intermediating species needs the drastic reaction conditions resulting in leading the poor selectivity when acyl-acceptant arene has conventional reactivity. This situation also affects the consecutiveness of the polycondensation reaction system. That is, the introduced aroyl group withdraws the electron of aromatic ring resulting in deactivation of it below the required level of acyl-acceptant ability. Furthermore, when the acyl cation or the equivalent has high electron deficiency by strong electron-withdrawing groups and have sufficient reactivity against second aroylation, it means low selectivity in the first aroylation step. This circumstance implies almost contradictory requirements for the reactivity of the acyl-acceptant/acyl-donor monomers, *i.e.*, satisfactory and constant acyl-acceptant/acyl-donating ability is needed throughout electrophilic aromatic aroylation, both before and after aroylation. At the same time, regioselectivity in addition to chemoselectivity must be maintained during the course of diaroylation. These suggest the large difficulty of the consecutive diaroylation of one arene system.

Another factor of electrophilic aromatic acylation reaction is the choice of acidic mediators. In Friedel–Crafts aroylation, Lewis acids, represented by AlCl_3 , afford the electrophiles from activated carboxylic acid derivatives such as acid halides or acid anhydrides, which attack arenes electrophilically to give aryl–aryl ketones.

Direct condensation reagents give diaryl ketones from free carboxylic acids and arenes.⁸¹ The representative of this type of reagents is polyphosphoric acid (PPA).^{82,83} As analogous reagents derived from phosphorus(V) oxide (P_2O_5 , diphosphorus pentoxide), P_2O_5 – MsOH mixture (P_2O_5 – MsOH),^{84,85} P_2O_5 –diethyl ether mixture,⁸⁶ and P_2O_5 –bis(triethylsilyl) ether mixture are available.^{87,88} Among these P_2O_5 based direct condensation reagents, only P_2O_5 – MsOH is liquid at room temperature. Other reagents are highly viscous or glassy. So P_2O_5 – MsOH is widely used as a convenient direct condensation reagent despite of the troublesome methanesulfonylated side product formation.^{85,89–95}

Direct condensation giving diaryl ketones is also possible by the aid of strong acid, such as methanesulfonic acid or sulfuric acid. However, the applicable substrates are limited. Recently, superacid-mediated electrophilic aromatic substitution has been utilized.⁹⁶ It is explained that superacid might transform carboxylic acids or the derivatives to dicationic superelectrophiles, which smoothly react with acceptants such as arenes to undergo ketone formation. In this case, the resulting superelectrophiles have the reactivity in the order of the precursors of ester, free carboxylic acid, and carboxylic acid halide from high to low level.^{97–100}

Among the transition metal complex aryl–aryl coupling reactions, the authors' group has focused nickel-complex catalyzed aromatic coupling reaction as polymerization step. This choice was made mainly by the reason on the basis of practical feasibility and economical efficiency, as described above.

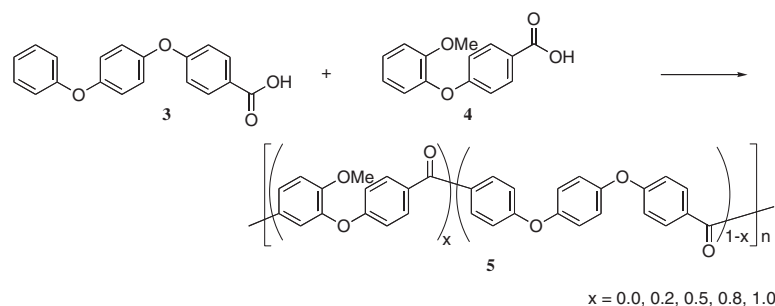
DESIGN OF REACTION

To undergo the investigation of the synthesis of wholly aromatic polyketones, the authors' group has managed the design of the reaction *via* combination of monomer molecular design and reagent modification.

The enchainment manners in the synthetic processes of wholly aromatic polyketones are classified into following two types: electrophilic aromatic aroylation polycondensation of arenedicarboxylic acid or the activated derivatives and bifunctional acyl-acceptant arene monomers and aromatic coupling polycondensation of dihalogenated aromatic ketone monomers. As a former type of polycondensation, that of the self-complementary monomers having an aroyl-donor moiety and an acyl-acceptant moiety in the same molecule is also applicable.

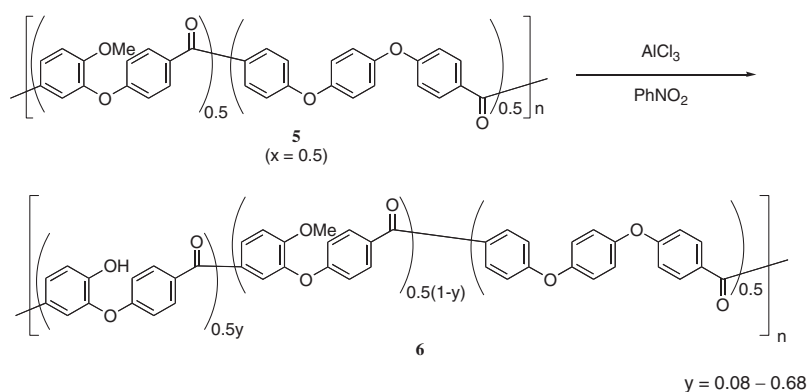
In both of the two routes for the synthesis of wholly aromatic polyketones, the electrophilic aromatic substitution aroylation is *de facto* common process. The aroyl ketone formation is ordinary included in both or one of the steps of the monomer synthesis and polymerization process. On the other hand, aromatic coupling is not always included. For some monomers, aromatic ring assembly compounds able to be purchased are employed as the starting materials.

In the series of the study on the synthesis of wholly aromatic polyketones to be discussed in this account, the following compounds and reagents are employed.



Polymerization was carried out with monomers **1** and **4** (sum of the two monomers: 2 mmol) in 3.6 mL or 6.0 mL of P_2O_5 -MsOH at 60°C, 80°C, or 100°C for 24 h under nitrogen.

Scheme 2.



Conversion of polymer **5** to polymer **6** was carried out with 100 mg (0.45 mmol repeating unit) of polymer **5** ($x = 0.5$) and 200 mg (1.5 mmol) of $AlCl_3$ in 5 g of nitrobenzene at 120°C, 150°C, 180°C, or 210°C for 1 h or 3 h under nitrogen.

Scheme 3.

Bifunctional Acyl-Acceptant Molecules

As the bifunctional acyl-acceptant monomer or the monomer precursor, 2,2'-dimethoxybiphenyl (**7**), 2,2'-bis(aryloxy) biphenyls (**65–67**), 2,2'-dimethoxy-1,1'-binaphthyl (**135**), *o*-terphenyl (**117**), and *m*-terphenyl were employed.

Bifunctional Acyl-Donor Molecules

As acyl-donor monomers, arenedicarboxylic acids/arenedicarbonyl chlorides having following arylenedicarbonyl units were employed: 1,4-phenylenedicarbonyl, 1,3-phenylenedicarbonyl, 4,4'-oxybisphenylenedicarbonyl, and so on.

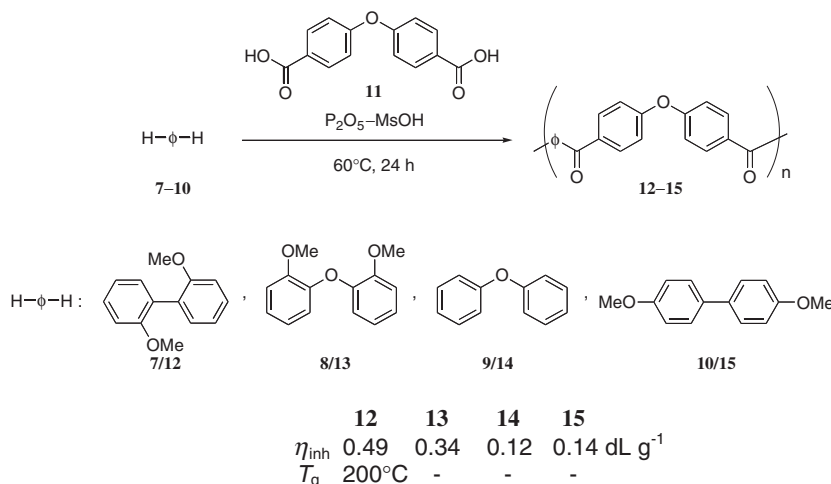
In addition to the above two types of monomers, the self-complementary monomers having acyl-acceptant moiety and electrophilic acyl-donor precursory moiety were prepared and subjected to polycondensation.

Acidic Mediator

As acidic mediators, $AlCl_3$, P_2O_5 -MsOH, and trifluoromethanesulfonic acid (TfOH) were employed for typical Lewis acid-mediated Friedel-Crafts reaction, direct condensation, and modified Friedel-Crafts acylation, respectively.

Prior to the series of study on the synthesis of wholly aromatic polyketones, the authors' group investigated the synthesis of aromatic poly(ether ketone) copolymer bearing adhesive functional groups in order to develop a novel coating material on steel surface.⁵³ The authors' group intended to create the high-performed polymer consisting of only carbon, hydrogen, and oxygen excluding hetero atoms such as sulfur, nitrogen, halogens, and so on.

The synthesis of the polymers with expectation to have such property was performed by the direct condensation copolymerization of 4-(4-phenoxyphenoxy)benzoic acid (**3**) and 4-(2-methoxyphenoxy)benzoic acid (**4**) followed by partial hydrolysis of aryl methyl ether linkages to be converted to phenolic hydroxy groups (Schemes 2 and 3). The homo condensation polymer of the former monomer has the same structure with PEEK® (**1**), and the polymerization of the latter monomer has reported to be susceptible to direct polycondensation with P_2O_5 -MsOH by Ueda and his co-workers.⁹² Though good adhesiveness to steel surface was satisfactorily achieved, the thermal stability of the partially hydrolyzed copolymer, *i.e.*, aromatic copoly(ether ketone)s bearing hydroxy groups showed thermal decomposition behavior at far lower temper-



Polymerization was carried out with 1.0 mol of monomers 7–10 and 1.0 mmol of dicarboxylic acid monomer **11** in 3 g of P₂O₅–MsOH at 60°C for 24 h under nitrogen.

Scheme 4.

ature than expected. This is probably caused by oxidation of phenol moiety *via* formation of quinoid intermediate. Though cross-linked phenolic resins have also phenolic hydroxy groups, they show excellent thermal stability. The low thermal stability of the partially hydrolyzed poly(ether ketone) is considered to be due to the participation of ketonic carbonyl group, which might function as the pool of electron resulting in promotion of the oxidative cleavage of aryl–aryl linkages. Contrary to the hydroxylated aromatic copoly(ether ketone)s, phenolic resins have only phenolic hydroxy groups, without ketonic carbonyl ones, which presumably avoid the cooperative oxidation to retain good thermal resistance.

Though hydroxylated aromatic copoly(ether ketone)s **6** have rather ordinary heat resistance, not only hydrolyzed aromatic copoly(ether ketone)s **6** but also non-hydrolyzed copolymer, *i.e.*, partially methoxylated copoly(ether ketone)s **5** show good adhesiveness to the surface of steel. This result prompted the authors' group to construct aromatic polyketones having ether moiety only as side groups. It means formation of the polymer skeleton composed of aromatic rings and ketonic carbonyl groups solely.

SYNTHESIS OF WHOLLY AROMATIC POLYKETONES HAVING 2,2'-DIMETHOXYBIPHENYLENE MOIETY

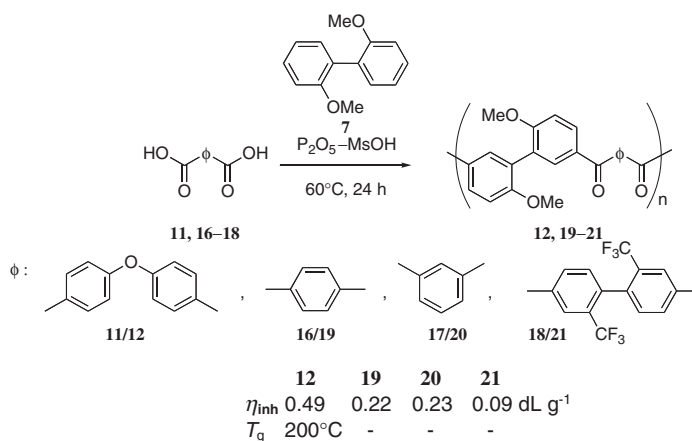
The investigation on the synthesis of wholly aromatic polyketones started by the utilization of chemical and structural properties of acyl-acceptant monomer/repeating unit of 2,2'-dimethoxybiphenyl (**7**)/2,2'-dimethoxybiphenylene. In this section, the syntheses of the titled structured wholly aromatic polyketones are described as the leading study of this series of investigation.

Electrophilic Aromatic Aroylation Polycondensation^{101,102}

As the initial stage of the investigation, acyl-acceptant ability of several candidate arenes was surveyed (Scheme 4). When the candidates were allowed to react with 4,4'-oxybis(benzoic acid) (**11**), 2,2'-dimethoxybiphenyl (**7**) showed the highest polymerizability. Contrary to the expectation, bis(2-methoxyphenyl) ether (**8**) showed moderate reactivity. Diphenyl ether (**9**) showed lower polymerizability than others. 4,4'-Dimethoxybiphenyl (**10**) also demonstrated rather moderate polymerizability. The preferred polymerizability of 2,2'-dimethoxybiphenyl (**7**) clearly proves that tandem aroylations proceed readily and consecutively. It means that the acyl-accepting ability of the bianisyl (**7**) should be maintained throughout the polymerization. That is, after the first aroylation, the resulting aroylated bianisyl compound has still sufficient level of acyl-accepting ability.

