A Novel Type of Polycondensation Utilizing Transition Metal-Catalyzed C–C Coupling. I. Preparation of Thermostable Polyphenylene Type Polymers

Takakazu YAMAMOTO,* Yasuhiro HAYASHI, and Akio YAMAMOTO

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 227

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Transition metal compounds including $NiCl_2(bpy)$ (bpy=2,2′-bipyridine), $NiBr_2(PPh_3)_2$ (PPh_3=triphenylphosphine), $PdCl_2(bpy)$, $NiCl_2$, $CoCl_2$, $FeCl_2$, and $FeCl_3$ catalyze polycondensation of di- and polyhalogenated organic aromatic compounds by dehalogenation with magnesium under mild conditions. Poly(*p*-phenylene), poly(*m*-phenylene), poly(oxybiphenylene), and poly(phenylenemethylene) were prepared from *p*-dihalobenzene, *m*-dichlorobenzene, bis(*p*-bromophenyl) ether, and α,*p*-dichlorotoluene. They have a high degree of polymerization and high thermal stability. Poly(*p*-phenylene), poly(oxybiphenylene), and poly(phenylenemethylene) have regularly repeated structures as proved by IR spectroscopy and X-ray powder diffraction. Polymerization of polyhalogenated aromatic compounds (1,3,5-trichlorobenzene and hexachlorobiphenyl) in tetrahydrofuran (THF) gave copolymers having aromatic nuclei and THF units. Polymerization of the haloaromatic compounds is considered to proceed through a mechanism in which consecutive cycles of oxidative addition of haloaromatic compounds (R–X) to the transition metal catalyst take place so as to cause alkylation (arylation) by the Grignard reagent formed in the system (R′MgX) and elimination of R–R′ from an active transition metal compound having R and R′ groups.

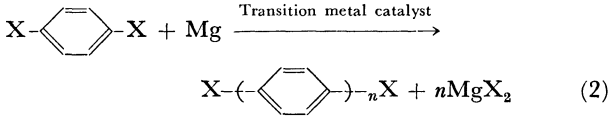
Polyphenylene type polymers consisting of coupled aromatic nuclei have high heat-resistance. Some of them have been utilized as material for rocket nozzles, electrical insulation, and fabrics which must withstand high temperatures.[1] Numerous reactions which produce the polyphenylene-type polymers have been developed over the past 15 years. The preparative methods include: (1) oxidative cationic polymerization of aromatic compounds by use of Friedel-Crafts type catalysts,[2] (2) dehalogenation of di- and poly-halogenated aromatic compounds with metals such as copper (Ullmann reaction)[3] and alkali metals (Wurtz-Fittig reaction),[4] (3) denitrogenation polymerization of diazonium compounds.[5] Of these methods the dehalogenation of di- and poly-halogenated aromatic compounds with metals such as copper[3] and alkali metals[4] serve as one of the most convenient and versatile routes for the preparation of the polyphenylene type polymers. However, the dehalogenation reaction by metals generally requires high temperatures, the polymers obtained having some structural irregularity and/or branching due to the radical nature of the conventional dehalogenation reactions by metals.

It was recently reported that transition metals or their compounds catalyze the coupling of Grignard reagents with aryl halides.[6]

$$RMgX + R'X \xrightarrow{\text{Transition metal}} R\text{-}R' + MgX_2 \qquad (1)$$

Since the transition metal-catalyzed coupling reaction proceeds selectively and quantitatively under mild conditions, it has been applied to the preparation of various organic aromatic compounds.[6]

Extension of the principle of the transition metal catalyzed coupling led us to its application to the preparation of polyphenylene-type polymers having regular recurring units by starting from dihalogenated aromatics. *p*-Dihalobenzene, for example, can be readily dehalogenated by coupling on reaction with magnesium which is promoted by transition metal catalysts, a linear polyphenylene being formed.



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The net reaction resembles the conventional dehalogenation polymerization of haloaromatic compounds with Cu and Na. However, the reaction by the new method proceeds under much milder conditions, and can be applied more widely. A part of the results was reported previously.[7]

Results and Discussion

Polymerization of Halo Aromatic Compounds. The results of polymerization of di- and poly-halogenated aromatic compounds are given in Table 1. Although the halo aromatic compounds are not polymerized with magnesium alone in the absence of transition metal catalyst (Exp. No.1, Table 1), addition of a catalytic amount of a suitable transition metal compound to the reaction mixtures initiates very smooth polymerization to yield polyphenylene-type polymers in high yields.

Dihalo Aromatic Compounds: A variety of transition metal compounds catalyze the polymerization of *p*-dibromobenzene. Of the transition metal complexes, $NiCl_2(bpy)$ (bpy=2,2′-bipyridine) acts as one of the most effective catalysts. Even a minor amount of the compound (*e.g.*, 5 mg of the complex with Ni/monomer of 3.4×10^{-4} in Exp. No. 3) gives a polymer in a high yield in 4 h at refluxing temperature of tetrahydrofuran (THF).

