

균일촉매반응 (제1보).  $[\text{Ir}(\text{ClO}_4)(\text{CO})(\text{Ph}_3\text{P})_2]$ 의 존재하에서  
아크릴로니트릴의 중합반응

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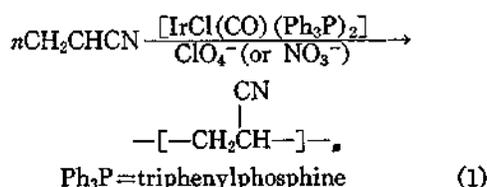
Homogeneous Catalysis (I). Polymerization of Acrylonitrile  
in the Presence of  $[\text{Ir}(\text{ClO}_4)(\text{CO})(\text{Ph}_3\text{P})_2]$

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We recently observed the polymerization of AN in the presence of Vaska's catalyst (1) and an anion,  $\text{ClO}_4^-$  or  $\text{NO}_3^-$ , in AN under  $\text{N}_2$  at  $25^\circ\text{C}$  in darkness.<sup>1</sup> Freshly distilled AN (originally stabilized by *p*-methoxyphenol) does not polymerize in the absence of either Vaska's catalyst or the anion, or both under the same conditions. Therefore, it is apparent that the polymerization is not a spontaneous one due to the removal of the stabilizer, but a catalytic reaction by iridium complex(es) (see equation 1).



In a typical experiment,  $[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$  (1, 0.15 mmole) was added to AN (10 ml) under  $\text{N}_2$  at  $25^\circ\text{C}$  to give a suspension of AN adduct,  $[(\text{AN})\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$  (2),<sup>2</sup> which is not catalytically active for the polymerization at the same conditions described above. Addition of  $\text{AgClO}_4$  (0.15 mmole) to the suspension yielded a clear pale yellow solution (I) and

$\text{AgCl}$  precipitation which was readily removed by filtration. Stirring the solution (I) under  $\text{N}_2$  in darkness at  $25^\circ\text{C}$  led slow formation of white precipitation (polycrylonitrile). This observation suggests that the reaction is a homogeneous catalysis. The solution solidified completely within 3 days. Addition of  $\text{AgNO}_3$ ,  $\text{Pb}(\text{ClO}_4) \cdot 3\text{H}_2\text{O}$ ,  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ , or  $\text{HClO}_4$ , to the suspension of 2 in AN also initiated the polymerization of AN under the same conditions described above.<sup>3</sup>

In order to obtain information on the nature of the polymerization, a free-radical scavenger,  $\alpha$ -naphthol (2.0 mmole) was added into the catalytically active solution (I) containing 0.05 mmole of iridium. It was found that the rate of the polymerization was not affected by the presence of  $\alpha$ -naphthol. Therefore, the reaction may not proceed via free-radical mechanism, but probably through anionic mechanism (polymerization of AN is known thus far to proceed via either free-radical or anionic mechanism<sup>4</sup>). Detailed mechanistic investigation would be carried out for further information.

It is apparent that Vaska's catalyst (1) is merely a precursor of the actual catalyst(s) for

equation 1 since **1** reacts with AN to produce the suspension of **2** in AN, and the polymerization does not occur until  $\text{AgClO}_4$  is added to the suspension to give the catalytically active solution (I) and  $\text{AgCl}$ . The conductance measurement of the solution (I) suggests that it contains some electrolyte(s).<sup>5</sup>

Addition of hexane to the solution (I) resulted in pale yellow precipitation (II) which was separated by filtration. Infrared spectrum of the solid (II) (wet sample immediately after separation) show two  $\nu_{\text{CN}}$  bands at 2270 and 2220  $\text{cm}^{-1}$ , and two  $\nu_{\text{CO}}$  bands at 2080 and 2020  $\text{cm}^{-1}$  (see Fig. 1 (a)). It was observed that the solid (II) loses 2080 and 2270  $\text{cm}^{-1}$  bands slowly under  $\text{N}_2$  at 25 °C, and a new one appears at 1990  $\text{cm}^{-1}$ , and 2020  $\text{cm}^{-1}$  band increases in its intensity (see Fig. 1 (b), (c)). No additional change in the spectrum was found for the next 24 hours.

It is known so far that Vaska's catalyst and its derivatives show a single  $\nu_{\text{CO}}$  band in their infrared spectra.<sup>6</sup> Therefore, it may be said that each  $\nu_{\text{CO}}$  band observed in our experiments represents a individual iridium complex, respectively. Accordingly, the solid (II) seems to contain two different iridium complexes, **3** (with 2020  $\text{cm}^{-1}$  band) and **4** (with 2080  $\text{cm}^{-1}$  band) which decomposes to give **5** (with 1990  $\text{cm}^{-1}$  band) and **3** (with 2020  $\text{cm}^{-1}$  band). It is well known that **1** reacts with  $\text{AgClO}_4$  to give  $\text{AgCl}$  and  $[\text{Ir}(\text{ClO}_4)(\text{CO})(\text{Ph}_3\text{P})_2]$ , and the latter undergoes complete ionization in some polar solvents (equation 2)<sup>6a</sup> and the novel addition-substitution reactions qualitatively (equation 3).<sup>6a</sup> It is also well known that