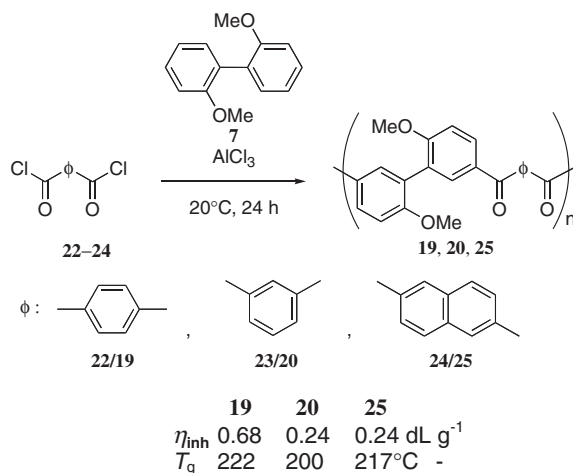
The reactivity of bianisyl **7** in the first aroylation is expected to be as high as anisole, which is in good agreement with the experimental results. Furthermore, the second aroylation also proceeded smoothly as opposed to the anxiety that the reactivity might be drastically dropped by electron-withdrawing effect of the introduced ketonic carbonyl groups. This behavior is interpreted from electronic effect. The formation of polymer from bianisyl **7** clearly means that electron-withdrawing effect scarcely propagated in this skeleton, *i.e.*, conjugation between two phenylene rings functioned incompletely. So the aromatic ring other than aroylated one behaves independently just like isolated anisole molecule.

In addition, high polymerizability is plausibly due to the assistance of the characteristic weak aggregative interaction of the resulting polymer molecules. The polycondensation synthesis of aromatic polymers in solution often suffers from the precipitation of the resulting low-molecular-weight polymers. The tendency that solution condensation polymerization for



Polymerization was carried out with 1.0 mol of monomer **7** and 1.0 mmol of dicarboxylic acid monomers **11**, **16–18** in 3 g of P₂O₅–MsOH at 60°C for 24 h under nitrogen.

Scheme 5.



Polymerization was carried out with 1.0 mol of monomer **7** and 1.0 mmol of dicarbonyl dichloride monomers **22–24** in 4 mL of ClCH₂CH₂Cl (1,2-dichloroethane) at 20°C for 24 h under nitrogen using 2.7 mmol of AlCl₃.

Scheme 6.

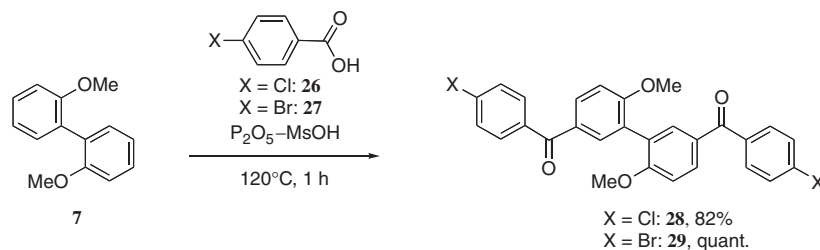
aromatic conjugated polymers hardly gives high-molecular-weight polymers is largely attributable to the drastic drop of the solubility of the intermediately formed low-molecular-weight polymer with progress of polymerization. Hence, the polymerizability of bianisyl **7** apparently demonstrates the good solubility of the polyketone having 2,2'-dimethoxy-5,5'-biphenylene moiety (**12**).

On the basis of above consideration, 2,2'-dimethoxybiphenyl (**7**) has conclusively proved to have excellent properties as an acyl-acceptant monomer for electrophilic aromatic arylation polycondensation. The potential of the bianisyl monomer (**7**) is far higher than those of the related candidate molecules.

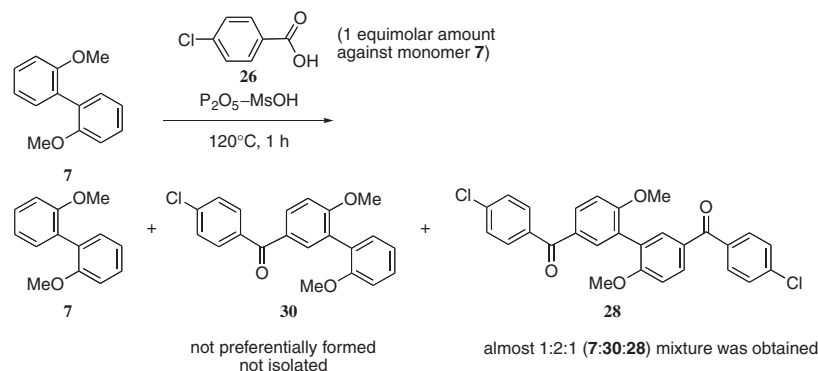
The susceptibility to tandem arylation of 2,2'-dimethoxybiphenyl (**7**) is plausibly brought about by the presence of the two methoxy groups and the twisted conformation. The

methoxy groups should activate the 3(3')- and 5(5')-positions of 2,2'-dimethoxybiphenyl (**7**). And the arylation occurs at the 5(5')-position selectively due to the steric hindrance. At the same time, steric repulsion of the methoxy group restricts the rotation of biphenylene moiety to forbid coplanar conformation. This means that the conjugation between two benzene rings is largely weakened resulting in preventing the electron-withdrawing effect of the aryl group introduced from reaching to the other ring through aryl–aryl bond. Moreover, the conjugation is considered to retain partially because the thermal property of the resulting polyketone is as high as those of the conjugated aromatic polymers as described above.

As the next stage of the study, the polycondensation of 2,2'-dimethoxybiphenyl (**7**) with several acyl-donor monomers by the aid of P₂O₅–MsOH or AlCl₃ was investigated (Schemes 5



Scheme 7.



A mixture of monomer 7, monoaroylated product 30, and diaroylated product 28 was obtained in almost 1:2:1 (7:30:28) distribution.

Scheme 8.

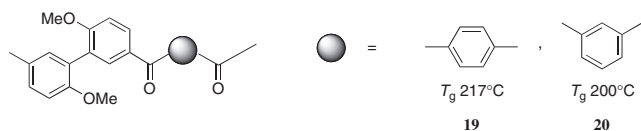


Figure 5. Glass transition temperatures of wholly aromatic polyketones 19 and 20.

and 6). Both of the acidic mediators promoted the reaction well. And for this polymerization, Friedel-Crafts acylation type polycondensation gave somewhat better results than those with P_2O_5 -MsOH.

Among the diaroil chlorides surveyed, terephthaloyl chloride (22) gave the best result. The polymers obtained are amorphous and have higher T_g than PEEK[®] (1) (Figure 5). Furthermore, some of the polymers obtained afforded flexible film by cast method.

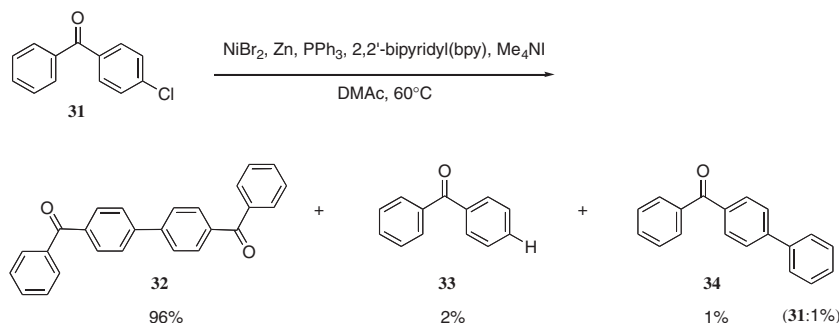
Aromatic Coupling Polycondensation¹⁰³

As described in the preceding section, the successful synthesis of wholly aromatic polyketones by $AlCl_3$ -mediated electrophilic aromatic arylation employing 2,2'-dimethoxybiphenyl (7) and arenedicarbonyl chlorides are considered to depend at least partially on the particular conformation of the intermediating medium molecular weight oligo- to polyketones brought about by 2,2'-dimethoxy-5,5'-biphenylene moiety. The twisted configuration is considered to depress the regular

aggregation of the polymer resulting in the stabilization of the molecule as a solute.

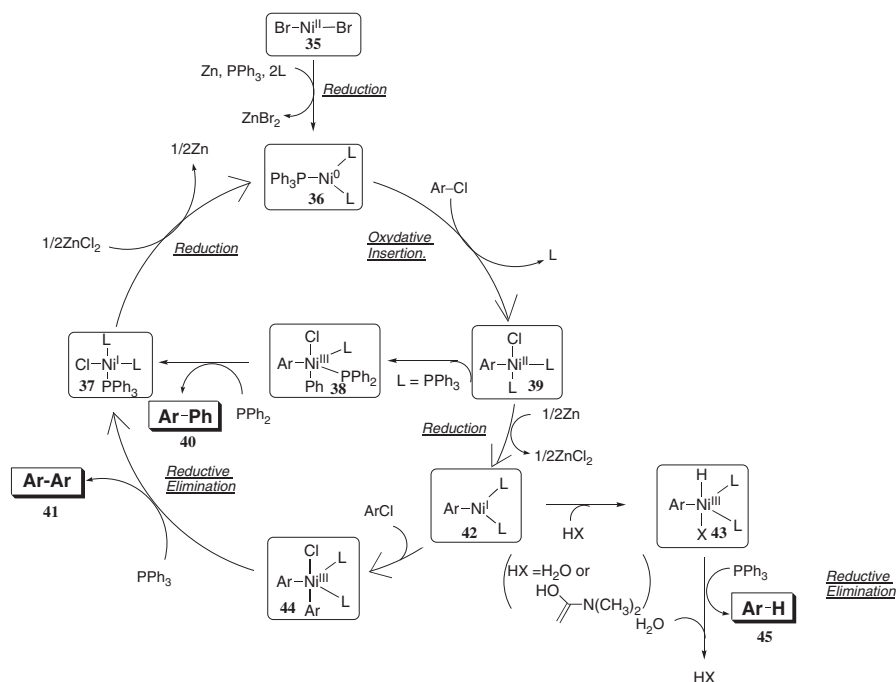
This structural promoting effect is considered to be applicable in other polymerization methods. This prompted the authors' group to utilize the molecular structure to the monomer of other type of polymerization reaction.

In a natural course, design of the monomer having two bond-forming functional groups on 2,2'-dimethoxybiphenylene backbone was attempted. The synthesis of the designed monomers for aromatic coupling polycondensation was undertaken by electrophilic aromatic arylation of 2,2'-dimethoxybiphenyl (7) with chloro- or bromobenzoic acids (26/27) (Scheme 7). The arylation reaction smoothly proceeded to give the targeted bifunctional derivatives in good yields with sufficient regioselectivity. However, selective synthesis of monoaroylated product by this method was unsuccessful. The reaction of equimolar amounts of 2,2'-dimethoxybiphenyl (7) and arenecarboxylic acid (26) gave a *ca.* 1:2:1 mixture of the starting material (7), the monoaroylated product (30), and the diaroylated product (28) (Scheme 8). Furthermore, silica gel column chromatographical separation of this mixture was unsuccessful. The polarity of the monoaroylated product (30) and diaroylated one (28) shows almost no difference. These facts mean that the chemical circumstances of the reaction sites in these compounds are essentially same, and susceptibility to the electrophilic aromatic arylation reaction of the starting material (7) and the monoaroylated derivative (30) is substan-



Nickel-complex-catalyzed aryl–aryl coupling reaction was carried out with 5 mmol of 4-chlorobenzophenone (**31**) in 10 mL of DMAc at rt for 30 min and 60°C for 5 h using 2.5 mmol of NiBr₂, 3.75 mmol of Zn, 2.5 mmol of PPh₃, 2.5 mmol of 2,2'-bipyridyl (bpy), and 2.5 mmol of Me₄NI.

Scheme 9.



Scheme 10.

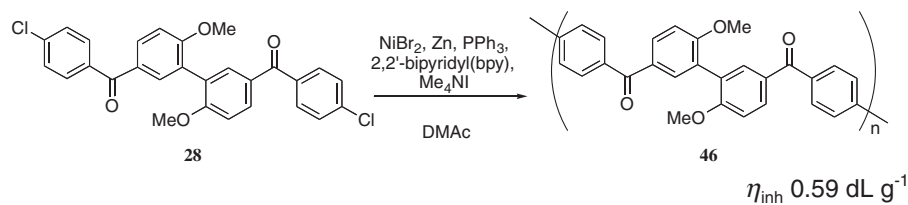
tially equivalent. This behavior is also in accordance with the high polymerizability of the 2,2'-dimethoxybiphenyl (**7**), which means this biaryl has almost equal acyl-accepting ability before and after first arylation.

The nickel-complex-mediated aromatic coupling reaction of aryl halides has been recognized as highly applicable synthetic reaction with good tolerance against various coexisting functional groups.^{77,78} However, nickel-complex mediated aromatic coupling reaction of chloroarenes bearing aroyl groups, *i.e.*, chlorinated benzophenone homologues, was not reported as the best of authors' group's knowledge.

The authors' group examined the reaction conditions for the coupling with the aid of the model reaction of the corresponding monohaloarene compound (**32**) (Scheme 9). The major by-

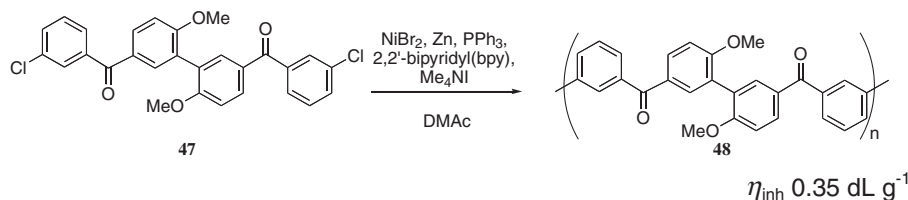
products of this coupling reaction are reduced arene (**33**) and phenyl substituted arene (**34**).

The nickel-complex-mediated aromatic coupling reaction is explained to proceed *via* the process depicted in Scheme 10: reduction (if needed) to Ni(0) species **36**, oxidative insertion of aryl halide giving Ni(II) species of Ni(II)ArCl(ligand)_n **39**, reduction by zinc or appropriate reductant giving Ni(I) species of Ni(I)Ar(ligand)_n **42**, oxidative insertion of second aryl halide to give Ni(III)Ar₂Cl(ligand) species **44**, reductive elimination of Ar–Ar **41** giving Ni(I)Cl species **37**, and reduction to Ni(0) species of the initial stage. When a phenyl group of triphenylphosphine, a conventional and typical monodentate ligand, moves on the nickel metal at the stage after the first oxidative insertion, the phenyl transferred by-



Polymerization was carried out with 0.7 mmol of monomer **28** in 2 mL of DMAc at rt for 30 min an 50°C for 1 h under nitrogen using 0.7 mmol of NiBr₂, 1.5 mmol of Zn, 1 mmol of PPh₃, 1 mmol of 2,2'-bipyridyl (bpy), and 1 mmol of Me₄NI.

