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Polymerization of 4-Vinylpyridine by Lanthanide Coordination Catalyst

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Abstract: Polymerization of 4-vinylpyridine was carried out with the lanthanide coordination catalyst. The influence of the component in catalytic system and solvents had been examined. The molecular weight of poly(4-vinylpyridine) obtained in CH_2Cl_2 with $Ln(P_{204})_3$ /$Al(i\text{-}Bu)_3$ is more than 20×10^4.

Keywords: 4-Vinylpyridine, rare earth coordination catalyst, polymerization.

Polyvinylpyridines are an important class of polymers that exhibit interesting properties due to the presence of the nitrogen atom in the pyridine ring. The weakly basic nitrogen atom makes possible a variety of reactions on vinylpyridine polymers, *e.g.* reaction with acids, quaternization and complexation of metals. In addition, these polymers are mainly attractive in applications as polyelectrolytes, polymeric reagents *etc.* Few papers about polymerization of 4-vinylpyridine (4-Vpy) with coordination catalyst are reported. In this paper, polymerization of 4-Vpy with lanthanide catalyst system was studied for the first time and the polymers with high molecular weight were obtained in CH_2Cl_2.

Table 1 shows the effect of different lanthanide compound on polymerization. The results indicate $Ln(P_{204})_3/Al(i\text{-}Bu)_3$ can catalyze the polymerization of 4-Vpy. The activity order of rare earth metal is as follows: Nd ~ Sm ~ Ho ~ Dy ~ La > Pr ~ Er. The effect of organometallic compounds on activity of catalyst was studied (**Table 2**).

Table 1 Effect of different rare earth compound on polymerization

$Ln(P_{204})_3$	La	Pr	Nd	Sm	Dy	Ho	Er
Conv.(%)	100	77	100	100	98	100	70
$M_n\times10^4$	33	93	25	38	87	34	40
mp(°C)	104.6	102.4	97.6	101.7	89.6	102.8	100.7

Polymerization conditions: [4-Vpy] = 0.01mol/L, [4-Vpy]/[Nd]=1500, Al/Nd =15 (molar ratio) , temperature: 30°C, time:30min, V_{tol}=8mL, solvent:CH_2Cl_2

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$Nd(P_{204})_3/AlEt_3$ is inactive for 4-Vpy polymerization. The activity of $Nd(P_{204})_3/Mg(n\text{-}Bu)_2$ is so high that the reaction is too fast to be controlled. However, the catalytic activity of $Nd(P_{204})_3$/ $Al(i\text{-}Bu)_3$(or $Al(i\text{-}Bu)_2H$) is also high but the reaction is mild.

Solvents have a great influence upon polymerization of 4-Vpy (**Table 3**). The catalytic activity in various solvents shows following sequence: dichloromethane > toluene ~ benzene > cyclohexane >>THF. This is probably because alkane and aromatic hydrocarbon is precipitant of poly4-Vpy. The catalyst was buried in polymers, so it is disadvantageous to monomer diffusion and chain growth.

The molecular weight of polymers is more than 20×10^4 measured by viscosity method. It is far higher than that obtained with $AlEt_3/VCl_3$ and $TiCl_3$/MAO *etc*[1,2]. Thermal analysis by DSC showed that the melting points of poly4-Vpy were about 88.7~104.6°C. The polymers produced by organobarium in THF are non-stereospecific as the polymers obtained with viscosity method as shown in ^{1}H-NMR.

Table 2 Effect of different organometallic compounds on polymerization

MR_n	$AlEt_3$	$Al(i\text{-}Bu)_3$	$Al(i\text{-}Bu)_2H$	$Mg(n\text{-}Bu)_2$
Conv.(%)	trace	100	100	100
$M_\eta\times10^4$	/	25	77	/
mp(°C)	/	97.4	88.7	/

Polymerization conditions are the same as **Table 1**.

Table 3 Effect of various solvents on polymerization

solvent	n-hexane	THF	toluene	benzene	Dichloromethane
Conv.(%)	24	trace	41	38	100
$M_\eta\times10^3$	110	/	144	166	252

Polymerization conditions are the same as **Table 1**.

References

1. M. L.Dias, M. I.Bruno, *Eur. Polym. J.*, **1997**, *33* (9), 1559.
2. Y. Benito, J. G. Rodriguez, *Eur. Polym. J.*, **1994**, *30* (6), 661.

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