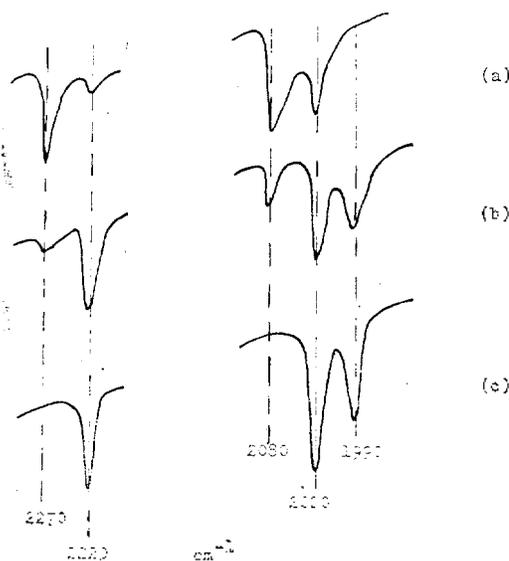
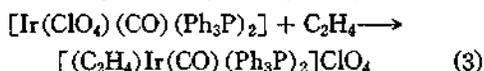
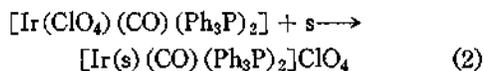


Fig. 1. Infrared spectra of the solid(II) measured in Nujol mull: (a) immediately after isolation from acrylonitrile, (b) after 1 hour under  $\text{N}_2$  at 25 °C, (c) after 24 hours under  $\text{N}_2$  at 25 °C.

Vaska's catalyst and its derivatives react with olefins to give olefin adducts (**2** for example).

Now, one may deduce three iridium complexes,  $[\text{Ir}(\text{ClO}_4)(\text{CO})(\text{Ph}_3\text{P})_2]$ ,  $[(\text{AN})\text{Ir}(\text{CO})(\text{Ph}_3\text{P})_2]\text{ClO}_4$  and  $[(\text{AN})\text{Ir}(\text{ClO}_4)(\text{CO})(\text{Ph}_3\text{P})_2]$  as the possible compounds which may be obtained from the solution (I). **5** seems to be  $[\text{Ir}(\text{ClO}_4)(\text{CO})(\text{Ph}_3\text{P})_2]$  which has been known to show a  $\nu_{\text{CO}}$  at 1990  $\text{cm}^{-1}$ .<sup>6a</sup> The  $\nu_{\text{CO}}$  would be higher in  $[(\text{AN})\text{Ir}(\text{ClO}_4)(\text{CO})(\text{Ph}_3\text{P})_2]$  than in  $[(\text{AN})\text{Ir}(\text{CO})(\text{Ph}_3\text{P})_2]\text{ClO}_4$  because of the higher coordination number for the former and high electronegativity of  $\text{ClO}_4^-$ , which causes decrease in  $\pi$ -donation from Ir to  $\text{CO}$ <sup>6a</sup> in  $[(\text{AN})\text{Ir}(\text{ClO}_4)(\text{CO})(\text{Ph}_3\text{P})_2]$  while such effect would be negligible in  $[(\text{AN})\text{Ir}(\text{CO})(\text{Ph}_3\text{P})_2]\text{ClO}_4$ . It is now easily seen that **3** (with  $\nu_{\text{CO}}$  at 2020  $\text{cm}^{-1}$ ) and **4** (with  $\nu_{\text{CO}}$  at 2080  $\text{cm}^{-1}$ ) would be  $[(\text{AN})\text{Ir}(\text{CO})(\text{Ph}_3\text{P})_2]\text{ClO}_4$  and  $[(\text{AN})\text{Ir}(\text{ClO}_4)(\text{CO})(\text{Ph}_3\text{P})_2]$ , respectively. The conductance value of the solution (I) described above

also supports the presence of  $[(AN)Ir(CO)(Ph_3P)_2]ClO_4$ .

It is seen in Fig. 1 that (i) the intensity of  $2270\text{ cm}^{-1}$  band decreases with decrease of  $2080\text{ cm}^{-1}$  band intensity while the intensity of  $2220\text{ cm}^{-1}$  band increases with increase of  $2020\text{ cm}^{-1}$  band intensity, and (ii) the intensity of  $2220\text{ cm}^{-1}$  band increases at the expense of  $2270\text{ cm}^{-1}$  band. This observation suggests that the bands at  $2270$  and  $2220\text{ cm}^{-1}$  are due to  $\nu_{CN}$  for **4** ( $[(AN)Ir(ClO_4)(CO)(Ph_3P)_2]$ ) and **3** ( $[(AN)Ir(CO)(Ph_3P)_2]ClO_4$ ), respectively.

Both of **3** and **4** may be catalytically active for the polymerization of AN although **3** may be more favorable one since it provides more room around iridium. Further investigation is being undertaken for a detailed reaction mechanism.

### ACKNOWLEDGEMENTS

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