

Polymerization of Styrene and 1,3-Butadiene by Catalyst Systems Based on Calix[4]arene Neodymium Complexes

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Abstract: Polymerization of styrene and 1,3-butadiene were performed by calix[4]arene-neodymium complexes using di-*n*-butylmagnesium and tri-*iso*-butylaluminum as cocatalyst respectively. The effect of the substituent groups in calix[4]arene on the catalytic activity was first investigated.

Keywords: Calix[4]arene-neodymium complexes, polymerization, catalyst.

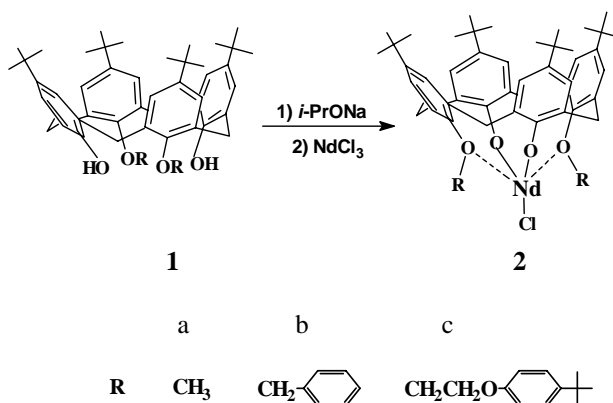
Interaction of calixarenes with metals is always a very intriguing subject in calixarene chemistry because the calixarene metal complexes may be potential catalysts for chemical reaction besides other application. Although a large number of metal complexes of calixarenes have been synthesized and characterized, yet the investigation on their catalytic activity for chemical reaction, especially for polymerization is scarce^{1,2,3}. Recently we have found that calix[4]arene-neodymium **2a** is a highly active catalyst for polymerization of styrene (St) in the presence of di-*n*-butylmagnesium (MgBuⁿ₂) and hexamethyl phosphoramidate⁴. Here we report the polymerization of styrene and 1,3-butadiene with **2** using MgBuⁿ₂ and tri-*iso*-butylaluminum (Al(*i*-Bu)₃) as cocatalyst respectively, and the effect of the substituent groups in calix[4]arene on the catalytic activity of **2**.

Experimental

The calix[4]arene-neodymium complexes **2a-2c** were synthesized following the method for the preparation of neodymium phenoxide⁵ (see **Scheme 1**). After removal of the phenolic protons in calix[4]arene by sodium *iso*-propoxide in a mixed solvent of *iso*-propanol-benzene, the calix[4]arene derivative **1a**, **1b** or **1c** was refluxed with anhydrous neodymium chloride for 4 h. The solvent was removed by evaporation. To the solid residue 1:1 mixed solvent of benzene and hexane was added. The solution was refluxed for about 0.5 h, cooled to room temperature, left stand overnight, and filtered. The filtrate was evaporated to dryness. The processes were repeated two times. Finally the complex was dried in vacuum. Yields are 73.2%, 68.5% and 83.8% for **2a**, **2b** and **2c**

respectively. The content of neodymium measured by EDTA titration in all cases is consistent with that calculated.

Scheme 1. Synthesis of calix[4]arene neodymium complexes



Di-*n*-butylmagnesium was prepared as follows⁶. A 150 ml flask equipped with a 100 ml pressure-equalizing addition funnel, reflux condenser, and mechanical stirrer was heated in vacuum and then purged with purified nitrogen for three times. The dried flask was charged 5.2g (0.22mol) of magnesium powder which was freshly filed, a few crystals of iodine and 30 ml of dry toluene. In the pressure-equalizing addition funnel 21 ml (0.20 mol) of *n*-butylchloride dried over 4 Å molecular sieve was mixed with 70 ml of toluene. 10 ml of the above solution in the funnel was previously added to the flask. The reaction mixture was heated to reflux. The initiation reaction occurred within 10-20 min. Then the remained solution of *n*-butylchloride in the funnel was slowly dropped into the flask over a 3 h period. During addition of *n*-butylchloride the temperature of oil bath was adjusted to maintain the refluxing of reaction mixture. After the addition was completed the reaction mixture was refluxed for another 1 h. Then stopped refluxing, 1 ml (0.014 mol) of triethylaluminum was carefully added with stirring and the mixture was refluxed for 2 h. Cooled to room temperature, the reaction mixture was centrifugalized to obtain a clear, colorless toluene solution of di-*n*-butylmagnesium. Magnesium and aluminum were measured by EDTA titration.