The polymerization proceeds most smoothly in THF under reflux conditions. However, since the catalytic activity of the complex is very high, it proceeds even at 0 °C (No. 4) though there is some induction period in this case. Employment of other ethereal solvents such as dibutyl ether (No. 5) and diglyme

TABLE 1. DEHALOGENATION POLYMERIZATION OF HALO ALOMATIC COMPOUNDS WITH MAGNESIUM IN THE PRESENCE OF TRANSITION METAL CATALYSTS[a)]

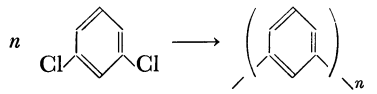
No.	Monomer	g (mmol)	Mg g (mmol)	Catalyst[b)] (mg)	Solvent[c)] (ml)	Time h	Yield[d)] g(%)	Remarks
1	*p*-Dibromobenzene	11.8(50)	1.22(50)	none	THF	4.0	0	
2	*p*-Dibromobenzene	11.8(50)	1.22(50)	$NiCl_2$(bpy) (51)	THF	4.0	3.8(95)	
3	*p*-Dibromobenzene	11.8(50)	1.22(50)	$NiCl_2$(bpy) (5)	THF	4.0	2.7(64)	
4	*p*-Dibromobenzene	11.8(50)	1.22(50)	$NiCl_2$(bpy) (50)	THF	6.0	4.0(94)	e)
5	*p*-Dibromobenzene	11.8(50)	1.22(50)	$NiCl_2$(bpy) (50)	Bu_2O	4.5	2.8(68)	
6	*p*-Dibromobenzene	11.8(50)	1.35(56)	$NiBr_2(PPh_3)_2$ (50)	THF	4.0	2.7(64)	
7	*p*-Dibromobenzene	11.8(50)	1.22(50)	$PdCl_2$(bpy) (50)	THF	4.0	4.1(95)	
8	*p*-Dibromobenzene	11.8(50)	1.35(56)	$FeEt_2(bpy)_2$ (100)	THF	6.0	0.8(18)	
9	*p*-Dibromobenzene	11.8(50)	1.35(56)	$CrMeCl_2(THF)_3$ (50)	THF	7.0	0.5(11)	
10	*p*-Dibromobenzene	11.8(50)	1.22(50)	$Ni(cod)(PPh_3)_2$ (50)	THF	4.0	3.8(86)	
11	*p*-Dibromobenzene	11.8(50)	1.22(50)	$NiCl_2$ (54)	THF	4.0	4.0(83)	
12	*p*-Dibromobenzene	11.8(50)	1.22(50)	$FeCl_2$ (50)	THF	4.0	3.2(76)	
13	*p*-Dibromobenzene	11.8(50)	1.22(50)	$FeCl_3$ (50)	THF	4.0	3.0(68)	
14	*p*-Dibromobenzene	11.8(50)	1.22(50)	$CoCl_2$ (50)	THF	4.0	3.2(77)	
15	*p*-Dichlorobenzene	7.4(50)	1.32(54)	$NiCl_2$(bpy) (70) (50)	THF	6.0	2.5(60)	
16	*p*-Diiodobenzene	3.3(10)	0.24(10)	$NiCl_2$(bpy) (8)	THF	4.0	0.4(50)	
17	*m*-Dichlorobenzene	7.2(49)	1.22(50)	$NiCl_2$(bpy) (50)	THF	6.0	3.6(92)	
18	Bis(*p*-bromophenyl)ether	12.8(40)	1.33(55)	$NiCl_2$(bpy) (100)	THF	5.0	4.0(60)	
19	Bis(*p*-bromophenyl)ether	11.9(36)	1.33(55)	$NiBr_2(PPh_3)_2$ (55)	THF	9.0	2.4(39)	
20	α,*p*-Dichlorotoluene	8.09(50)	1.28(53)	$NiCl_2$(bpy) (50)	THF	7.0	3.3(69)	
21	2,5-Dibromopyridine	11.9(50)	1.22(50)	$NiCl_2$(bpy) (50)	THF	8.0	3.9(62)	
22	2,5-Dibromopyridine	11.9(50)	1.22(50)	$NiBr_2(PPh_3)_2$ (50)	THF	8.0	4.5(64)	
23	2,5-Dibromopyridine	11.9(50)	1.22(50)	$NiCl_2$ (50)	THF	8.0	1.4(23)	
24	9,10-Dibromoanthracene	8.4(25)	0.64(26)	$NiCl_2$(bpy) (50)	THF	6.0	1.25(22)	
25	1,3,5-Trichlorobenzene	9.07(50)	3.65(150)	$NiCl_2$(bpy) (50)	THF	15	2.15	f)
26	1,3,5-Trichlorobenzene	4.53(25)	1.83(75)	$NiCl_2$(bpy) (50)	Diglyme	10.5	1.76(72)	
27	Hexachlorobiphenyl	18.0(50)	3.65(150)	$NiCl_2$(bpy) (50)	THF	15.0	8.2	f)