Scheme 11.



Polymerization was carried out with 0.7 mmol of monomer **47** in 2 mL of DMAc at rt for 30 min an 50°C for 3 h under nitrogen using 0.7 mmol of NiBr₂, 1.5 mmol of Zn, 1 mmol of PPh₃, 1 mmol of 2,2'-bipyridyl (bpy), and 1 mmol of Me₄NI.

Scheme 12.

product (**40**) is obtained. On the other hand, the compounds having nickel–aryl bondings are subjected to hydrolytic work-up, the reduced by-product (**45**) is produced. The former by-product is obtained when the process of catalytic cycle after the first oxidative insertion is relatively slow. Especially, it is said that the presence of vacant site on nickel atom promotes the transfer. These situations might be brought about by deficiency of ligands in the reaction system. The latter by-product is apt to be gained when the reductive elimination is the rate determining step.

On the other hand, the nickel-complex-mediated aromatic coupling requires the best conditions for two different cycles of oxidation–reduction processes. It is rather difficult to elucidate the common conditions against all steps of the reaction. To find the applicable conditions minimizing the amounts of the two types of by-products, molar-balances and other conditions were examined by the reaction with the relating monohalogenated compounds.

With some perturbation of the reaction conditions, the nickel-complex-mediated polycondensation reaction of 5,5'-bis(4-chlorobenzoyl)-2,2'-dimethoxybiphenyl (**28**) has been performed to give high-molecular-weight wholly aromatic polyketone (**46**, Scheme 11). In the same manner, another regioisomeric monomer of 5,5'-bis(3-chlorobenzoyl)-2,2'-dimethoxybiphenyl (**47**) was allowed to polymerize to give regioisomeric wholly aromatic polyketone (**48**) (Scheme 12). However, the latter polymerization proceeded rather moderately. The obtained polymer (**48**) from monomer **47** is assumed to have lower molecular weight.

The obtained polyketones (**46** and **48**) are amorphous and able to give flexible cast film.

The cause of the difference in polymerizability of two monomers is not clarified at the present stage.

On the other hand, the molecular structures and the T_g 's of the isomeric or homologous four wholly aromatic polyketones (**19**, **20**, **46**, and **48**) obtained by aromatic coupling polycondensation and AlCl₃-mediated electrophilic aromatic arylation polycondensation show curious relationship. Figure 6 demonstrates the molecular structure of the repeating unit of the wholly aromatic polyketones mentioned above.

These polyketones show T_g 's ranging from 200°C to 218°C, which are far higher than that of PEEK® (**1**), 153°C. Furthermore, there seems to be apparent relationship between the structure of the arylenedicarbonyl moiety and the T_g . The T_g of the polyketone having 1,4-phenylene moiety (**19**) is almost the same with that of the polyketone having 4,4'-biphenylene moiety (**46**). On the other hand, T_g of the isomeric polyketone having 1,3-phenylene moiety (**20**) is lower than that of the isomeric polyketone having 1,4-phenylene moiety (**19**). Furthermore, the polyketone having 3,3'-biphenylene moiety (**48**) has the lowest T_g among these isomeric or homologous polyketones.

This tendency is qualitatively interpreted from the conformation of the polymers. On assumption that T_g 's are directly influenced by the stability of the glass state, it might be governed by the susceptibility of the polymer molecules to assembling together. As 2,2'-dimethoxybiphenylene unit has screwed conformation of two phenylene rings, the whole chain of a molecule is not able to have straightly aligned structure. Then, the molecules do not possess stable crystalline structure. The amorphous state thus obtained is plausibly supported by partial aggregation of the other parts of the polymers. As the

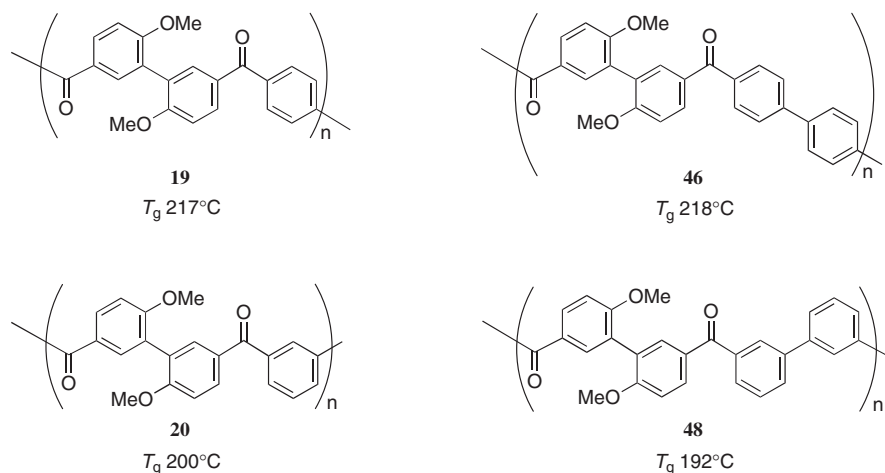


Figure 6. Glass transition temperatures of wholly aromatic polyketones.

twisted biphenylene units are linked with rigid moiety composed of arylenedicarbonyl units, such units plausibly aggregate tightly to make stable amorphous state. Therefore, more straightly aligned aromatic ring assembly moiety might afford more stable glass states by good piling-up, resulting in high T_g . From this viewpoint, the extended 1,4-phenylene moieties of polyketone **19** should effectively contribute to stabilize the amorphous state. The *m*-phenylene moiety in polyketone also functions as well to stabilize the amorphous state, resulting in a little lower but still sufficiently high T_g . However, the *m,m'*-biphenylene moiety in polyketone probably makes the polymer take conformations made up by flexible crank-shaft and screwed structures. Then, the T_g should become lower than other polyketones having rather extended structures.

Unsymmetrically Sequenced and Regularly Sequenced Wholly Aromatic Polyketones

The polyketones bearing *p,p'*- and *m,m'*-biphenylenedicarbonyl moieties (**46** and **48**) have distinct T_g 's, which suggests the large difference of these moieties in stabilizing potential.

This interpretation prompted the authors' group to synthesize the regioisomeric polyketones having biphenylenedicarbonyl units possessing various level of unsymmetry to clarify the determining factors of the thermal properties of the polyketones such as T_g .

In the first stage of this series of study on the synthesis of regioisomeric poly(biphenylenedicarbonyl biphenylene)s, the copolymerization of 5,5'-bis(4-chlorobenzoyl)-2,2'-dimethoxybiphenyl (**28**) and 5,5'-bis(3-chlorobenzoyl)-2,2'-dimethoxybiphenyl (**47**) was undertaken.

For the next stage, nickel-complex-mediated aromatic coupling polycondensation of the monomers having *m,p'*-biphenylenedicarbonyl moiety was attempted.

As the third stage of the study, the synthesis of the polyketones with sequential tacticity was undertaken.

Nickel-Complex-Mediated Aromatic Coupling Copolycondensation of Two Symmetrical Monomers.¹⁰⁴ The copolymeriza-

tion of 5,5'-bis(4-chlorobenzoyl)-2,2'-dimethoxybiphenyl (**28**) and 5,5'-bis(3-chlorobenzoyl)-2,2'-dimethoxybiphenyl (**47**) with various molar fractions demonstrates somewhat curious polymerization behavior.

The polymerizability of the 4-chlorobenzoylated monomer (**28**) is apparently higher than that of 3-chlorobenzoylated one (**47**) on the basis of the inherent viscosity of the resulting homopolymers derived from these monomers. However, inherent viscosity of the obtained copolymer (**49**) does not always correlate with the molar fraction of the monomers (Scheme 13).

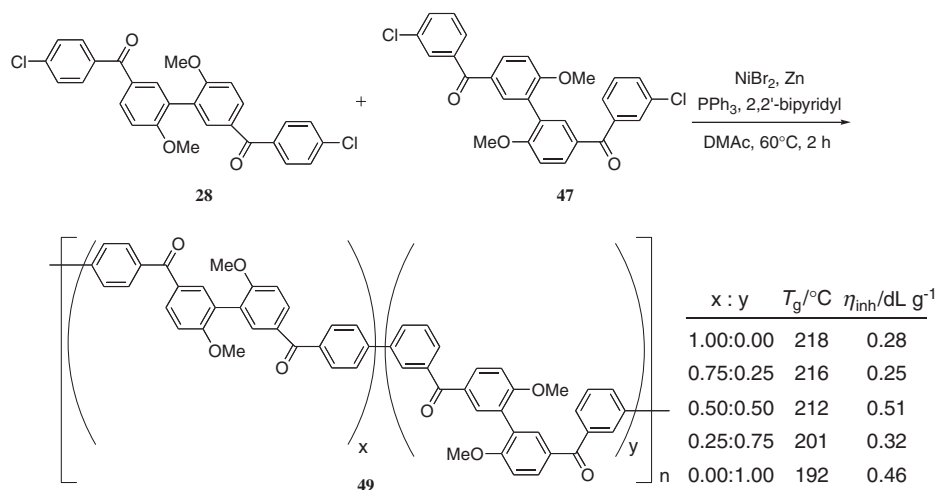
It suggests that the monomers have characteristic reactivity against the same or another kind regioisomeric structure of the monomers or terminal group of the intermediate polymer. At the present stage, the questions of the exact copolymerization reaction behavior and the determining factors remain still open. **Aromatic Coupling Polycondensation of the *m,p'*-bis(chlorobenzoyl)-2,2'-Dimethoxybiphenyl Monomer.**¹⁰⁵ Synthesis of another type of unsymmetrical isomeric polymer was planned by aromatic coupling polycondensation of the *m,p'*-substituted monomer (**51**). The target polymer was expected to have characteristic properties on the basis of highly enhanced unsymmetrical structure.

The fine design of the synthetic sequence for this unsymmetrical monomer (**51**) was achieved. According to this reaction sequence, the synthesis was successfully undertaken (Schemes 14 and 15).

The polycondensation reaction of the monomer proceeded satisfactorily to give the copolyketone (**55**) capable to afford flexible cast film (Scheme 16).

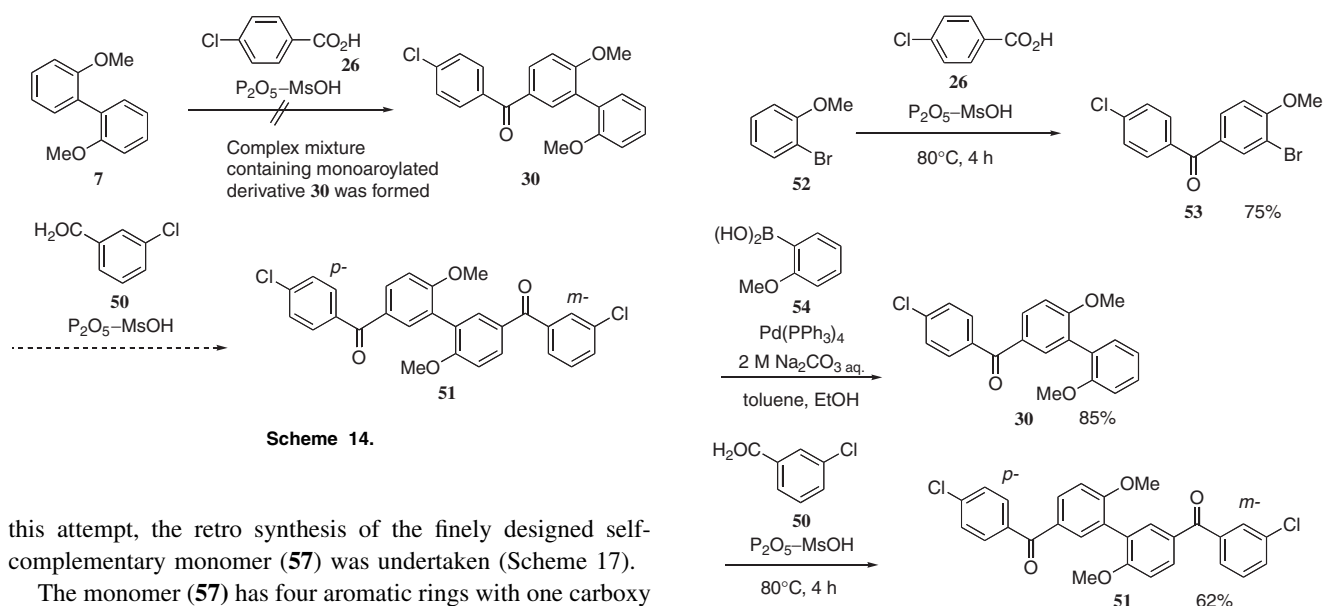
Synthesis of Self-Complementary Monomer Able to Act Roles of Both Acyl-Acceptor and Acyl-Donor and the Self-Complementary Polycondensation of the Monomer.¹⁰⁶ The synthesis of the sequential polyketone (**56**) is attractive not only from the polymer property aspect but also from the interest of the polymer synthetic chemistry.

The synthetic route was planned on the basis of the electrophilic aromatic arylation polycondensation. Against



Polymerization was carried out with 1 mmol of a mixture of monomers **28** and **47** in 1 mL of DMAc at rt for 30 min and 50°C for 3 h under nitrogen using 0.25 mmol of NiBr₂, 1.55 mmol of Zn, 1.75 mmol of PPh₃, 1.75 mmol of 2,2'-bipyridyl (bpy), and 1 mmol of Me₄NI.

Scheme 13.



Scheme 14.

Scheme 15.

this attempt, the retro synthesis of the finely designed self-complementary monomer (**57**) was undertaken (Scheme 17).

The monomer (**57**) has four aromatic rings with one carboxy group. Among the aromatic carbons having hydrogen atom, that situated at the *p*-position against the methoxy group on the terminal *o*-anisyl moiety is solely expected to undergo electrophilic arylation on condition that the reaction is undertaken under the specified conditions. The ortho position of the same *o*-anisyl ring is sterically blocked. All of the carbons of the different aromatic rings are deactivated electronically.

