

Table 2 Effect of Polymerization Time on St Polymerization

Time (h)	Yield(%)	Mn × 10 ⁴	Mw × 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, CHCl₃, 60°C, N₂

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 microstructure¹⁰ which almost consist with that of PS radically prepared by AIBN in CHCl₃ at 60°C. These results indicate undoubtedly that the styrene polymerization with NBP in CHCl₃ 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(PBu₃)₂Cl₂-based initiator system, here no polymerization occurred when Ni(PBu₃)₂Cl₂ was employed in CHCl₃ at 60°C. This result suggests that the metal-carbon bond is necessary for the formation of radical species in the present polymerization.

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