a) Under reflux except for No. 4. b) bpy=2,2′-bipyridine, PPh_3=triphenylphosphine, cod=1,5-cyclooctadiene, Me=methyl, Et=ethyl. c) THF=tetrahydrofuran, Bu_2O=dibutyl ether. d) Based on the amount of carbon taken into the polymer. e) At 0 °C. f) Copolymer with THF (see the text).

gives similar results.

Other nickel and palladium complexes such as $NiBr_2(PPh_3)_2$ (PPh_3=triphenylphosphine) and $PdCl_2$(bpy) also show high catalytic activities, but the catalytic activities of iron and chromium complexes, $Fe(C_2H_5)_2(bpy)_2$ and $CrCl_2(CH_3)(THF)_3$, are relatively low. Simple transition metal compounds such as $NiCl_2$, $FeCl_2$, and $CoCl_2$ catalyse the polymerization as well. In contrast to these transtion metal compounds metallic Pd and Ni, $PdCl_2$, $CuBr_2$, Cu(acetylacetonato)$_2$, and $MnCl_2$ have negligible or no catalytic activity for the polymerization, although Pd metal and $PdCl_2$ are known to act as effective catalysts for the preparation of low molecular weight aromatic compounds by Reaction 1.[6d,6e)] Cuprous halides do not catalyze the polymerization of halo aromatic compounds, either, but they catalyze the polymerization of halo aliphatic compounds to yield aliphatic polymers having high molecular weight. *p*-Dichlorobenzene and *p*-diiodobenzene are also polymerized by the transition metal catalysts, the yields being lower than in the polymerization with *p*-dibromobenzene.

Polymerization is not restricted to *p*-dihalobenzene. *m*-Dichlorobenzene (No. 17, Table 1) and other dihalo aromatic compounds such as bis(*p*-bromophenyl) ether and α,*p*-dichlorotoluene can be polymerized by using the transition metal catalysts.



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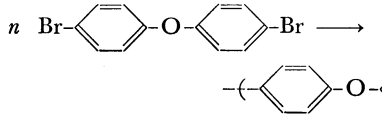

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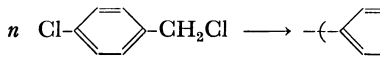

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Some transition metal compounds catalyze the coupling between organolithiums and organic halides:[8)]

$$RLi + R'X \xrightarrow{[M]} R\text{-}R' + LiX \quad (6)$$

However, attempts to utilize lithium instead of magnesium as the dehalogenating reagent in the preparation of polyphenylene type polymers from aromatic halides were unsuccessful.

Polyhalo Aromatic Compounds: When the dehalogenation polymerization of aromatic compounds having three or more halogen atoms is carried out in THF (Nos. 25 and 27, Table 1), the polymers obtined

Table 2. Properties of the polyphenylene type polymers

No.[a]	Polymer	Color	Mp (°C)	Soluble fraction in hot toluene (%)[b]
2	$-(-p\text{-}C_6H_4-)-_n$	light yellow	550 dec	20
6	$-(-p\text{-}C_6H_4-)-_n$	light yellow	550 dec	16
14	$-(-p\text{-}C_6H_4-)-_n$	light yellow	550 dec	35
17	$-(-m\text{-}C_6H_4-)-_n$	white	190—200[c]	39
			280—295[d]	
18	$-(-C_6H_4\text{-}O\text{-}C_6H_4-)-_n$	white	250—280	18
20	$-(-C_6H_4CH_2-)-_n$	white	230—235[c]	52
			>400[d]	
21	$-(-C_5H_3N-)-_n$	brown	260	e)
25	$C_6H_3Cl_3$-THF copolymer[f]	yellow	190—195	
26	$-(-C_6H_3-)-_n$	brown	290 dec	
27	$C_{12}H_4Cl_6$-THF copolymer[f]	brown	185—200	

a) Numbers correspond to those in Table 1. b) Extracted with hot toluene in a Soxhlet extractor for 50 h. c) For polymers soluble in hot toluene. d) For polymers insoluble in hot toluene. e) Soluble in acidic water. f) See the text.