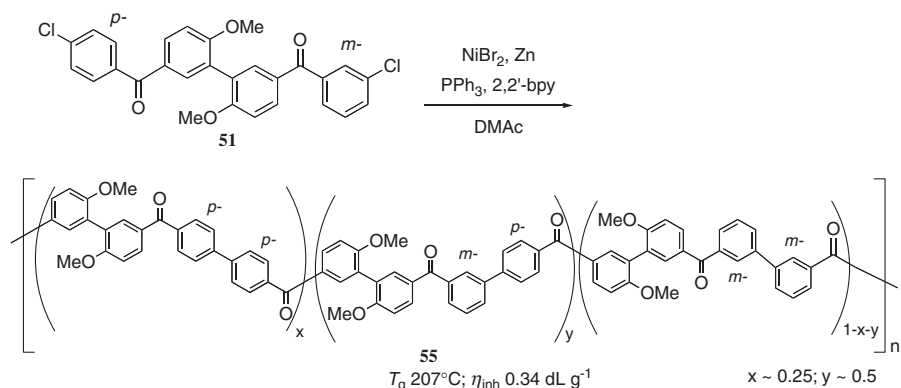
The synthesis of the monomer was performed according to the finely designed reaction sequence as shown in Scheme 18.

The polymerization of the monomer successfully proceeded regioselectively with the aid of P₂O₅-MsOH. As P₂O₅-MsOH, one of the useful direct acylation reagents, is able to mediate the arylation under mild reaction conditions, the difference in reactivity of the aromatic carbons should be satisfactorily distinguishable (Scheme 19).

The excellent polymerizability is considered to depend largely on the high solubility of the intermediating oligomer assisted by the twisted structure of the 2,2'-dimethoxy-5,5'-biphenylene nuclei.

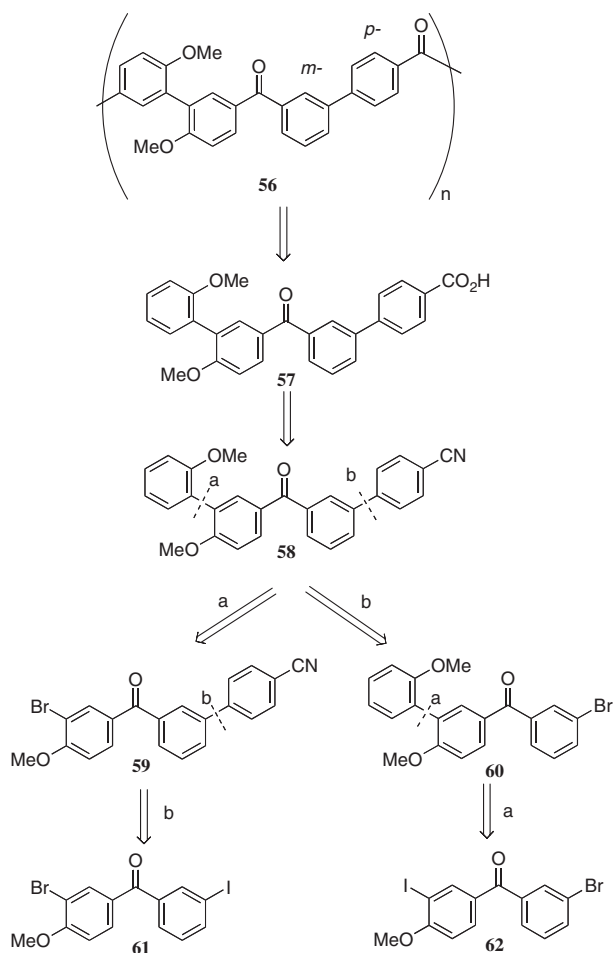
The copolyketones composed of *m,m'*-biphenylenedicarbonyl unit and *p,p'*-biphenylenedicarbonyl one excluding the *m,p'*-counter part is expected to have medium regularity.

Though this type of isomeric polyketones is attractive, the synthesis of them has not been undertaken. For this synthesis, polymerization by the bond formation reaction other than biphenylene unit of the arenedicarbonyl moiety or the corresponding strategy is required.



Polymerization was carried out with 0.15 mmol of a mixture of monomer **51** in 0.15 mL of DMAc at 60°C for 2 h under nitrogen using 0.15 mmol of NiBr₂, 0.47 mmol of Zn, 0.30 mmol of PPh₃, and 0.15 mmol of 2,2'-bipyridyl (bpy).

Scheme 16.



Scheme 17.

Synthesis and Electrophilic Aromatic Aroylation Polycondensation of 2,2'-bis(aroylaryloxy)biphenyls^{107,108}

The polymerizability of 2,2'-dimethoxybiphenyl (**7**) is excellent as an acyl-acceptant monomer in aromatic polyketone

synthesis. The structural driving force for this reactivity has proved sufficient to be applied to the monomer for other type of polymerization method.

On the other hand, the methoxy group in this monomer brings about intrinsic limitation of the thermal and chemical stability of the resulting polymers, though they realize the excellent acyl-acceptant ability electronically *via* both resonance and inductive manners.

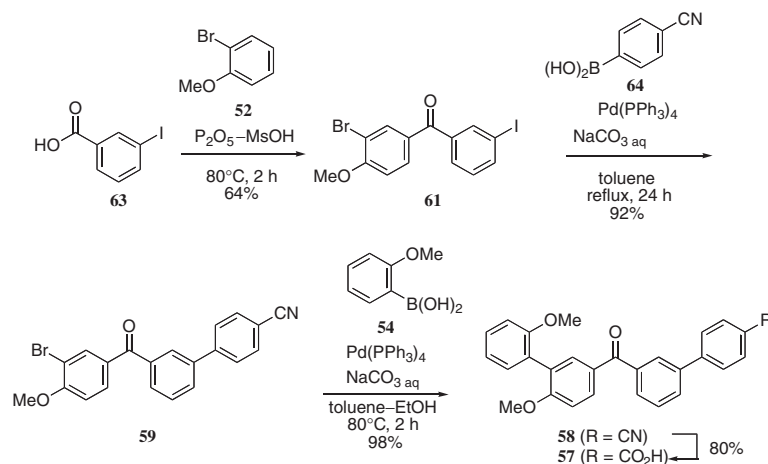
The C-O bond in Me-OAr is susceptible to scission by strong Lewis acids or protic ones. In fact, the methoxy groups on arene ring were readily cleaved to hydroxy groups with treatment of AlCl₃ as shown in Scheme 3. Furthermore, this bond is thermally cleaved at the lower temperature than that for aryl-aryl ethers. This tendency clearly affects the heat resistance of the resulting polyketones as the scission of the adjacent ketonic carbonyl-aryl bond is probably initiated *via* quinoid intermediates formed by scission of aryl methyl ether moiety.

To make the most of the electronic driving force in the electrophilic aromatic aroylation polycondensation and to utilize this structural advantage with increase of the thermal stability of the repeating unit, the aroylaryloxy analogues (**65–67**) of 2,2'-dimethoxybiphenyl (**7**) were designed as acyl-acceptant molecules (Scheme 20).

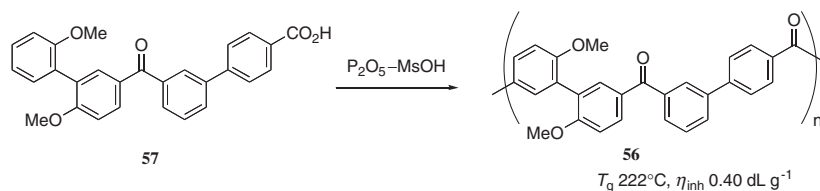
Several molecules of above category were successfully synthesized according to Scheme 21.

Monomer **65** successfully gave polyketones of high-molecular-weight (Scheme 22). Monomer **65** shows sufficiently high but somewhat lower acyl-acceptant ability against electrophilic aromatic aroylation polycondensation than 2,2'-dimethoxybiphenyl (**7**). Monomers **66** and **67** only gave aromatic polyketones of low-molecular-weight. With increase of the volume of aroyl groups, drastic drop of solubility is supposed to occur resulting in the precipitation.

The obtained aromatic polyketones (**77–79**) have T_g 's ranging from 156 to 176 °C. The temperature range is almost equal with that of that of PEEK[®]. This result suggests that the T_g 's are largely attributed to the basic polymer structures, as these wholly aromatic polyketones have the skeletons bearing

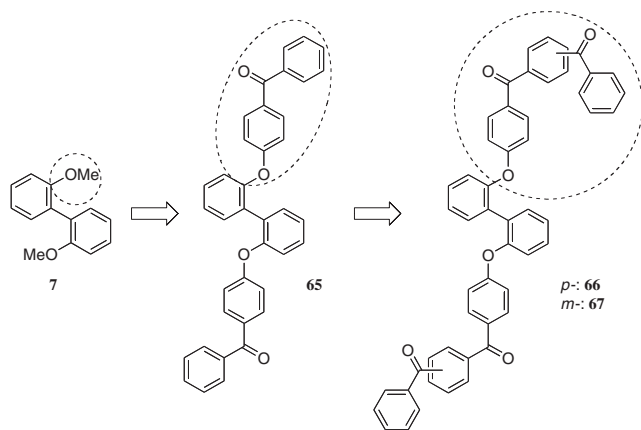


Scheme 18.



Polymerization was carried out with 0.1 mol of monomer **57** in 2 mL of P_2O_5 -MsOH at $60^\circ C$ for 3 h under nitrogen.

Scheme 19.



Scheme 20.

aromatic ketone side chains bonded *via* ether linkages. Such a characteristic polymer structure plausibly behaves essentially in the same manner with that of accumulation of aromatic oligo(ether ketone) macromonomers.

SYNTHESIS OF WHOLLY AROMATIC POLYKETONE SKELETONS BEARING FLUORINE ATOMS^{109–117}

Introduction of fluorine atom into wholly aromatic poly-

ketone skeleton is attractive subject not only from the interest in the property of the resulting polyketones but also from that of the synthetic methods. From the point of the property of the polymer, the very weak aggregation force among the fluorine substituents brings about the specific physical property, low viscosity, and surface property.^{118–122} This also obliges the preparation of such polymers to be undertaken with the specific procedure suppressing the inhibition by this factor.

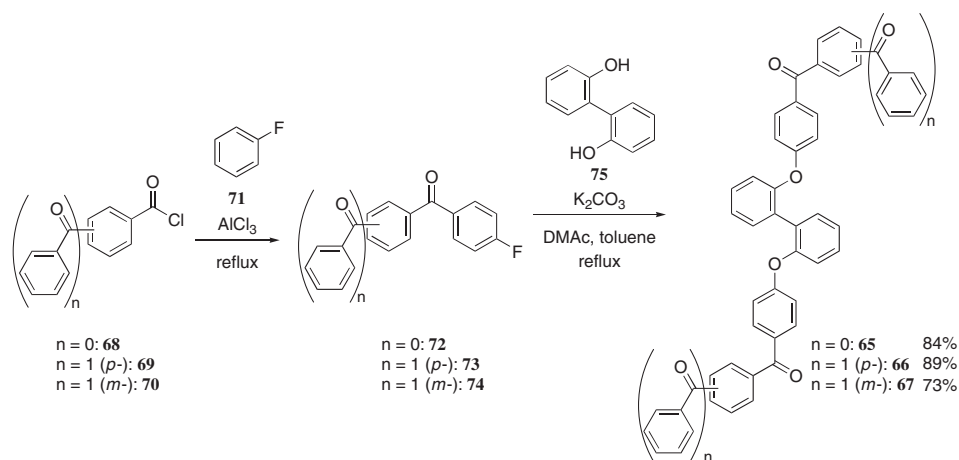
The authors' group has been investigating the synthesis of aromatic polyketones bearing CF_3 groups *via* three approaches.

First, biphenylylenedicarboxylic acid having two CF_3 groups (**81**) was designed, synthesized, and subjected to polycondensation with arenes (Schemes 23 and 24).

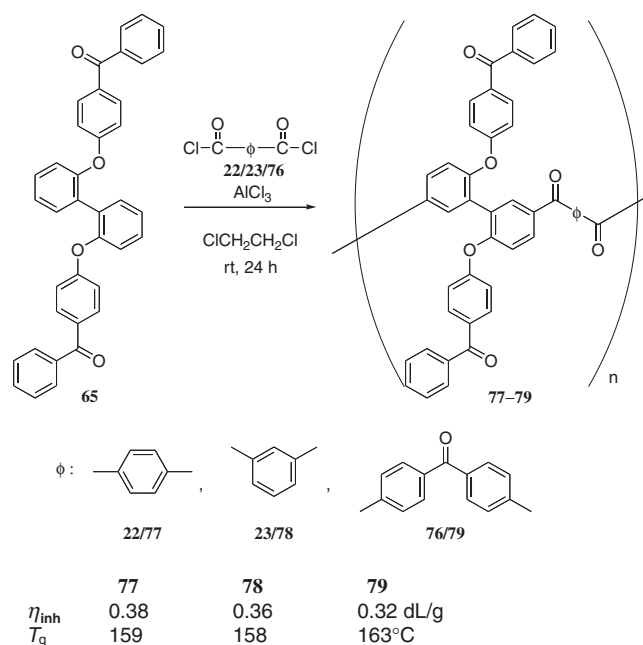
Second, biphenylylenedicarboxylic acid having one CF_3 group (**92**) was designed as a polymer constructing unit (Scheme 25).

Especially, sequential control in the synthesis of such polyketones bearing this unit has been the major subject of this part of the study. The targeted polyketones are formulated in Scheme 26.

Some of the monomers were prepared according to the finely designed synthetic sequences and applied to polymerization. Furthermore, regioselective electrophilic arylation polycondensation successfully gave the sequenced wholly aromatic polyketones bearing CF_3 groups (Schemes 27, 28, and 29).



Scheme 21.



Polymerization was carried out with 0.4 mol of monomer **65** and 0.4 mmol of dicarbonyl dichlorides **22**, **23**, or **76** in 2 mL of $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1,2-dichloroethane) at 5°C for 1 h and rt for 24 h under nitrogen using 3.6 mmol of AlCl_3 .

Scheme 22.

