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A NOVEL TYPE OF POLYCONDENSATION OF POLYHALOGENATED ORGANIC AROMATIC COMPOUNDS PRODUCING THERMOSTABLE POLYPHENYLENE TYPE POLYMERS PROMOTED BY NICKEL COMPLEXES

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Nickel complexes ($NiCl_2$(2,2'-bipyridine) and $NiBr_2$(triphenylphosphine)$_2$) catalyze polycondensation of di- and polyhalogenated aromatic compounds including p-dibromobenzene, p-dichlorobenzene, m-dichlorobenzene, bis(4-bromophenyl)ether, p-chlorobenzyl chloride and 1,3,5-trichlorobenzene by dehalogenation with magnesium to give polyphenylene type polymers in high yields.

The great emphasis has been placed on the development of thermally stable polymers. Polyphenylene type polymers which are composed of coupled aromatic rings have high heat-resistance and some of them have been utilized as materials for rocket nozzles, electrical insulation, and fabrics which must stand against high temperatures.[1)] The dehalogenation of the haloaromatic compounds with metals such as copper (Ullmann reaction) and sodium (Wurtz-Fittig reaction) gives the polyphenylene type polymers,[1,2)] e.g.,

$$nC_6H_4X_2 \xrightarrow{\text{Cu or Na}} \left(C_6H_4 \right)_n \tag{1}$$

However, the dehalogenation requires high temperatures (commonly above 200°C) and the polymers prepared may have some steric irregularities or branching due to the radical nature of the conventional coupling reactions.

Recently Tamao and coworkers reported that nickel complexes catalyze the coupling of Grignard reagents and aryl(or alkenyl) halides.

$$RMgX + R'X \xrightarrow{NiY_2L_2} R\text{-}R' + MgX_2 \tag{2}$$

Since the nickel-catalyzed coupling reaction proceeds selectively and quantitatively under mild conditions, it is expected that the utilization of the coupling reaction in the preparation of the polyphenylene type polymers gives sterically regular polymers in high yield under mild conditions.

In this paper we report the polycondensation of di- or polyhalogenated aromatic compounds to polyphenylene type polymers by using the coupling reaction as expressed by Eq. 2, e.g.,

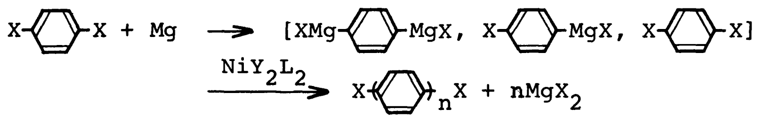
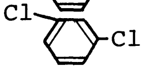
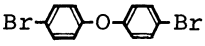
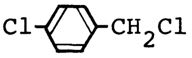


Table 1 Polymerization of Dihalogenated Aromatic Compounds by Dehalogenation with Magnesium Catalyzed by Nickel Complexes[a]

No	Monomer	g(mmol)	Mg g(mmol)	Catalyst(mg)[b]	Time	Yield,g(%)	Soluble in hot toluene	Insoluble in hot toluene[c]
1		11.8(50)	1.22(50)	$NiCl_2$(bpy)(25)	4.0h	3.5(94)	0.70 g	2.8 g
2	"	11.8(50)	1.22(50)	" (50)	6.5h	3.3(87)	0.20	3.1
3	"	11.8(50)	1.35(56)	$NiBr_2(PPh_3)_2$(50)	7.0h	2.7(71)	0.43	2.2
4	"	11.8(50)	1.35(56)	$FeEt_2(bpy)_2$(100)	6.0h	0.8(21)		
5	"	11.8(50)	1.35(56)	$CrMeCl_2(THF)_3$(50)	7.0h	0.5(13)		
6		7.4(50)	1.32(54)	$NiCl_2$(bpy)(70)	15.0h	2.5(66)	0.87	1.6
7		7.2(49)	1.22(50)	" (50)	6.0h	3.6(95)	1.4	2.2
8		12.8(40)	1.33(55)	" (100)	5.0h	4.0(50)	0.72	3.3
9	"	11.9(36)	1.33(55)	$NiBr_2(PPh_3)_3$(55)	9.0h	2.4(39)		
10		8.1(50)	1.28(53)	$NiCl_2$(bpy)(50)	7.0h	3.3(73)	1.7	1.6

a. In 60 ml of tetrahydrofuran, under reflux.

b. bpy = 2,2'-bipyridine, PPh_3 = triphenylphosphine, THF = tetrahydrofuran.

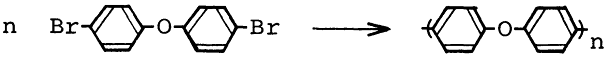
c. Extracted with hot toluene in a Soxhlet extractor for 50 hr.

where NiY_2L_2 represents a nickel complex (Y = halogen, L = ligand).

Table 1 shows the results of the polycondensation of the dihalogenated aromatic compounds by the dehalogenation with magnesium in the presence of nickel complexes. It is seen in Table 1 that dihalogenated aromatic compounds are readily polymerized to polyphenylene type polymers by the dehalogenation with magnesium in the presence of nickel complexes.