contain both the aromatic nuclei and THF units. The IR spectra show bands characteristic of not only aromatic compounds but also of polytetrahydrofuran $-(-O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2-)-_n$. The NMR spectra show signals of aromatic protons at δ 7—8 ppm and those of THF-protons at δ 1.8 ppm $-(-CH_2\text{-}\underline{CH_2}\text{-}CH_2-)-$, δ 2.4 ppm $-(-C_6H_4\text{-}\underline{CH_2}-)-$, δ 3.7 ppm $-(-O\text{-}\underline{CH_2}-)-$, and δ 4.1 ppm $-(-C_6H_4\text{-}O\text{-}\underline{CH_2}-)-$. The polymers are not soluble in THF, which dissolves polytetrahydrofuran, but soluble in chloroform, which does not dissolve polyphenylene type polymers. The resutls suggest that the polymers are copolymer such as

$$-(-A-)\overline{_m}-(-O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2-)-_n,$$

where A represents the aromatic units.

In the case of hexachlorobiphenyl polymerized with magnesium in THF, the NMR spectrum indicates that the copolymer contains the two monomer units in about 1:1 ratio in line with the analytical data. The peak areas of methylene protons at δ 2.4 ppm and δ 4.1 ppm contained in the THF units adjacent to the aromatic unit are considerably small, although the copolymer contains the two monomer units in about 1:1 ratio. This suggests that the copolymer has a block structure rather than a random structure.

The copolymers of polyhaloaromatic compounds and THF melt without decomposition at considerably high temperatures (Table 2). The polymerization of polyhalogenated aromatic compounds in other ethereal solvents such as dibutyl ether and diglyme gives normal dehalogenated homopolymers of the polyhalogenated aromatic compounds (No. 26).

Properties of Polymers. Physical Properties: The color, melting point, and solubility of the polymers obtained are given in Table 2. The polymers prepared by the present method are much less colored than those prepared by conventional methods such as oxidative cationic polymerization of benzene and dehalogenation polymerization of halo aromatic compounds. For example, poly(*p*-phenylene) prepared by the present method is light yellow, whereas the one prepared by conventional methods is brown or black.[1-5] Poly(*m*-phenylene) prepared by the Wurtz-Fittig reaction[4b] of $m\text{-}C_6H_4Br_2$ and poly(oxybiphenylene) prepared by the polycondensation of potassium *p*-(*p*-bromophenyl)phenoxide[9] were reported to be yellow and gray, respectively.

The polymers prepared here generally have high thermal stability. The thermal stability of poly(*p*-phenylene) prepared by the present method is comparable with that prepared by the oxidative cationic polymerization of benzene. It does not melt up to 550 °C, where it begins to decompose in the air. Differential thermoanalysis (DTA) of poly(*p*-phenylene) in the air showed an exothermic peak at 580 °C due to the oxidation of the polymer. Poly(*m*-phenylene), poly(oxybiphenylene), poly(phenylenemethylene), and poly(2,5-pyridinediyl) melt above 200 °C. Poly(1,3,5-benzene-triyl)(No. 26) which appears to have a three dimentional structure decomposes at 290 °C without melting. The copolymers with THF melt at relatively low temperatures, their melting points being much higher than the melting point of the THF homopolymer.

The solubility of the polyphenylene-type polymers is low. Poly(*p*-phenylene), poly(*m*-phenylene), poly(oxybiphenylene), and poly(phenylenemethylene) are partially extracted by hot toluene as shown in Table 2, but the extracted fractions do not dissolve in toluene at room temperature. Poly(pyridinediyl) (No. 21—23) is soluble in an aqueous solution containing HCl with the concentration higher than 3 M. Dilution or neutralization of the solution caused precipitation of the polymer. The copolymers with THF are soluble in chlorinated hydrocarbons such as $CHCl_3$ and CCl_4.

IR Spectra and Molecular Weight: Figute 1 shows IR spectra of typical polymers. The IR spectrum of poly(*p*-phenylene) prepared by the present method is essentially of poly(*p*-phenylene)s prepared by conventional methods such as oxidative cationic polymerization of benzene. The out-of-plane vibration of *p*-phenylene units, δ(para), in poly(*p*-phenylene)s prepared under various conditions appears in the region 805±