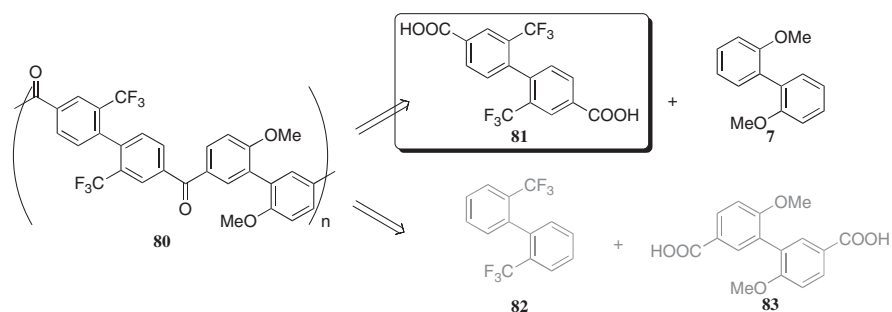
As the third protocol for this category of wholly aromatic polyketones, CF_3 -bearing aryloxyated biphenyl homologues (**111**–**113**) were prepared and subjected to electrophilic aromatic arylation polycondensation (Scheme 30).

The details for the series of the studies on fluorine-containing wholly aromatic polyketones are discussed in a separate article.¹⁰⁹

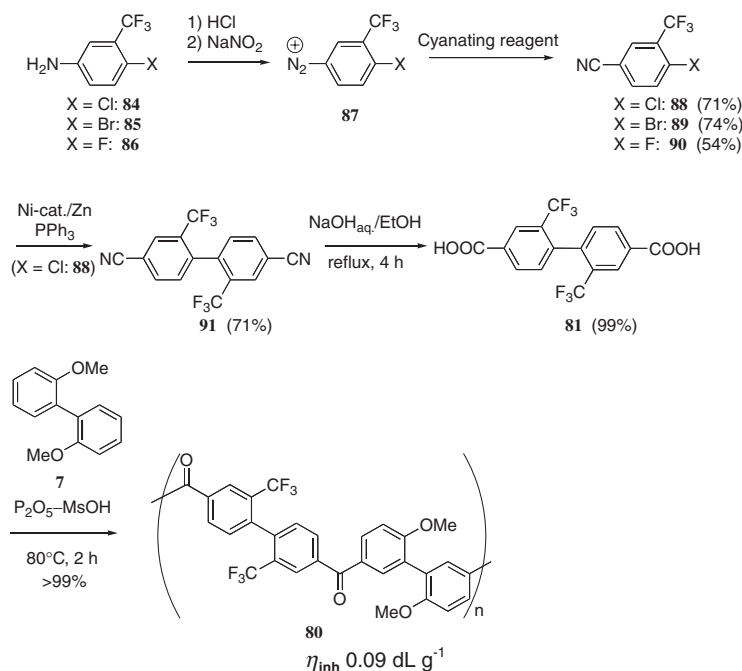
SYNTHESIS OF WHOLLY AROMATIC POLYKETONES BEARING TERPHENYLENE UNITS—A PROTOCOL FOR FULLY AROMATIC POLYKETONES

The successful synthesis of wholly aromatic polyketones

bearing 2,2'-dioxybiphenylene moieties is largely attributed to the twisted structure of the 2,2'-disubstituted biphenylene unit. Utilization of this structural advantage to analogous molecules promises extension of the variety of this type of polymer. From this point, *o*- and *m*-terphenyls are potential candidates for constructional aromatic ring assembly moiety. As the *o*-hydrogen atoms to the bridgehead carbons of biphenylene unit sterically repel to each other, the phenylene rings are expected to have screwed conformation. In this course, the terminal phenyl groups of the *o*-terphenyl (**117**) should take the similar space position with that of 2,2'-dimethoxybiphenyl (**7**). Furthermore, this unit is expected to play a role of crankshaft unit suppressing regular aggregation of the polymer chains. As a natural consequence, synthesis and

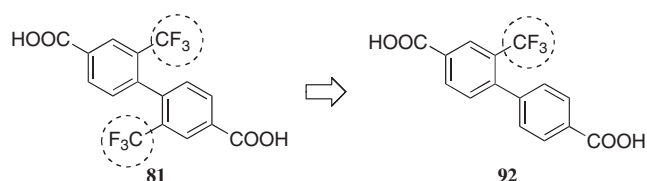


Scheme 23.



Polymerization was carried out with 0.25 mol of dicarboxylic acid monomer **81** and 0.25 mmol of monomer **7** in 2.5 mL of P_2O_5 -MsOH at 80°C for 2 h under nitrogen.

Scheme 24.



Scheme 25.

polymerization of bis(halobenzoylated) *o*- and *m*-terphenyls were attempted.

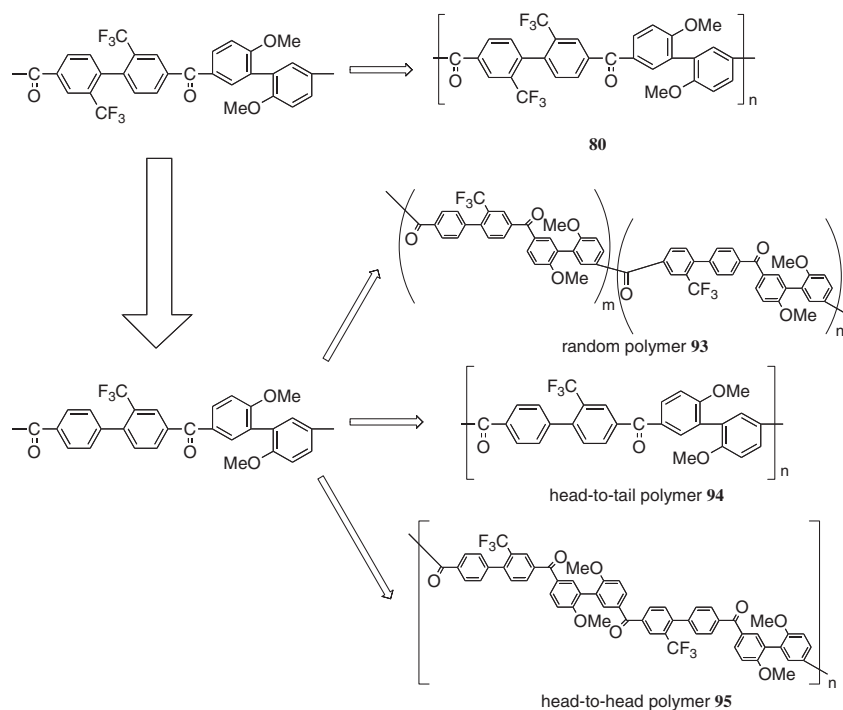
Aromatic Coupling Polycondensation of the bis(halobenzoylated) Monomer Bearing *o*-Terphenylene Moiety^{123–126}

Previous to the polymerization study, the regioselectivity of the electrophilic aromatic arylation of *o*-terphenyl (**117**) was investigated. The results are tabulated in Table I. The arylation

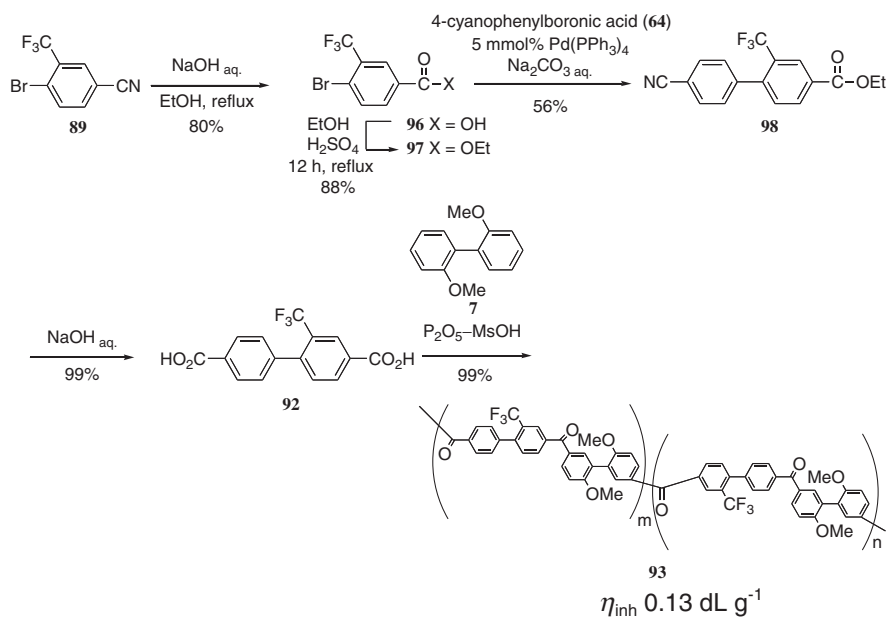
clearly shows distinct *p'*,*p''*-regioselectivity. Furthermore, the reactivity of the second arylation has proved somewhat lower than that of the first one.

These behaviors are interpreted by the mechanisms composed of conventional molecular conversions.

The arylation or the equivalent approaches the aromatic ring along the perpendicular direction to form π -complex, then it gradually converts to σ -complex with one of the carbon atom of the aromatic ring. As acylium ion generally has highly stabilized structure compared to alkyl cation, the obtained π -complex is considered to be also stabilized and inert enough to give sufficient regioselectivity. In this course, the electrically and sterically preferred *p*-positioned carbon atom of the terminal phenyl group should react predominantly. Furthermore, the absence of the strong electron-donating group probably brings about insufficient electron density of the arene ring resulting in the electron-withdrawing deactivation of the



Scheme 26.

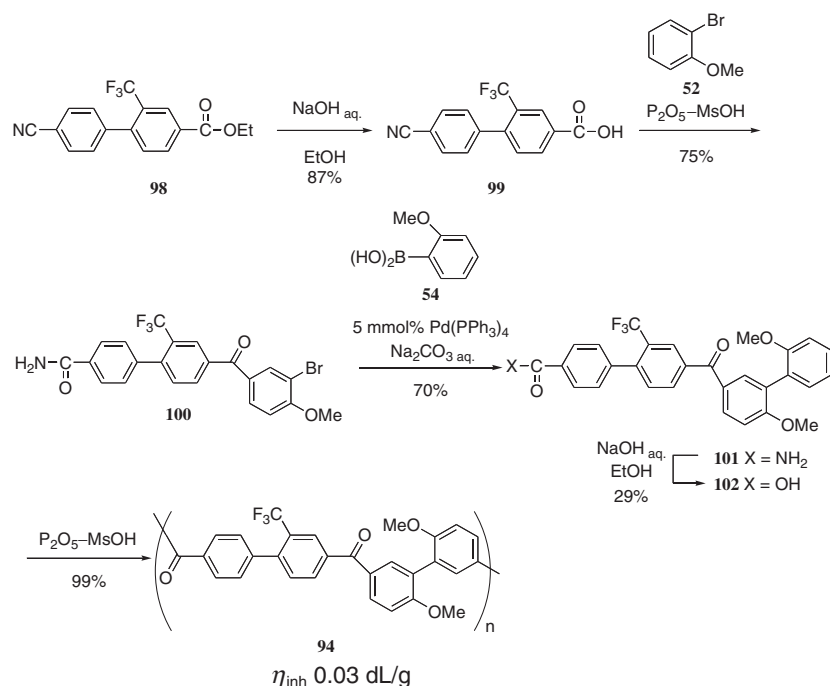


Polymerization was carried out with 0.25 mol of dicarboxylic acid monomer **93** and 0.25 mmol of monomer **7** in 2.5 mL of P₂O₅-MsOH at 80°C for 2 h under nitrogen.

Scheme 27.

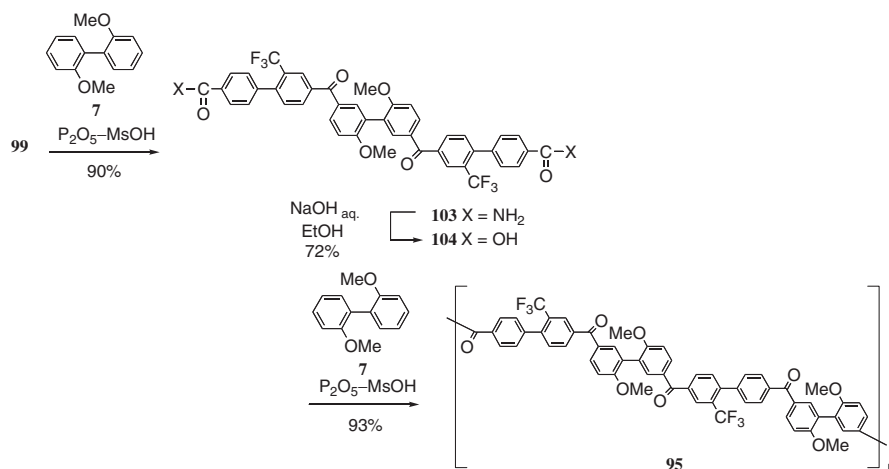
central phenylene ring by the aroyl group introduced in the terminal phenyl group. The other terminal phenyl group should also receive the rather small electron withdrawing deactivation effect along with the steric hindrance of the aroyl group. This situation plausibly causes the difference in susceptibility to

aroylation between the non-aroylated substrate and the mono-aroylated one. In addition, the authors' group has confirmed that the third aroylation is possible to proceed on the central phenylene ring under the somewhat drastic reaction conditions.¹²⁷



Polymerization was carried out with 0.04 mol of carboxylic acid monomer **102** in 1 mL of P_2O_5 -MsOH at 80°C for 2 h under nitrogen.

Scheme 28.

