Chinese Chemical Letters Vol. 12, No. 11, pp 1033 – 1036, 2001
http://www.imm.ac.cn/journal/ccl.html

Polymerization of Styrene by Neutral Ni (II) Acetylide Complex

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Abstract: Neutral nickel σ-acetylide complex $[Ni(C\equiv CPh)_2(PBu_3)_2]$ is a novel initiator for the polymerization of styrene in $CHCl_3$ over a range of polymerization temperature from 40°C to 60°C. The polystyrene obtained was a syndio-rich atactic polymer and its weight-average molecular weight reached 279000. The mechanism of the polymerization was discussed and a radical mechanism was proposed.

Keywords: Styrene, nickel acetylide complex, initiator, polymerization, syndio-rich.

Over the past few years, the utilization of late transition metal-based soluble complexes as styrene polymerization catalysts has received considerable attention[1]. Various systems have been explored. For example, cationic η^3-allylnickel complexes alone[2] or modified by P (III) ligands[3] as well as a few other systems (*e. g.*, cationic η^3-benzylic nickel complexes[4]) are active homogeneous catalysts for the low molecular weight polymerization of styrene by simple cationic mechanism[2,3,4]. Neutral allylnickel complexes alone[5] or activated by addition of electron-poor additives[5a,6] as well as homogeneous organometallic catalytic systems containing methylaluminoxane [*e.g.*, $Ni(acac)_2$/methylaluminoxane[7]] are known to produce high molecular weight polystyrene, and a coordination mechanism was proposed[5a, 6].

Since 1995[8], an increasing number of late transition metals, like copper, iron, ruthenium, in conjunction with different organic halides and ligands have been known to be able to catalyze the atom transfer radical polymerization (ATRP) of styrene. The ATRP gives polystyrene with controlled molecular weights and narrow molecular weight distributions. However, up to now, except for the ATRP of MMA[9], no nickel or palladium based systems were found to be active for the ATRP of styrene. Furthermore, there was also little report concerning neutral nickel complexes alone being used for radical polymerization of styrene so far.

More recently[10], we have found that a series of neutral nickel and palladium σ-acetylide complexes $[M(C\equiv CR)_2(PR'_3)_2$, M=Ni, Pd; R=Ph, CH_2OH, CH_2OOCH_3, CH_2OOCPh, $CH_2OOCPhOH$-*o*; R′=Ph, Bu] were efficient initiator for styrene polymerization. Among them, $Ni(C\equiv CPh)_2(PBu_3)_2$ (NBP) shows the highest catalytic activity. In this paper, some features of the styrene polymerization with NBP together with the polymerization mechanism are investigated for the first time.

Experimental

$Ni(PBu_3)_2Cl_2$[11] and $Ni(C{\equiv}CPh)_2(PBu_3)_2$ (NBP)[12] were prepared according to the literatures.

Polymerization

All procedures for polymerization were carried out under purified nitrogen atmosphere. A typical polymerization procedure is as follows: into a 30 mL well-dried ampoule, NBP (10.65 mg, 0.016 mmol) as the catalyst, $CHCl_3$ (0.2 mL) as solvent were added in turn, shook to obtain a homogeneous solution, and then styrene (0.8 mL, 6.84 mmol) was injected. After the mixture stood at 60°C for a definite reaction time, HCl/ethanol (10%, 0.5 mL) was added to decompose the catalyst, and THF (5 mL) was added to dissolve the resulting polymers, which were precipitated as a white wadding by the addition of large excess of ethanol. Polystyrene (PS) was washed with ethanol and dried in *vacuo* at room temperature for 24 h.

Results and Discussion

The solvents have great influence on the catalytic activity of NBP towards St polymerization. The polymerization system shows high reaction activities in chlorinated solvents. For example, the polymer yields reaches about 22% in either $CHCl_3$ or CCl_4 at 60°C for 24 h polymerization while the monomer concentration and the catalyst concentration are 6.6 $mol{\cdot}L^{-1}$ and $6.6{\times}10^{-3}$ $mol{\cdot}L^{-1}$, respectively. It is found that chloroform is a favorable solvent for the homogenous polymerization of styrene. However, NBP exhibits little catalytic activity neither in high-polarity solvents containing N, O, and S (such as 1,4-dioxane, THF, DMSO, and $HNEt_2$), nor in non-polarity solvents (such as toluene). Blank experiments demonstrated that $CHCl_3$ or CCl_4 alone cannot catalyze the styrene polymerization.

The effect of polymerization temperature on the St polymerization was summarized in **Table 1**. The polymer yields rapidly increase from 11% to 56% while polymerization temperature increases from 40°C to 60°C, accompanied by the decreasing of the number-average molecular weight of PS and the broaden of the molecular weight distribution. The polystyrene with high molecular weight ($Mn=14.7{\times}10^4$) and molecular weight distribution (Mw/Mn=1.88) can be obtained at 40°C, which may be due to the less side-reaction at low temperature.

Table 1 effect of Polymerization Temperature on St Polymerization

Temperature (°C)	Yield (%)	$Mn\times10^4$	$Mw\times10^4$	Mw/Mn
40	11	14.7	27.7	1.88
50	25	13.9	27.4	1.97
60	56	11.9	27.9	2.34

Conditions: [St]=6.84 mol/L, [NBP]=0.016 mol/L, $CHCl_3$, 47 h, N_2

Table 2 Effect of Polymerization Time on St Polymerization

Time (h)	Yield(%)	$Mn \times 10^4$	$Mw \times 10^4$	Mw/Mn
3	3	9.7	17.7	1.82
12	12	/	/	/
24	30	9.8	18.9	1.94
36	52	10.9	21.9	2.02
47	56	11.8	27.9	2.34

Conditions: [St]=6.84 mol/L, [NBP]=0.016 mol/L, $CHCl_3$, 60°C, N_2

Table 2 illustrates the effect of polymerization time on the St polymerization. The molecular weight and polydispersity of PS progressively increased with prolonging polymerization time.

In order to understand the polymerization mechanism of this system, two experiments were designed. First, is to add 2 equiv of hydroquinone, which is well-known inhibitor for radical reactions, to NBP into the system prior to the initiation of the styrene polymerization. The second is to add the same amount of hydroquinone into the system after the polymerization had proceeded at the stage of 20% conversion of monomer. In the former case, the polymerization was stopped completely and no polymer was obtained after 24 h. In the later case, the polymerization conversion has no more increased and the polymerization was also immediately and completely stopped at that stage. Furthermore, the polystyrene obtained has a syndio-rich atactic microstructure[10] which almost consist with that of PS radically prepared by AIBN in $CHCl_3$ at 60°C. These results indicate undoubtedly that the styrene polymerization with NBP in $CHCl_3$ proceeds by a radical mechanism. The radical species may be produced by the homolytical activation of the carbon-chlorine bond *via* the single electron redox reaction between Ni(II) and Ni(III)[9]. It is worth to note that, in contrast to the atom transfer radical polymerization of MMA with $Ni(PBu_3)_2Cl_2$-based initiator system, here no polymerization occurred when $Ni(PBu_3)_2Cl_2$ was employed in $CHCl_3$ at 60°C. This result suggests that the metal-carbon bond is necessary for the formation of radical species in the present polymerization.

Acknowledgment

Financial support from the Key Laboratory of Organic Synthesis of Jiangsu Province is gratefully acknowledged.

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Received 16 April, 2001