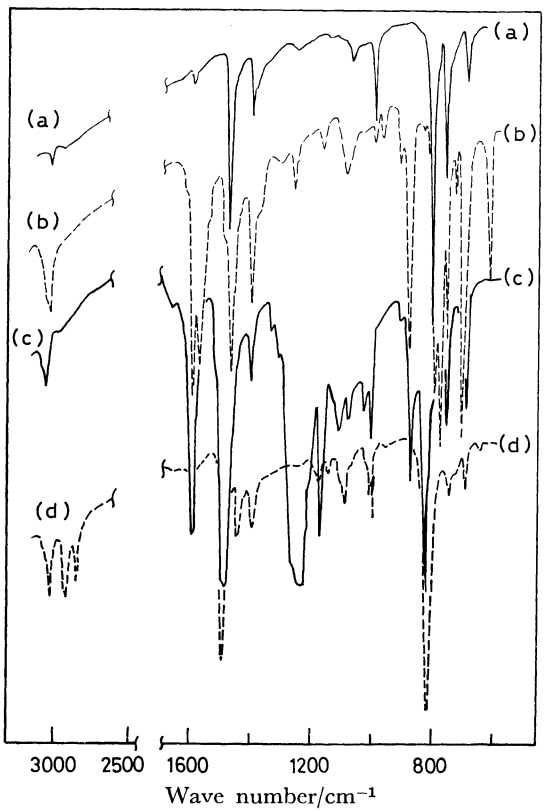
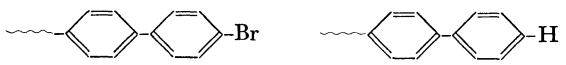


Fig. 1. IR spectra of (a) poly(*p*-phenylene) prepared from *p*-dibromobenzene, (b) poly(*m*-phenylene), (c) poly(oxybiphenylene), and (d) poly(phenylenemethylene).

5 cm^{-1}. Weak ν(C–Cl), ν(C–Br), and ν(C–I) bands of terminal *p*-halophenyl groups are observed at 1085, 1065, and 1055 cm^{-1}, respectively, in the IR spectra of poly(*p*-phenylene)s prepared from the corresponding *p*-dihalobenzenes. In addition to the δ(para) band at 805±5 cm^{-1} assignable to the *p*-phenylene units the IR spectrum of poly(*p*-phenylene) shows two out-of-plane vibration bands due to terminal phenyl group at 760 cm^{-1} (δ(mono$_1$)) and 690 cm^{-1} (δ(mono$_2$)).[2b] These IR spectroscopic data suggest that the poly(*p*-phenylene) has both *p*-halophenyl and phenyl groups as the terminal groups:



The fact that the intensities of the bands due to the terminal phenyl group (δ(mono$_1$) and δ(mono$_2$)) are much greater than the ν(C–X) band suggests that the proportion of the terminal group bearing the halogen is not so high.

Kovacic and Oziomek took the relative intensity of δ(para) to that of δ(mono$_1$) and δ(mono$_2$), $A(\delta(\text{para}))/\{A(\delta(\text{mono}_1))+A(\delta(\text{mono}_2))\}$ (A=absorbance of the peak), as a measure for the degree of polymerization.[2b,2c] The value $A(\delta(\text{para}))/\{A(\delta(\text{mono}_1)+A(\delta(\text{mono}_2)\}$ for poly(*p*-phenylene) prepared from dibromobenzene with various catalysts lies between 1.92 (No. 2, Table 1) and 3.85 (No. 7, Table 1), indicating that poly(*p*-phenylene)s obtained have considerably high degrees of polymerization, comparable to that

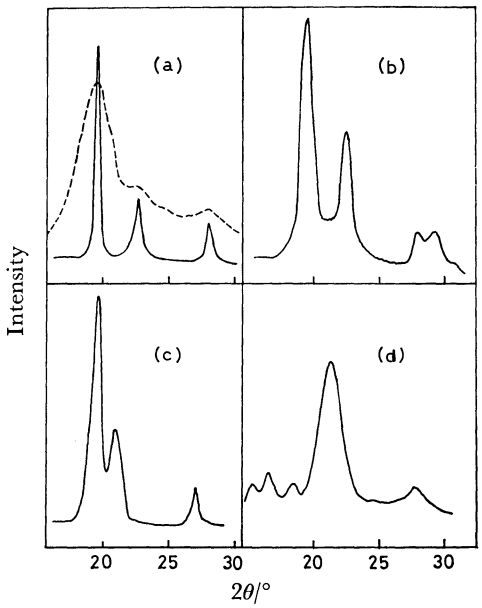


Fig. 2. X-Ray diffraction patterns of (a) poly(*p*-phenylene), (b) poly(oxybiphenylene), (c) poly(phenylenemethylene), and (d) poly(*m*-phenylene). See the text for the broken line in Fig. 2a.