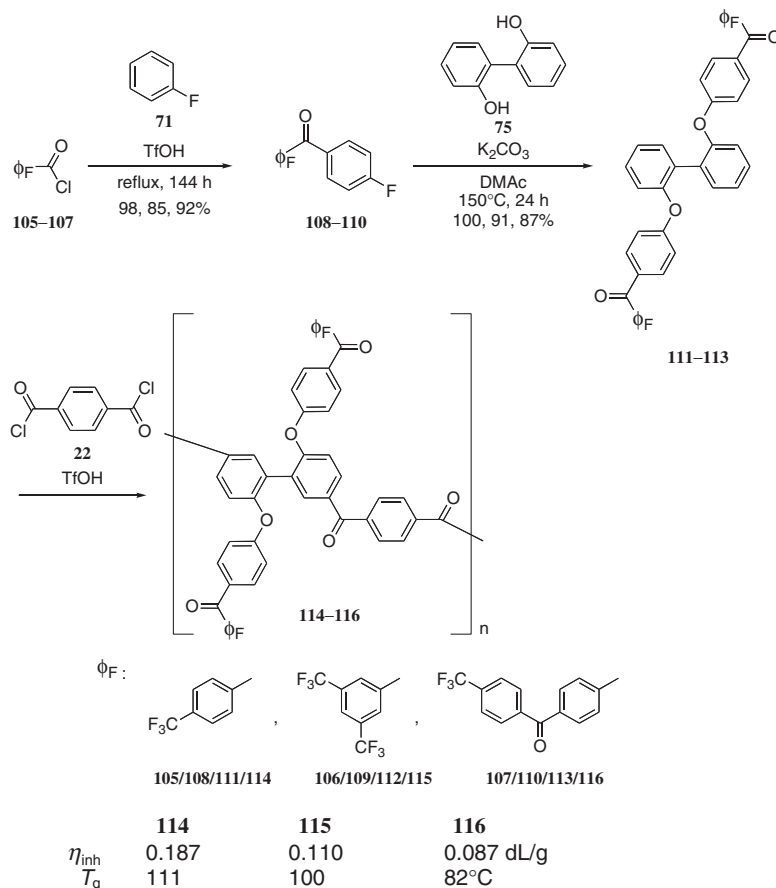


Polymerization was carried out with 0.25 mol of dicarboxylic acid monomer **104** and 0.25 mmol of monomer **7** in 2 mL of P_2O_5 -MsOH at 80°C for 2 h under nitrogen.

Scheme 29.

Based on the results of the reaction of *o*-terphenyl (**117**) with *p*-chlorobenzoic acid (**26**), the P_2O_5 -MsOH-mediated polycondensation of *o*-terphenyl (**117**) with arenedicarboxylic acids were attempted. However, electrophilic aromatic arylation polycondensation was unsuccessful, probably due to the insufficient acyl-acceptant ability of the phenyl terminal in the monoarylated terphenyl species to achieve quantitative arylation.

Though the reactivity of *o*-terphenyl (**117**) against electrophilic arylation condensation is rather low, it is still sufficiently high for dual functionalization by diarylation to prepare the other types of monomers as an aromatic ring assembly precursor. 4,4''-Bis(4-chlorobenzoylated) *o*-terphenyl (**119**) obtained in the electrophilic aromatic arylation reaction has just the requisite of the monomer for aromatic coupling polycondensation. The terphenyl derivative (**119**) was sub-



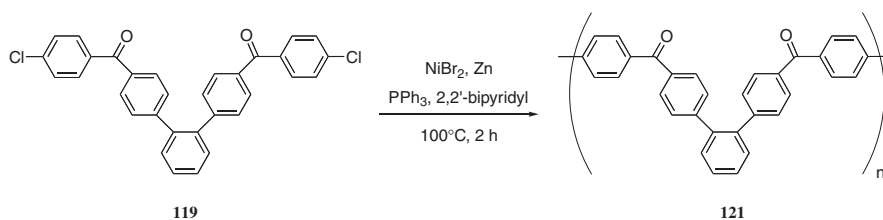
Polymerization was carried out with 0.2 mol of monomers **111–113** in 0.5 mL of $\text{ClCH}_2\text{CH}_2\text{Cl}$ (1,2-dichloroethane) and 0.2 mmol of dicarbonyl dichlorides **22** (added by portion at rt) followed by reflux for 30 min under nitrogen using 0.1 mmol of TfOH.

Scheme 30.

Table I. Regioselective bis(*p*-chlorobenzoylation) of *o*-terphenyl (**117**)^a

Run	X	Reagent	Amount of Reagent ^b	Temp/°C	Time/h	Yield/%	
						119	120
1	Cl	AlCl_3^c	0.6 mmol	20	5	0	57
2	Cl	$\text{Fe}_2(\text{SO}_4)_3$	0.2 mmol	150	24	37	11
3	OH	PPA ^d	3 mL	100	24	0	0
4	OH	$\text{P}_2\text{O}_5\text{-MsOH}^e$	1 mL	100	4	14	62
5	OH	$\text{P}_2\text{O}_5\text{-MsOH}^e$	1 mL	100	8	57	17
6	OH	$\text{P}_2\text{O}_5\text{-MsOH}^e$	1 mL	100	24	38	5

^aReaction conditions: *p*-chlorobenzoyl chloride (**118**) or *p*-chlorobenzoic acid (**26**), 3 mmol; *o*-terphenyl (**117**), 1 mmol. ^bAmount of reagent against 1 mmol of *o*-terphenyl (**117**). ^c4 mL of 1,2-dichloroethane was added as a solvent. ^dPPA: polyphosphoric acid. ^e $\text{P}_2\text{O}_5\text{-MsOH}$: 1/10 (w/w) mixture of P_2O_5 and methanesulfonic acid.



Polymerization was carried out with 0.25 mmol of monomer **119** in 0.25 mL of DMAc at 100°C for 2 h under nitrogen using 0.125 mmol of NiBr₂, 0.776 mmol of Zn, 0.25 mmol of PPh₃, and 0.125 mmol of 2,2'-bipyridyl (bpy).

Scheme 31.

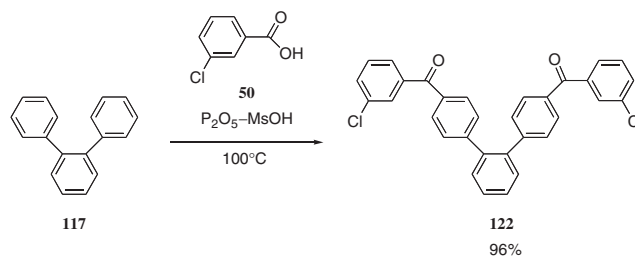
jected to nickel-complex-mediated aromatic coupling polycondensation (Scheme 31).

The nickel-complex-mediated aromatic coupling polycondensation of monomer **119** was performed under the almost same reaction conditions with those for bis(chlorobenzoyl)-2,2'-dioxybiphenyls (**28**, **47**, and **51**). As a result, the polycondensation gave the polyketone having amorphous property and good film-forming ability. The resulting polyketone (**121**) has T_g of 176 °C and T_{d5} of 560 °C, where T_{d5} means the temperature of 5% weight loss recorded in the thermogravimetric thermogram recorded under N₂ atmosphere. On comparison of the thermal indices of the resulting polyketone (**121**) with those of the polyketone derived from 5,5'-bis(4-chlorobenzoyl)-2,2'-dimethoxybiphenyl (**28**), the T_g is lower by 42 K and the T_{d5} is higher by 110 K. These phenomena indicate that the amorphous state of the polyketone bearing *o*-terphenylene unit (**121**) is less stable than that of the polyketone derived from 5,5'-bis(4-chlorobenzoyl)-2,2'-dimethoxybiphenyl (**28**). They also mean that polyketone **121** has far higher heat resistance than the latter polyketone (**28**).

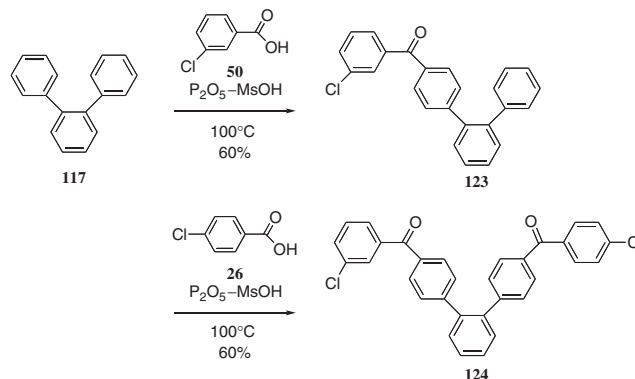
The obtained polyketone (**121**) is perfectly free from ether bondings both in the main chain and the side ones. This structural characteristic is considered to reflect the thermal property of the resulting polyketone distinctively. The unique thermal behavior of this polyketone described above is interpreted from the molecular structure and the conformation. The presence of two kinds of twisted aromatic ring assembly moieties in the *o*-terphenylene-bearing polyketone (**121**), *i.e.*, biphenylene and *o*-terphenylene, should lead the loosely stacked mass of the aromatic ring units resulting in less stable amorphous state. On the contrary, the absence of the methoxy groups in the entire molecule probably affords tolerance to thermal decomposition.

In a natural consequence of this, other monomers having *o*-terphenylene units for aromatic coupling polycondensation were designed. First, an isomeric symmetrical monomer of 4,4''-bis(3-chlorobenzoyl)-*o*-terphenyl (**122**) was successfully synthesized by the same method as the corresponding 4-chloro isomeric monomer (**119**) (Scheme 32).

Another isomeric monomer having unsymmetrical structure, 4-(3-chlorobenzoyl)- and 4''-(4-chlorobenzoyl)-*o*-terphenyl (**124**), was also synthesized successfully *via* P₂O₅-



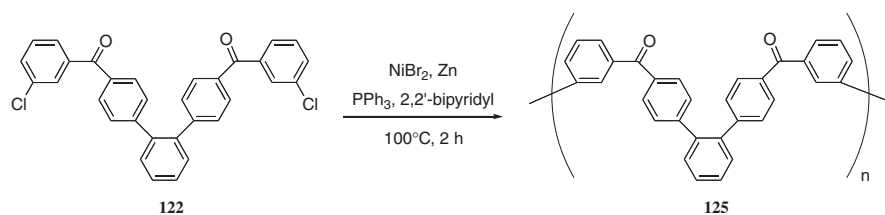
Scheme 32.



Scheme 33.

MsOH-mediated monoaroylation with 3-chlorobenzoic acid (**50**) followed by the second aroylation with the 4-chlorobenzoic acid (**26**) (Scheme 33).

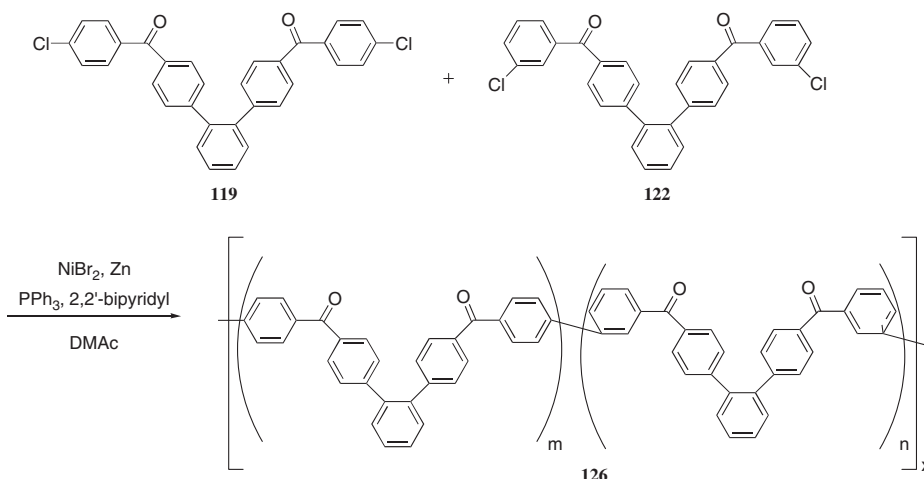
In contrast to the aroylation of 2,2'-dimethoxybiphenyl (**7**), that of *o*-terphenyl (**117**) gave monoaroylated product in a good yield. The column chromatographical separation of the crude product of the reaction of equimolar amounts of *o*-terphenyl and *p*-chlorobenzoic (**26**) acid or *m*-chlorobenzoic acid (**50**) satisfactorily gave pure monoaroylated derivative. The successful synthesis of monoaroylated derivatives of *o*-terphenyl (**117**) is interpreted by the following mechanism. The susceptibility to aroylation reaction of *o*-terphenyl (**117**) is sufficiently high to yield the regioselectively aroylated product in a preparative scale. However, the reactivity of *o*-terphenyl (**117**) is somewhat lower than that of 2,2'-dimethoxybiphenyl (**7**). Furthermore, deactivation by the introduced aroyl group



Polymerization was carried out with 0.25 mmol of monomer **122** in 0.25 mL of DMAc at 100°C for 2 h under nitrogen using 0.125 mmol of NiBr₂, 0.388 mmol of Zn, 0.125 mmol of PPh₃, and 0.25 mmol of 2,2'-bipyridyl (bpy).

Scheme 34.

Table II. Copolymerization of monomers **119** and **122**



Run	NiBr ₂ /mol%	Temp./°C	Time/h	Yield/%	$\eta_{inh}/dL\ g^{-1a}$	M_n^b
1	25	100	2	99	0.21	9100
2	50	100	2	96	0.30	10200
3	100	100	2	96	0.18	7400
4	50	80	2	96	0.14	6200
5	50	120	2	99	0.11	5200
6	50	100	1	96	0.26	10200
7	50	100	3	96	0.30	9700

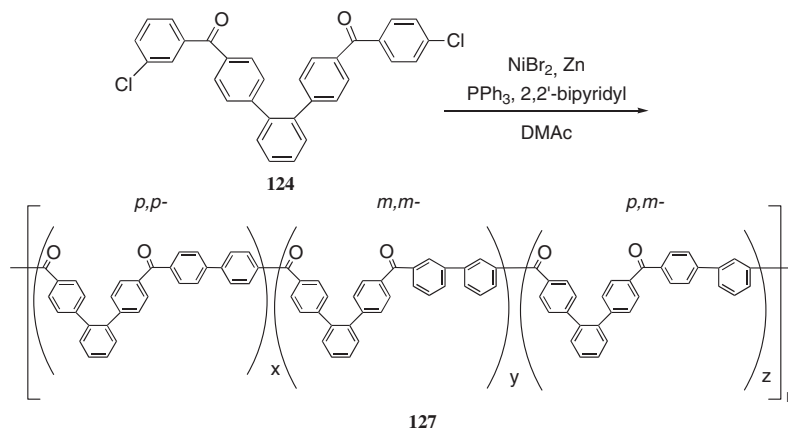
Reaction conditions: each monomer (**119**, **122**), 0.0625 mmol; Zn, 0.388 mmol; NiBr₂: 2,2'-bipyridyl: PPh₃ = 1:1:2; DMAc, 0.25 mL. ^aDetermined in a concentrated H₂SO₄ solution (0.3 g dL⁻¹) at 30 °C. ^bCalculated on the basis of GPC measurement (Column, Shodex; GPC KD-806M. Eluent, CHCl₃, UV detector, 300 nm).

might affect the other terminal phenyl group in the monoaroylated *o*-terphenyl derivative probably by interaction *via* space. So the reactivity of monoaroylated derivative of *o*-terphenyl (**117**) is lower than that of *o*-terphenyl (**117**) itself. Then the aroylation reaction might be controlled to cease at the monoaroylated state by the choice of the specified reaction conditions. These situations should also lead the separation of the monoaroylated product and *o*-terphenyl (**117**) possible due to the different polarity between the two compounds.

