フェニルアセチレンおよびフェニルアセチレン誘導体のイリジウム触媒による重合の検討

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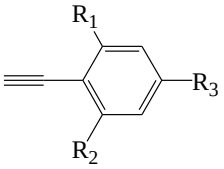
Synthetic Study of Poly(phenylacetylene) and Poly(phenylacetylene) Derivatives by Iridium Catalysts (*Graduate School of Science and Technology, Niigata University*)○Keisuke Terashima, Takashi Kaneko, Toshiki Aoki, Masahiro Teraguchi

Polymerization of monosubstituted acetylenes is generally carried out using Mo, W or Rh catalysts. There are a few studies on the polymerization of phenylacetylenes using Ir complex, despite it is expected to exhibit polymerization ability. In this study, we investigated the polymerization of phenylacetylenes (**1**) and ortho-substituted phenylacetylenes (**2** and **3**) using $[Ir(cod)CI]_2$ and $[Ir(cod)OMe]_2$. Polymerization of **1** with $[Ir(cod)X]_2$ (X = CI, OMe) alone yielded only low molecular-weight polymers (M_n < 3,000). On the other hand, in the presence of additives such as triphenylvinyllithium (Ph_2C=C(Ph)Li), PPh_3, and 2, 5-norbornadiene(nbd), polymers containing a high molecular-weight part (M_n ca. 90,000) were obtained.
Keywords : Polyphenylacetylenes; Polymerization; Iridium catalyst

一般に一置換アセチレン類の重合はMo、W及びRh触媒が有効であることが知られている。[1,2] Irは Rhの同族元素でありフェニルアセチレン類の潜在的な重合活性が期待できるが研究例は少ない。本研究では $[Ir(cod)Cl]_2$ 及び$[Ir(cod)OMe]_2$ を用いてフェニルアセチレン(**1**)及びオルト置換フェニルアセチレン(**2**, **3**)の重合を検討した。



1 : R_1, R_2, R_3 = H
2 : R_1=CH_3, R_2, R_3 = H
3 : R_1, R_2 = CH_3, R_3 = O-(*n*-$C_{12}H_{25}$)

$[Ir(cod)X]_2$(X = Cl, OMe)触媒単独での **1** の重合では、分子量3,000以下の重合体のみしか生成しなかったのに対して、Rh触媒[3]での重合に効果のあるトリフェニルビニルリチウム(Ph_2C=C(Ph)Li)、PPh_3、2,5-ノルボルナジエン(nbd)を共存させた触媒系では数平均分子量が最大90,000程度の成分を含む重合体が得られた。

Table. Polymerization of **1** using $[Ir(cod)Cl]_2$-Ph_2C=C(Ph)Li-PPh_3-nbd in toluene [a]

Temp. (°C)	Monomer Convn.(%) [b]	Yield(%) [c]	M_n(×10^3) [d]	M_w/M_n [d]	Area(%) [d]
30	29.2	9.9	7.46	1.49	10.5
			3.35	1.86	86.8
			0.38	1.05	2.7
0	15.4	6.3	89.9	1.26	8.4
			4.36	1.88	87.5
			0.41	1.09	4.1

[a] $[M]_0$ = 0.20 M, [Ir] = 4.0 mM, [Ir] : [nbd] : [PPh_3] : [Li] = 1 : 1 : 1.1 : 2 for 24 h. [b] Determined by GC using mesitylene as internal standard. [c] Methanol-insoluble part. [d] Measured by GPC calibrated with polystyrene standard (eluent:THF).

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