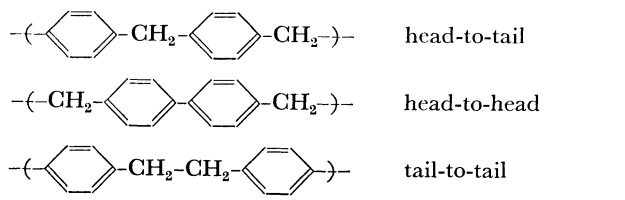
prepared by Kovacic and Oziomek through oxidative cationic polymerization of benzene.[2b]

The IR spectra of types of polymers other than poly(*p*-phenylene) are also in line with the expected structures as represented in Eqs. 3—5. The absorptions in the region of the out-of-plane vibration of poly(*m*-phenylene) are more complicated than those of poly(*p*-phenylene) since each *m*-phenylene unit has both isolated δ(C–H) and three adjacent δ(C–H)'s. Poly(oxybiphenylene) has strong ν(C–O) band at 1245 cm^{-1} and poly(phenylenemethylene) has aliphatic ν(C–H) bands at 2860 and 2960 cm^{-1}. Poly(oxybiphenylene) and poly(phenylenemethylene) have ν(C–X) (1050—1090 cm^{-1}) band of terminal halophenyl group and δ(C–H) (680—770 cm^{-1}) bands of terminal phenyl group. The fact that the relative intensities of these bands assignable to terminal phenyl and halophenyl groups are considerably weaker than those of δ(C–H) bands due to the inner repeating aromatic units (800—900 cm^{-1}) indicates that these polymers have high degree of polymerization.

X-Ray Diffraction: Figure 2 shows X-ray diffraction patterns of the powdery polymers prepared by polycondensation with magnesium. The X-ray diffraction spectrum of poly(*p*-phenylene) shows strong and sharp peaks even before annealing of the polymer, indicating that the polymer has high crystallinity due to the polymer structure having regularly repeated units in the polymer chain produced by highly selective condensation reaction between the Grignard reagents and aryl halides (Eq. 1). The poly(*p*-phenylene) prepared by the oxidative cationic polymerization of benzene shows only broad signals as represented by the broken line in Fig. 2a when it is not annealed; sharp peaks appear only after the annealing of the polymer.[2d]

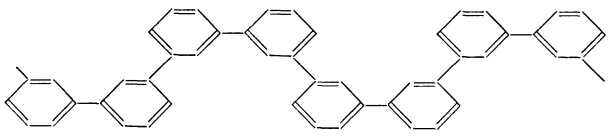
The X-ray diffraction patterns of poly(oxybiphenylene) and poly(phenylenemethylene) also show sharp

peaks before annealing. Formation of the following three units is possible in the polymerization of α,*p*-dichlorotoluene:

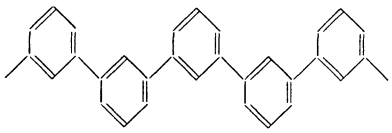


However, the sharp X-ray diffraction peaks of the polymer as well as the simple IR pattern in the region of the out-of-plane vibration suggest that the polymer contains mainly one of the three units, presumably the head-to-tail structure.

The X-ray diffraction pattern of poly(*m*-phenylene) shows broad peaks and that of poly(2,5-pyridinediyl) shows no clear peaks. The broadness of the peaks in the X-ray pattern of poly(*m*-phenylene) might be due to the irregularities caused by the presence of both *cis-trans* and *trans-trans* configurations:



cis-trans



trans-trans

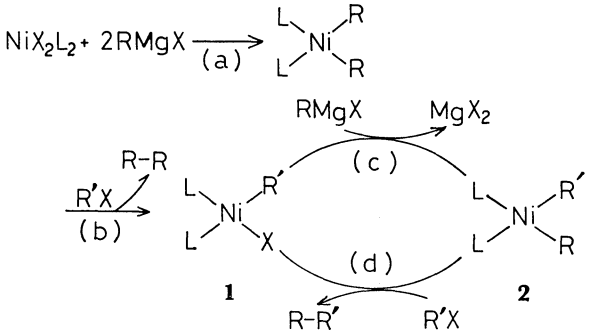
3. Polymerization Mechanism: The coupling between a Grignard reagent RMgX and an aryl halide R'X catalyzed by a dihalonickel complex NiX_2L_2 (L= ligand) (Eq. 1) seems to proceed through a mechanism comprised of

(a) formation of NiR_2L_2 by the reaction of NiX_2L_2 with RMgX,

(b) reaction of NiR_2L_2 with R'X to yield R–R and $NiR'(X)L_2$,

(c) alkylation of $NiR'(X)L_2$ with RMgX to yield $NiR(R')L_2$, and

(d) elimination of R–R' with formation of $NiR'(X)L_2$ in the reaction of $NiR(R')L_2$ with R'X:[6b]



In the mechanism the starting complex NiX_2L_2 is converted into the active species $NiR'(X)L_2$ by reactions (a) and (b). The catalytic formation of R–R' then proceeds through the key intermediates $NiR'(X)L_2$ and $NiR'(R)L_2$.