The nickel-complex-mediated aromatic coupling polycondensation of these monomers were performed under the almost same reaction conditions with those for bis(4-chlorobenzoylated) homologue (Scheme 34 and Tables II and III). Furthermore, there seems scarce difference between the reactivity of 3-chlorobenzoyl moiety and 4-chloro counter part. The

copolymerization of 4,4''-bis(3-chlorobenzoylated) *o*-terphenyl (**122**) and 4,4''-bis(4-chlorobenzoylated) *o*-terphenyl (**119**) successfully proceeded. The copolymerization proceeds in the arbitrary ratio of two symmetric monomers. And the polymerization of unsymmetrically bis(chlorobenzoylated) *o*-terphenyl, *i.e.*, 4-(3-chlorobenzoylated) and 4''-(4-chlorobenzoylated) *o*-terphenyl (**124**), also proceeded successfully.

By these polycondensation, two types of copolyketones were obtained. Table IV shows the four isomeric fully aromatic polyketones composed of *o*-terphenylene units. The T_{d5} 's of the four polyketones are essentially same. On the other hand, the T_g 's spread in the range of 156 °C to 189 °C. These results suggest that the thermal resistance of these polyketones depends essentially on the common structure of the repeating units and the stability of the glassy state of the polymers

Table III. Polymerization of unsymmetrical monomer **127**


Run	NiBr ₂ /mol %	Temp./°C	Time/h	Yield/%	$\eta_{inh}/dL g^{-1}$ ^a	M_n ^b
1	50	100	2	98	0.18	8000
2	25	100	2	89	0.11	5100
3	100	100	2	91	0.14	6800
4	50	100	1	94	0.19	8000
5	50	60	2	97	0.18	6100
6	50	80	2	98	0.20	6800
7	50	120	2	98	0.20	8200

^aReaction conditions: Monomer, 0.125 mmol; Zn, 0.388 mmol; NiBr₂: 2,2'-bipyridyl: PPh₃ = 1:1:2; DMAc, 0.25 mL. ^aDetermined in a concentrated H₂SO₄ solution (0.3 g dL⁻¹) at 30 °C. ^bCalculated on the basis of GPC measurement (Column, Shodex GPC KD-806M; Eluent, CHCl₃; UV detector, 300 nm).

Table IV. Thermal properties of polyketones **121**, **125–127**, **46**, **48**

polymer	$T_g/^\circ C$	$T_d/^\circ C^a$
121	176	560
125	156	563
126	189	562
127	183	564
46	218	450
48	189	— ^b

^aTemperature where a 5 wt% weight loss was recorded by TG. ^bNot measured.

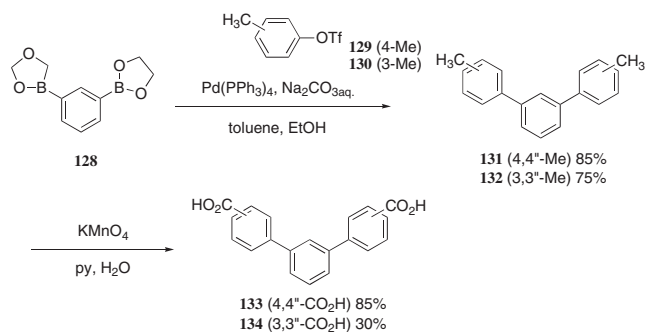
depends clearly on the sequence of the combination of the regioisomeric repeating units. The four polyketones are aligned as random (unsymmetrical), copolymer (1:1), *p,p'*-linked polymer, and *m,m'*-linked polymer on the basis of T_g by the order of low to high temperature. This phenomenon is interpreted from the point of the difference in the interaction of polymer chains on the basis of chain structure. The *m*-linked biphenylene units should afford the polymer extremely high flexibility resulting in weak interaction among macromolecular chains as shown in the comparison of isomeric polyketones derived from chlorobenzoylated 2,2'-dimethoxybiphenyl monomers (**28** and **47**) (polyketone **46** and polyketone **48**) described in the preceding section. In this case, *o*-terphenylene moiety should make the polymer main chain highly twisted. From this viewpoint, the repeating unit in the polyketone obtained from chlorobenzoylated *o*-terphenyl should have doubly folded structure. This is somewhat different structure compared to the corresponding polyketones derived from chlorobenzoylated 2,2'-dimethoxybiphenyl.

The polyketone derived from bis(*m*-chlorobenzoylated) *o*-terphenyl (**125**) shows the lowest T_g among the four isomeric polyketones (Table IV). In the *m,m'*-linked polyketone (**125**), both the 3,3'-biphenylene assembly and *o*-terphenylene assembly have doubly folded crankshaft structures excluding the rod-like rigid polymer main chain parts. Then, the aggregation state of the *m,m'*-linked polyketone (**125**) has scarce portion of the regularly aligned structure. This probably leads the lower T_g than those of the other isomeric polyketones.

The polyketone derived from *p,p'*-chlorobenzoylated *o*-terphenyl (**119**), which has rigid and extended non-substituted 4,4'-biphenylenedicarbonyl unit and highly twisted *o*-terphenylene one alternately, has the regularity of the aggregation state of polymer molecules almost equal with or somewhat lower level than polyketone **48**, which is obtained from bis(*m*-chlorobenzoylated) 2,2'-dimethoxybiphenylene (**47**).

On the other hand, the polyketones having the structures of ternary mixture of biphenylenedicarbonyl moieties show higher T_g than other two isomeric polyketones. It is probably due to the effective combination of doubly folded *o*-terphenylene units and the ternary mixture of biphenylene units bonded by ketonic carbonyl groups giving the more stable state than those of the polyketones having sole isomeric part of biphenylene unit. The alternating sequence of regular but highly twisted aromatic ring assemblies should cause the rather weak aggregation state compared with the mixed repeating unit structure.

On the basis of the observation described above, the mixing of the extended aromatic ring assembly moiety and the isomeric folded one in molecular size scale is considered to be effective to stabilize amorphous state of these polymers.



Scheme 35.

Contrary to the T_g , the thermogravimetric behaviors of these polymers are almost equal. It is speculated that the thermal decomposition depends largely on the nature of the intrinsic property of the individual bonding because the thermal decomposition accompanying with weight loss means at least the occurrence of the scission of bondings. In this process, the differences in the aggregation state scarcely affect the decomposition temperature. However, this interpretation is a mere conjecture at this stage. To confirm the thermal decomposition behavior accurately, model thermal reaction and/or quantitative analysis of the decomposition of the polyketone are required.

Synthesis of the bis(halobenzoylated) Monomer Bearing *m*-Terphenyl Moiety¹²⁸

The successful synthesis of the polyketones consisting of *o*-terphenylene unit and biphenylene one prompted the authors' group to attempt the synthesis of *m*-terphenyl analogues with expectation of novel expression of property of aromatic polymers. However, the synthesis of functionalized *m*-terphenyl has proved troublesome (Scheme 35). The electrophilic substitution of *m*-terphenyl often suffers from low regioselectivity. The alternative route for introduction of functional groups into *m*-terphenyl nuclei has been found very complicated. Furthermore, the solubility is rather unsuitably low for solution polymerization. At the present stage, it is better to conclude *m*-terphenylene moiety is difficult to be introduced into wholly aromatic polyketone skeletons.

SYNTHESIS OF WHOLLY AROMATIC POLYKETONES COMPRISING OF 2,2'-DIMETHOXY-1,1'-BINAPHTHYLYLENE MOIETY AND THE RELATING POLYKETONES AND COMPOUNDS¹²⁹⁻¹³³

As one of the most effective chiral sources for asymmetric synthesis, 2,2'-disubstituted 1,1'-binaphthyls have been widely employed. This chiral unit structure is also irreplaceable for the synthesis of artificial chiral polymers. On the other hand, the methyl ether derivatives of this unit structure, 2,2'-dimethoxy-1,1'-binaphthyl (**135**), has the structure of just the aromatic homologue of 2,2'-dimethoxybiphenyl (**7**). It means that binaphthyl compound **135** is expected to play a role of acyl-acceptant monomer in aromatic polyketone synthesis (Figure 7).

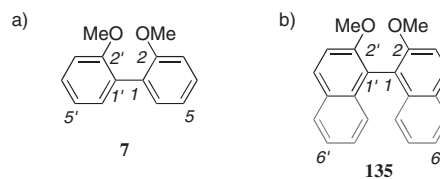
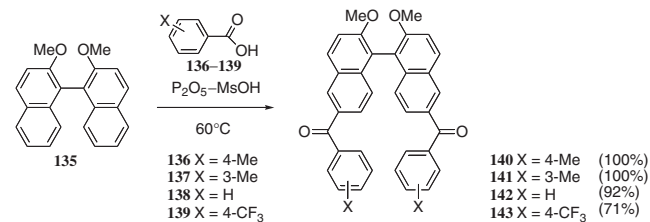


Figure 7. Acyl-acceptant aromatic compound and the analogue. a) 2,2'-dimethoxybiphenyl (**7**), b) 2,2'-dimethoxy-1,1'-binaphthyl (**135**).



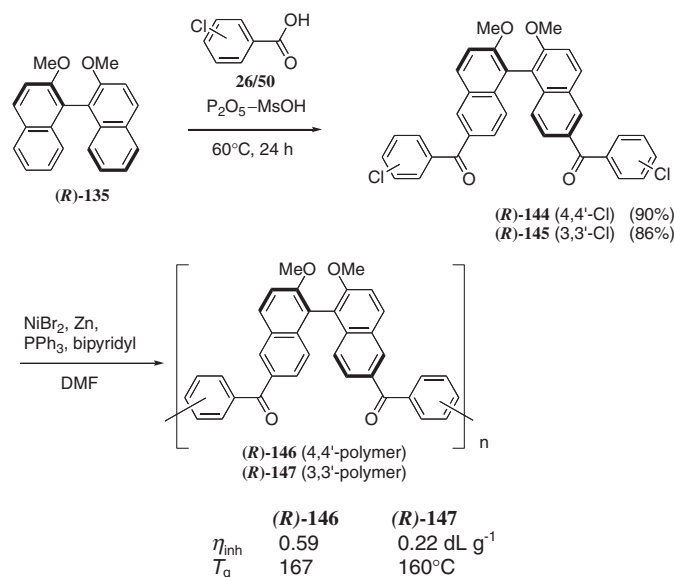
Scheme 36.

On these circumstances, it is valuable to utilize the molecule for the construction of the wholly aromatic polyketones and the relating compounds.

Regioselective Electrophilic Aromatic Acylation of 2,2'-Dimethoxy-1,1'-binaphthyl

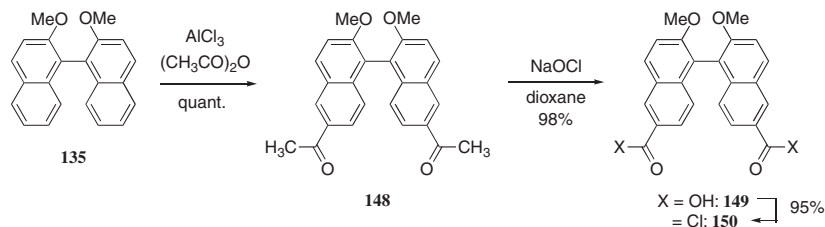
The binaphthyl derivative (**135**) has good regioselectivity on the 6- and 6'-carbons to accept acylium electrophiles (Scheme 36).¹²⁹ However, the reactivity of this molecule is somewhat lower than that of 2,2'-dimethoxybiphenyl (**7**). In fact, the electrophilic aromatic acylation polycondensation of 2,2'-dimethoxy-1,1'-binaphthyl molecule (**135**) gives the polymer only when the acyl-donor monomer of especially high reactivity such as oxybis(benzoic acid) (**11**)/isophthalic acid (**17**) or the acid chloride derivatives is employed.¹³⁰ On the other hand, the reactivity of the electrophilic aromatic acylation of 2,2'-dimethoxy-1,1'-binaphthyl (**135**) is sufficient for tandem introduction of acyl groups. Furthermore, the rather moderate reactivity allows the isolation of the mono-acylated derivative and the synthesis of the unsymmetrically 6,6'-diacylated or functionalized 2,2'-dimethoxy-1,1'-binaphthyl derivatives *via* step-wise acylation or functionalization. Thus, the utilization of 2,2'-dimethoxy-1,1'-binaphthyl (**135**) as a construction block for aromatic polyketones is more effective when it is employed as a monomer precursor rather than the direct acyl-acceptant arene.¹³¹

The synthesis of the polyketones containing 2,2'-dimethoxy-1,1'-binaphthylene unit has a lot of attractive facts and results. Especially, the resulting optically active polyketones are interesting as it affords a chiral π -conjugated molecular sphere. In a natural course of such background, the authors' group has been investigating the synthesis and characterization of aromatic polyketones having 2,2'-dimethoxy-1,1'-binaphthylene units. As briefly concerned above, introduction of 2,2'-dimethoxy-1,1'-binaphthylene unit into aromatic polyketones has been performed efficiently *via* regioselective



Polymerization was carried out with 0.4 mmol of monomer (*R*)-144 or (*R*)-145 in 0.8 mL of DMAc at 100°C for 2 h under nitrogen using 0.2 mmol of NiBr₂, 1.2 mmol of Zn, 0.4 mmol of PPh₃, and 0.2 mmol of 2,2'-bipyridyl (bpy).

