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Polymerization of Methyl Methacrylate with Samarocene Complex Supported on Mesoporous Silica

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Abstract: Samarocene complex was supported on a series of mesoporous silica with various pore sizes. Polymerization of methyl methacrylate (MMA) by these catalysts provide highly syndiotactic PMMAs with higher molecular weights compared with those obtained by solution polymerization with homogeneous catalyst system.

Keywords: Mesoporous silica, supported catalyst, samarocene complex.

Synthesis of polymers with controlled molecular weight and narrow polydispersity is of both fundamental interest and practical importance. In recent years, high molecular weight poly (methyl methacrylate) (PMMA) having an unusually narrow polydispersity has been synthesized by using the unique initiating property of $(C_5Me_5)_2Ln^{III}R$ (R=H, Me, Ln=Sm, Yb) complexes[1,2]. Herein we report the results of the first example of the polymerization of methyl methacrylate (MMA) with samarocene complex supported on a porous inorganic crystal called "mesoporous zeolite". Mesoporous zeolite MCM-41 is a new family of silicate/aluminosilicate molecular sieves with pore diameters within the mesoscopic range. A liquid crystal templating mechanism in which the structures of the surfactant liquid crystal serve as organic templates is proposed for the formation of these materials. Thus, a mesoporous silica has a honeycomb-like framework with a uniform, controllable pore diameter from 15 to 100 Å which is determined by the chain length of the surfactant[3,4]. It is used as a solid support of titanocene for the polymerization of ethylene and other monomers and provides the polymers with high molecular weight and narrow molecular weight distribution[4~9].

To methylate the SiOH functionalities of MCM-41, a toluene suspension of the zeolite was pretreated with $AlMe_3$, and the isolated solid was washed with toluene to remove the excess $AlMe_3$. The toluene solution of $(C_5Me_5)_2SmMe$ (THF) was added by hypodermic syringe into pretreated MCM-41, and stirred under argon overnight. After stirring, the solution was removed and the soluble samarocene complex was washed with toluene. MMA was added into the resulting suspension with vigorous magnetic stirring at 0°C. After polymerization the resulting polymer solution was poured into methanol to precipitate the polymer. The polymers were dried in vacuum at

room temperature overnight.

Polymerization results of MMA with $(C_5Me_5)_2SmMe$ (THF) supported on MCM-41, are shown in **Table 1**. The resulting PMMA (run 2) possesses a very high molecular weight (Mn=1,460,000), high syndiotacticity (rr%=86.2), and narrow MWD (Mn/Mw= 1.47). The pore diameter of MCM-41 has great influence on the catalytic activity, although the tacticity of PMMA is not much affected. MWD of PMMA is decreased with decreasing the pore size of MCM-41, and is wider than that of PMMA obtained by homogeneous solution polymerization. The catalyst systems have no polymerization activity when little pore diameter MCM-41 was used as a support (run 4, 5).

Compared with the PMMA obtained by solution polymerization with homogeneous catalyst (run 6), polymerization of MMA by mesoporous silica supported catalysts afforded highly syndiotactic PMMAs with higher molecular weights. Further studies on the mechanistic aspect and on the kind of alkylaluminum and on the polymerization of other acrylate monomers with this and related lanthanocene based system are under progress.

Table 1 Polymerization of MMA by $(C_5Me_5)_2SmMe$ (THF)/MCM-41

run	MCM-41[a]	yield (%)	Mn[c] (10^5)	Mw/Mn[c]	tacticity[d] (%)		
					mm	mr	Rr
1	C-22	>99	12.7	1.58	0.5	14.1	85.4
2	C-16	>99	14.6	1.47	0.5	13.3	86.2
3	C-14	12	1.21	1.17	3.5	12.5	84.0
4	C-12	no polymer	-	-	-	-	-
5	C-10	no polymer	-	-	-	-	-
6[b]	homogeneous	99	0.52	1.03	1.0	16.8	82.8

in toluene, 0°C, 4 h. [a] Alkyl chain length of the alkyl ammonium template for MCM-41. [b] Data from ref. 2. [c] Determined by GPC against PMMA standard in THF. [d] Measured by ^{1}H-NMR in $CDCl_3$.

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