If the same mechanism can be applied to the present polymerization of p-$C_6H_4Br_2$, it seems to proceed as follows:

$$\mathrm{BrNiL_2}\text{-}(\text{-}\mathrm{C_6H_4}\text{-})\text{-}_{n_1}\mathrm{MgBr} + \mathrm{Br}\text{-}(\text{-}\mathrm{C_6H_4}\text{-})\text{-}_{n_2}\mathrm{MgBr}$$
$$\mathbf{1}(n_1) \qquad\qquad \mathbf{P}(n_2)$$
$$\xrightarrow{\text{(c) type reaction}} \mathrm{Br}\text{-}(\text{-}\mathrm{C_6H_4}\text{-})\text{-}_{n_2}\mathrm{NiL_2}\text{-}(\text{-}\mathrm{C_6H_4}\text{-})\text{-}_{n_1}\mathrm{MgBr} + \mathrm{MgBr_2}$$
$$\mathbf{2}(n_1, n_2)$$
$$\mathbf{2}(n_1, n_2) + \mathrm{Br}\text{-}(\text{-}\mathrm{C_6H_4}\text{-})\text{-}_{n_3}\mathrm{MgBr}$$
$$\mathbf{P}(n_3)$$
$$\xrightarrow{\text{(d) type reaction}} \mathrm{BrNiL_2}\text{-}(\text{-}\mathrm{C_6H_4}\text{-})\text{-}_{n_3}\mathrm{MgBr} + \mathrm{Br}\text{-}(\text{-}\mathrm{C_6H_4}\text{-})_{\overline{n_1+n_2}}\mathrm{MgBr}$$
$$\mathbf{1}(n_3) \qquad\qquad \mathbf{P}(n_1+n_2)$$
$$\mathbf{1}(n_3) + \mathbf{P}(n_4) \rightarrow \mathbf{2}(n_3, n_4)$$
$$\mathbf{2}(n_3, n_4) + \mathbf{P}(n_5) \rightarrow \mathbf{1}(n_5) + \mathbf{P}(n_3+n_4)\cdots \textit{etc.}$$

Scheme 1.

where $\mathbf{P}(n)$ stands for the polymer having n phenylene units and $\mathbf{P}(1)$ represents the monomer p-BrC_6H_4MgBr which is the main product of the reaction between p $C_6H_4Br_2$ and Mg. $\mathbf{1}(n_1)$, $\mathbf{2}(n_1,n_2)$... represent intermediate nickel complexes **1** and **2** having phenylene groups bonded to nickel. We have examined the time course of the polycondensation by following the disappearance of the mono-Grignard reagent Br–C_6H_4–MgBr, di-Grignard reagent BrMg–C_6H_4–MgBr and intact dibromobenzene formed by the reaction of dibromobenzene with Mg in a 1:1 ratio by means of gas chromatography. The amounts of the di- and mono-Grignard reagents were measured as benzene and bromobenzene after hydrolysis of the reaction mixture.

Figure 3 shows time-course of the decrease of species in the $NiCl_2$(bpy)-catalyzed dehalogenation polymerization of p-$C_6H_4Br_2$ with Mg at 3±1 °C where the rate of polymerization is not very high. As shown in Fig. 3 the reaction of p-$C_6H_4Br_2$ with Mg in a 1:1 molar ratio gives a mixture of p-$C_6H_4(MgBr)_2$, p-BrC_6H_4MgBr, and intact p-$C_6H_4Br_2$. The rate of consumption of these chemical species is low at the early stage, becoming higher after the induction period. The dihalonickel complex $NiCl_2$(bpy) seems to be converted into the active species (*e.g.*, Ni(C_6H_4MgBr)(Br)(bpy), **1**(1)) during the induction period.

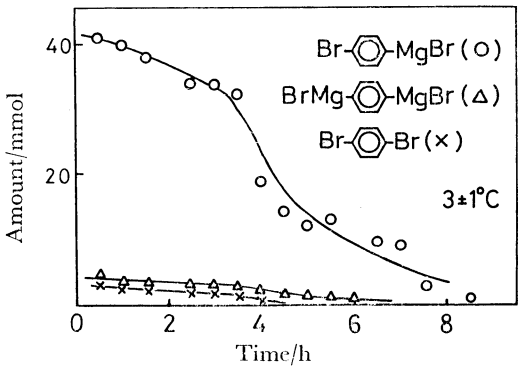
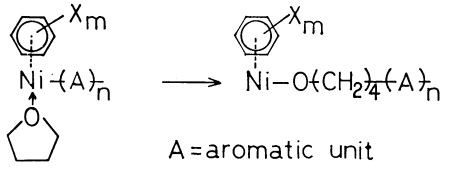


Fig. 3. Time course of mnomer consumption during the polymerization of p-$C_6H_4Br_2$ (11.8 g, 50 mmol) in THF (50 ml) at 3±1 °C; p-BrC_6H_4MgBr (○), p-$C_6H_4(MgBr)_2$ (△), and p-$C_6H_4Br_2$ (×), Catalyst = $NiCl_2$(bpy) (50 mg).