Scheme 37.



Scheme 38.

electrophilic aromatic arylation introduction of polymerizable functional groups into 2,2'-dimethoxy-1,1'-binaphthyl nuclei (**135**) followed by suitable polymerization such as transition metal complex aromatic coupling polycondensation (Scheme 37) and electrophilic aromatic arylation polycondensation (Schemes 38, 39).^{130,132}

In the same manner, utilization of nucleophilic aromatic substitution polymerization is far more convenient method to obtain optically active aromatic polymers of aromatic poly(ether ketone)s (Scheme 40).^{133,134}

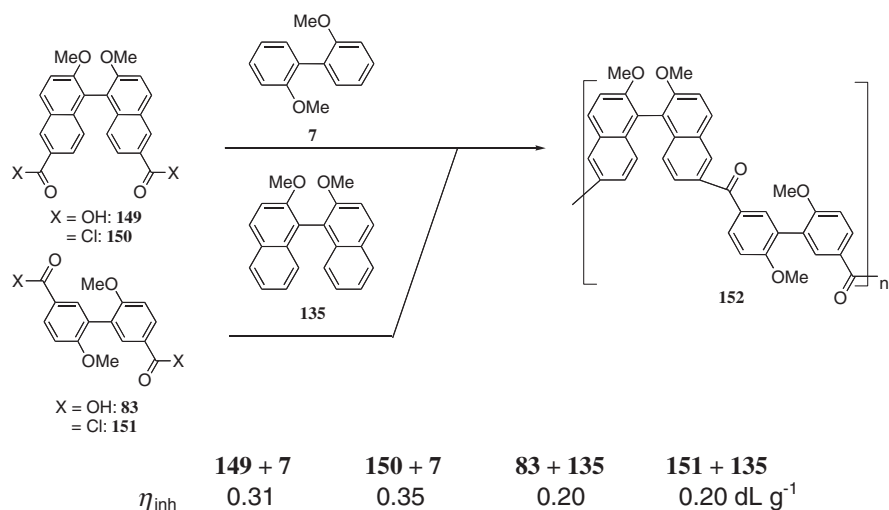
The chemistry of the wholly aromatic polyketones composed of 2,2'-dimethoxy-1,1'-binaphthyl (**135**) will be reviewed and discussed elsewhere in the future.

THE PROPERTIES OF WHOLLY AROMATIC POLYKETONES

The wholly aromatic polyketones prepared by the authors' group generally have highly amorphous nature. The melting of

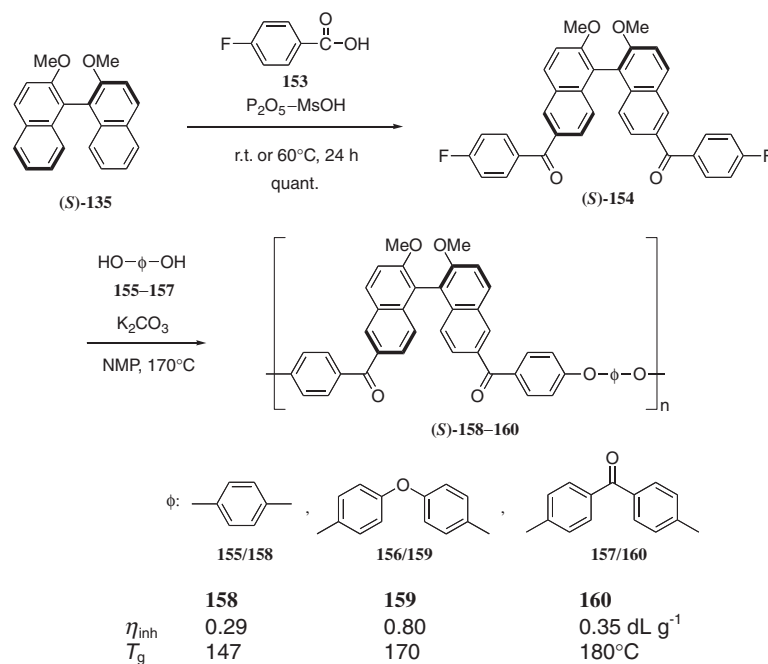
the polymers was hardly observed. Almost all of the polymers show only glass transition. The T_g 's are dispersed in rather wide range of over 100°C up to 220°C. The twisted geometry of the aromatic ring assembly moiety in the polymer main chain probably affords the isotropic tight-packed aggregation of aromatic ring parts of the polymer molecules. The polymers generally show high decomposition temperature (5 or 10%-weight loss temperature). Absence of ethereal linkage probably disturbs the thermal scission of polymer main chain. Before thermal decomposition, intramolecular pyrolytic coupling of aromatic rings should proceed to afford thermally stabilized organic solid.

The solubility of the polymers is essentially low. The wholly aromatic polyketones derived from 2,2'-dimethoxybiphenylene or 2,2'-dimethoxybinaphthylene acyl-acceptant monomer without fluorinated alkyl group are substantially insoluble in most of organic solvents. Contrarily, the wholly aromatic polyketones having terphenylene moiety show rather good solubility in wide range of organic solvents. For example,



Polymerization was carried out according to either of the following two procedures: 1) dicarboxylic acid monomer **149** or **83** (0.2 mmol) and the counter acyl-acceptant monomer (**7** or **135**, 0.2 mmol) were allowed to react in 0.4 mL of P₂O₅-MsOH at 80°C for 2 h under nitrogen, 2) dicarbonyl chloride monomer **150** or **151** (0.2 mmol) and the counter acyl-acceptant monomer (**7** or **135**, 0.2 mmol) were allowed to react in 0.5 mL of ClCH₂CH₂Cl (1,2-dichloroethane) at 50°C for 24 h under nitrogen using 1.2 mmol of TfOH.

Scheme 39.



Polymerization was carried out with 0.2 mmol of monomer (*S*)-**154** and 0.2 mmol of aromatic diols **155–157** in 0.5 mL of NMP at 170°C for 6 h under nitrogen using 1 mmol of potassium carbonates.

Scheme 40.

polymer **121** is soluble in chloroform, chlorobenzene, DMF, 1,4-dioxane, tetrahydrofuran, and toluene. The difference should be brought about by rather loose packing of the molecules due to the structural limitation of terphenylene moiety.

CONCLUSION

Nucleophilic aromatic substitution reaction is one of the most effective synthetic method for poly(ether ketone)s.

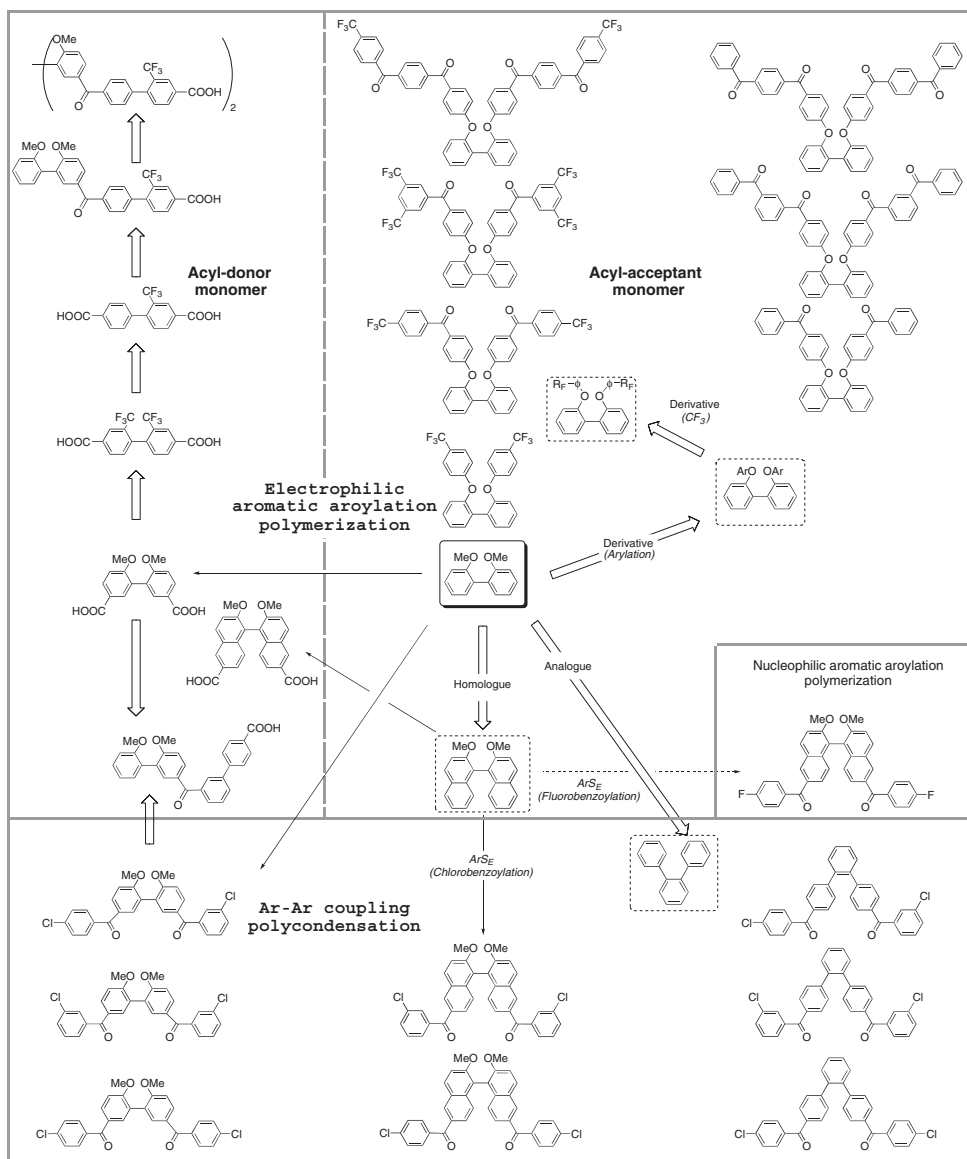


Figure 8. Family of monomers for syntheses of wholly aromatic polyketones.

However, this reaction inevitably places the ether linkage in the resulting polymer main chain. Therefore, it is unable to be applied for the synthesis of wholly aromatic polyketones. The strategy to construct novel aromatic polyketone skeleton with exclusion of ether bondings from the main chain, wholly aromatic polyketone, was performed by overcoming the problems.

For preparation of aromatic polyketones, several possible protocols are plausible. However, preparation of aromatic polyketones requires electrophilic aromatic arylation ketone construction as the final polymerization stage and/or the monomer/precursor synthesis. When the electrophilic aromatic arylation is the enchainment step, employment of equimolar amounts of bifunctional acyl-acceptant and bifunctional acyl-donor monomers or self-complementary compound having bifunctionality of both acyl-accepting and acyl-donating ability

is choice of the monomer. When the enchainment is undertaken by carbon-carbon bond formation with the aid of aromatic coupling-polymerization, introduction of ketonic carbonyl groups in the monomer preparation is ordinarily employed.

Under such circumstances, the syntheses of wholly aromatic polyketones are investigated by designing bifunctional aromatic compounds capable to undergo successive electrophilic aromatic arylation substitution were surveyed patiently. Against these candidate molecules, the electrophilic aromatic arylation reactions as direct polycondensation and as dual functionalization bringing about enchainment ability were investigated. The monomers described in this article are displayed with the correlations in Figure 8.

In the course of investigation, 2,2'-dimethoxybiphenyl (7) has proved to play a role of an excellent acyl-acceptant

monomer in electrophilic aromatic arylation polyketone synthesis. This molecule has proved highly enhanced electronically to realize subsequent reactivity and regioselectivity. Moreover, this advantage is assisted by characteristic structure of twisted biphenylene moiety. These electronic and structural merits of biphenyl monomer **7** also give the resulting intermediating polymeric molecules sufficient flexibility for polymerization to proceed to a satisfactory extent. This compound has been revealed as a potential precursor for monomers against nickel-complex-mediated aromatic coupling polycondensation synthesis of wholly aromatic polyketone. The strategic combination of aromatic coupling and electrophilic aromatic arylation enabled the syntheses of unsymmetrically chlorinated monomer and self-complementary monomer. These monomers afforded randomly sequenced and regularly sequenced wholly aromatic polyketones, respectively. Furthermore, the homologous 2,2'-diaryloxybiphenyl **65** has proved another potential acyl-acceptant monomer for electrophilic aromatic arylation polyketone synthesis.

The doubly folded structure of *o*-terphenyl (**117**) enables highly regioselective electrophilic aromatic arylation to give three regioisomeric monomers (**119**, **122**, and **124**) for aromatic coupling polycondensation. These monomers afford the fully aromatic polyketones, which exclude ether bondings from the entire polymer molecules. These polyketones show quite good resistance to thermal decomposition and characteristic glass transition behavior.

The regioselective electrophilic aromatic arylation has been also realized against 2,2'-dimethoxy-1,1'-binaphthyl (**135**). Employment of this chiral compound affords aromatic polyketones (**146**, **147**, **152**), composed of optically active π -conjugated aromatic ring assembly.

The syntheses of wholly aromatic polyketones bearing fluorine-containing groups (**80**, **93–95**) have been also achieved. Furthermore, sequence controlled syntheses of three kinds of the wholly aromatic polyketones, *i.e.*, homogeneously sequenced, irregularly sequenced, and regularly sequenced polyketones have been achieved by fine designing of the intermediate and the synthetic route.

This still novel type of aromatic polymer has characteristics of amorphous property, twisted and partially conjugated structure, and good heat residence. The polymers consist of only carbon, hydrogen, and oxygen atoms and achieve the high performance. In other words, it forms the environment friendly highly performed polymer group with other non-hetero atom polymers, such as polyarylates, polyethers, and so on. The results contain some facilitating facts and behaviors including other than polymer synthesis.^{135–138}

Furthermore, the structure of the wholly aromatic polyketones reminds the authors of the intermediating polymers which might be formed in the long term process of conversion from wood to charcoal where initially contained oxygen and hydrogen atoms are eliminated with carbon atoms as small molecules.

Conclusively, the synthesis and the characterization of wholly aromatic polyketones still remains much room to be studied.

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