When 25 mg of $NiCl_2$(bpy) (bpy = 2,2'-bipyridine)[4)] was added to a mixture of products which were 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, smooth polymerization started, and the polymerization was almost completed after refluxing for 1 hr. After further refluxing for 3 hr the reaction mixture was poured into 500 ml of ethyl alcohol, and the polymer precipitated was collected over a glass filter and dried in vacuum to yield 3.5 g (94 %) of light yellow poly(p-phenylene). Extraction of the polymer by hot toluene with Soxhlet extractor for 50 hr gave 0.70 g of extractable fraction. The IR spectrum of poly(p-phenylene) thus prepared showed the out-of-plane vibration (ν(C-H)) at 803 cm^{-1} indicating that the polymer was linear poly(p-phenylene) having high degree of polymerization.[5)]

p-Dichlorobenzene was polymerized analogously. The polymerization is not restricted to that of p-dihalogenated benzene, but m-dichlorobenzene and aromatic compounds having oxygen, methylene and other units may be readily polymerized likewise.



The IR spectrum of poly(oxybiphenylene) showed a ν(C-O) band at 1245 cm^{-1}, and that of poly(phenylenemethylene) showed aliphatic ν(C-H) bands at 2860 and 2960 cm^{-1}. Since the region of out-of-plane vibration (600-900 cm^{-1}) in the IR spectra of the polymers showed relatively simple patterns, the polymers are considered to have regularly repeated structures.

The polymers obtained had relatively poor solubilities. However, when the polymer main chain is not symmetric as in poly(m-phenylene) or has methylene unit as in poly(phenylenemethylene), considerable parts of the polymers were extracted by hot toluene (Table 1).

$NiBr_2(PPh_3)_2$ (PPh_3 = triphenylphosphine)[6)] has comparable catalytic activity for the condensation polymerization. Although complexes of other metals such as $Fe(C_2H_5)_2(bpy)_2$[7)] and $Cr(CH_3)Cl_2$(tetrahydrofuran)$_3$[8)] also catalyze the polycondensation, their catalytic activities are much less than those of the nickel complexes.

The nickel catalyzed polycondensation of 1,3,5-trichlorobenzene and hexabromobenzene also proceeds in tetrahydrofuran. However, the polycondensation of the polyhalogenated aromatic compounds was accompanied by the ring opening polymerization of tetrahydrofuran which was used as the solvent. A preliminary examination of the polymers by IR and NMR spectroscopy and solubility test showed that the polymers obtained were copolymers such as;

$$\text{-(A)}_m\text{-(O-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{)}_n$$

where A represents aromatic nucleus.

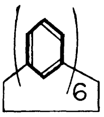
All of the polyphenylene type polymers obtained had high melting points as shown in Table 2. The melting points of poly(m-phenylene), poly(oxybiphenylene), and poly(phenylenemethylene) were lower than that of poly(p-phenylene) which has a linear structure. The introduction of oxygen atoms or methylene groups into the main chain may enhance the mobility of the polymer chain, thus lowering the melting point of poly(oxybiphenylene) and poly(phenylenemethylene).

Table 2 includes analytical data of the polymers. The degree of polymerization ($\overline{DP}$) was calculated from the analysis of halogen content on the assumption that the polymers have halogen at both ends and $\overline{DP}$'s thus calculated are given in the last column of Table 2. That the toluene-extractable fraction of poly(m-phenylene) contains less halogen than the toluene-unextractable fraction may be due to the

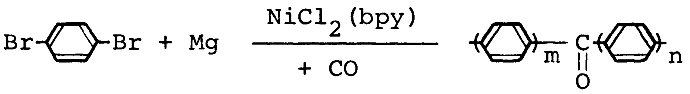
Table 2 Melting Points and Analytical Data of Polymers

Sample[a]	Mp(°C)	Analysis C	Analysis H	Analysis X	$\overline{DP}$
No.1	>400	83.8	5.14	7.86	24
No.7-Soluble	190-200	90.9	4.89	2.71	33
No.7-Insoluble	280-295	89.0	4.59	4.90	18
No.9	250-280	83.1	5.47	2.02	46
No.10-Soluble	230-235	87.8	6.41	6.13	12
No.10-Insoluble	>400	88.0	6.83	3.51	21

a. Numbers corresponding to those in Table 1. Soluble and Insoluble mean extractable and unextractable fractions by hot toluene.

contamination of cyclic oligomers like  ; in this case the assumption that the polymer has halogen at both ends does not hold and the $\overline{DP}$ of No.7-Soluble is less than the value given in Table 2.

When the polymerization of p-dibromobenzene was carried out in the atmosphere of carbon monoxide, incorporation of the CO molecules took place and the IR spectrum of the polymer showed a ν(C=O) band at 1660 cm^{-1}:



The elemental analysis of the copolymer showed that the ratio of phenylene units and carbon monoxide units was about 2 : 1. The incorporation of CO during the polymerization supports that the polymerization proceeds on the nickel complex.$^{9)}$ The copolymer melted at about 300°C. The incorporation of the CO group in the main chain appears to cause the lowering of the melting point.

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