According to Scheme 1 the polymer should have both $-C_6H_4MgBr$ and $-C_6H_4Br$ terminals. The phenyl terminal of poly(p-phenylene) was thought to be formed from the $-C_6H_4MgBr$ terminal during the work-up of the polymer. However, reactions of the raw polymer with D_2O or CO_2 did not introduce D or carboxyl group into the polymer. This excludes the presence of the $-C_6H_4MgBr$ terminal in the polymer. The phenyl terminal can be formed through the incorporation of mono-functional species such as C_6H_5MgBr and C_6H_5Br formed by the reactions of p-$C_6H_4(MgBr)_2$ and p-BrC_6H_4MgBr with trace amounts of water in the solvent. If these nomo-functional species should participate, the polymerization would be terminated with formation of the phenyl terminal(s). Under certain conditions the polymerization might be terminated mainly through this process, and most of the polymer end would be the phenyl group. The infrared spectra of some polymers suggest the formation of polymers with phenyl end group(s). Addition of C_6H_5Br or C_6H_5MgBr into the polymerization system decreases the degree of polymerization as judged from the increase in the intensities of $\delta(\text{mono}_1)$ and $\delta(\text{mono}_2)$ in the IR spectrum of the polymer obtained.

When an aromatic compound having three or more halogen atoms is employed for the polymerization, it may act as an electron acceptor, coordinating with the transition metal complex. Coordination of the electron acceptor to the transition metal would enhance the Lewis acidity of the transition metal and initiate the ring-opening polymerization of THF, which is usually catalyzed by Lewis acid, producing the copolymer with THF units:



Experimental

Material. Commercial haloaromatic compounds except for hexachlorobiphenyl were used. Hexachlorobiphenyl was supplied by Prof. Emeritus S. Kambara. Solvents were dried over sodium wire and distilled under nitrogen. $NiCl_2$(bpy),[10] $NiBr_2(PhP_3)_2$,[11] $PdCl_2$(bpy),[12] $Fe(C_2H_5)_2$-(bpy)$_2$,[13] $Cr(CH_3)Cl_2(THF)_3$,[14] and (1,5-cyclooctadiene)bis-(triphenylphosphine)nickel[15] were prepared according to the literature. Commercial products were used for simple transition metal compounds.

Polymerization. When 51 mg of $NiCl_2$(bpy) was added to a mixture of the products obtained by the reaction of 11.8 g (50 mmol) of p-dibromobenzene with 1.22 g (50 mg-atom) of magnesium in dry tetrahydrofuran (50 ml), smooth polymerization started. Polymerization was almost completed after refluxing the mixture for 1 h. After further refluxing for 4 h the reaction mixture was poured into 500 ml of ethyl alcohol. The polymer precipitated was collected over a glass filter, washed with dilute hydrochloric acid and ethyl alcohol, and dried in a vacuum to yield 3.8 g (95%) of light yellow poly(p-phenylene) (No. 2, Table 1). Extraction of the polymer by hot toluene with Soxhlet extractor for 50 h gave 0.70 g of the extractable fraction. Polymerization of p-dibromobenzene catalyzed by other transition metal compounds and that of other haloaromatic compounds were carried out in a similar manner. Analytical data of the polymers agreed with the structures given in the text. Percent yields in Table 1 are calculated based on the amount of carbon taken into the polymer.

The polyphenylene type polymers were also prepared by stirring the mixture of halo aromatic compound, magnesium, and the catalyst added before formation of the Grignard reagent. The yields and spectral data of the polymers prepared by this method were almost the same as those prepared by the method described above.

Kinetics. The reaction of p-dibromobenzene (11.8 g, 50 mmol) and magnesium (1.22 g, 50 mg-atom) was carried out in 50 ml of THF at room temperature. After completion of the reaction the reaction vessel was immersed in thermostatted water. Toluene (2.00 g) was added to the reaction mixture as an internal standard of gas chromatography and then 50 mg of $NiCl_2$(bpy) was added with stirring. The reaction mixture was occasionally pipetted out and treated with dil HCl. The amounts of p-$C_6H_4(MgBr)_2$, p-BrC_6H_4MgBr, and p-$C_6H_4Br_2$ were determined by measuring the amounts of benzene, bromobenzene, and p-dibromobenzene with a Shimadzu GC-3BT Gas Chromatogram.

Spectral Measurement and Analyses. IR spectra were recorded on a Hitachi Model 295 spectrometer. NMR spectra were taken with a Japan Electron Optics Laboratory SP-100 NMR spectrometer. Differential thermoanalyses were performed with a Shimadzu DT-30 thermal analyzer. X-Ray diffraction spectra were obtained with a Phillips PW-1051 X-Ray Diffractometer. Microanalyses of the polymers were performed by Mr. T. Saito with a Yanagimoto CHN Type MT-2 autocorder.

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