Anhydrous neodymium chloride was prepared by refluxing hydrated neodymium chloride in thionyl chloride. Triethylaluminum and tri-*iso*-butylaluminum were commercial products purchased from Roth Chemical Co. Other reagents, solvents and monomers were purified by conventional methods.

All polymerization procedures were carried out under dry nitrogen. Polymerization was performed in a glass cuvette which was previously heated in vacuum and then purged with nitrogen for at least three times. The polystyrene or polybutadiene was precipitated from reaction mixture by adding ethanol. The calixarene retained in polymer was removed by immersing the polymers in ethanol solution of potassium hydroxide.

Results and Discussion

The results of polymerization of styrene by **2a**, **2b** or **2c** / MgBu^n_2 catalyst system are shown in **Table 1**. Under the similar reaction conditions the yields of polystyrene (PSt.) with **2a**, **2b** and **2c** are 55.4%, 42.8% and 26.4% respectively. If no neodymium is present, only a trace of PSt. is obtained. So that the polymerization of styrene can be catalyzed by **2a**, **2b** or **2c** in the presence of cocatalyst, di-*n*-butylmagnesium. Maybe due to the steric factor of substitute groups, the order of catalytic activity is **2a**>**2b**>**2c**.

There is a little effect of substituent groups in calix[4]arene on the molecular weight (indicating viscosity-average molecular weight, the same below) of PSt..

Table 1. Polymerization of St. by **2a-2c**/ MgBu^n_2 catalyst system^a

Cat.	[Cat.] (mol/L)	[MgBu^n_2] (mol/L)	Mg/Nd	Yield (%)	Mv ^b $\times 10^{-4}$
2a	6.0×10^{-3}	4.5×10^{-2}	7.5	55.4	3.43
2b	6.0×10^{-3}	4.5×10^{-2}	7.5	42.8	4.14
2c	6.0×10^{-3}	4.5×10^{-2}	7.5	26.4	2.30

a. Other conditions: [MgBu^n_2] = 4.5×10^{-2} mol/L; [St.] = 4.28 mol/l; Time = 48h; T = 70°C; Solvent = toluene.

b. Mv was evaluated from $[\eta] = 0.75 \times 10^{-4} \times \text{Mv}^{0.783}$ (in benzene at 30°C)⁷.

Since rare earth metals, especially neodymium, are excellent catalysts for synthesis of *cis*-polybutadiene, **2a**, **2b** and **2c** are also applied to catalyze the polymerization of 1,3-butadiene.

As shown in **Table 2**, although the effect of substituent groups in calixarene on molecular weight and *cis*-content of polybutadiene is not obvious, the effect of substituent groups on activity of catalysts is marked. Polybutadienes with **2b** and **2c** were achieved in yields of 14.9% and 56.3% respectively, and almost no polybutadiene was got with **2a**. The order of catalytic activity is **2c**>**2b**>**2a** which is just the reverse of the order in polymerization of styrene. This order may be due to the polarity of substituent groups in calixarene, and the steric factor has less effect. Especially the oxygen atoms in substituent groups of **2c** being able to coordinate with neodymium is probably the reason why the activity of **2c** is far larger than that of **2b** and **2a**. This is conformable to the fact that polymerization of 1,3-butadiene with neodymium compounds can be accelerated by added alcohol⁸.

Table 2. Polymerization of butadiene by **2a-2c**/ $\text{Al}(i\text{-Bu})_3$ catalyst system^a

Cat.	[Cat.]	[$\text{Al}(i\text{-Bu})_3$] (mol/L)	Yield (%)	Mv ^b $\times 10^{-4}$	<i>Cis</i> ^b (%)
2a	4.0×10^{-3}	1.6×10^{-2}	trace	/	/
2b	4.0×10^{-3}	1.6×10^{-2}	14.9	2.85	95.7
2c	4.0×10^{-3}	1.6×10^{-2}	56.3	3.81	93.7

a. The other conditions: Time = 12h; T = 50°C; Solvent = toluene.

b. Mv and *cis* content of polybutadiene were evaluated by the method in literature⁸.

Conclusion

It is found for the first time that the substituent groups in calix[4]arene have a marked effect on the catalytic activity of calixarene-neodymium complexes for polymerization of styrene and 1,3-butadiene, which is important for us to look for better calixarene-neodymium catalysts.

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