

## ***Supporting Information for***

# ***In-situ X-ray absorption fine structure study on the polymerization of isoprene assisted by Nd-based ternary catalysts***

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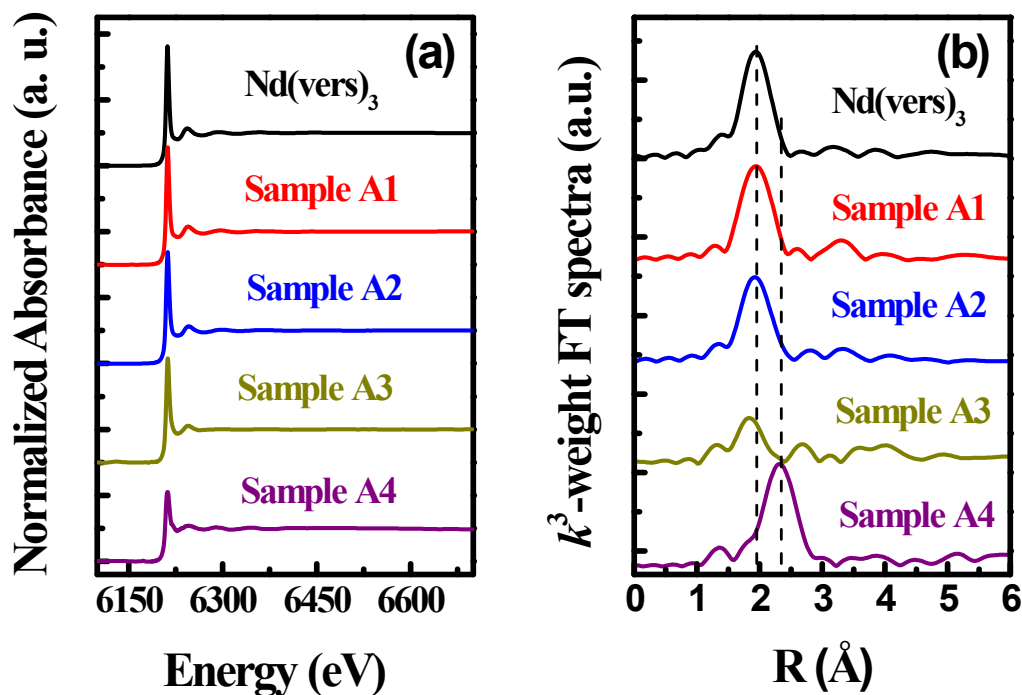
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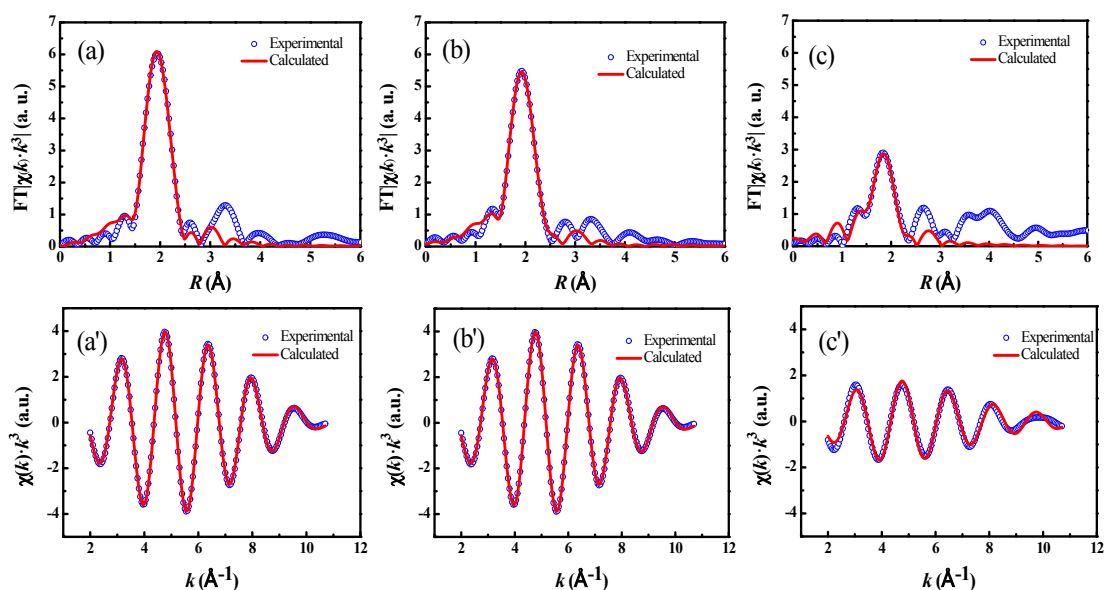
## 1. XAFS Analysis for Catalyst-II

**XAFS spectra:** Catalyst-II contains  $\text{Al}(i\text{Bu})_2\text{Cl}$ ,  $\text{AlEt}_3$ , and  $\text{Nd}(\text{vers})_3$ . The normalized Nd  $L_{\text{III}}$ -edge X-ray absorption spectra and the corresponding Fourier transform (FT) spectra for  $\text{Nd}(\text{vers})_3$  hexane solution, Samples A1-A4 are shown in Fig. S1. After removing the pre-edge and post-edge backgrounds, the normalized  $k^3$ -weight XAFS signals within the  $k$ -space region of  $2\text{-}11 \text{ \AA}^{-1}$  were Fourier-transferred to  $R$ -space. It has been claimed that Nd carboxylates presented predominantly the ionically bonding characters in complexes with O-ligating atoms <sup>[s1, s2]</sup> and was in absence of long-range <sup>[s3]</sup> order. The main coordination peak located at about  $1.95 \text{ \AA}$  in the FT spectrum of the  $\text{Nd}(\text{vers})_3$  solution has been confirmed <sup>[s4]</sup> to involve about 9-10 oxygen atoms distributed in two sub-shells. From Fig. S1, it can be seen that the Sample A1, A2, and A3 have similar spectral features with the sample  $\text{Nd}(\text{vers})_3$ , but the decrease of the white line intensity is still visible, which implies the change of electron state density. In other words, the coordination environments around Nd centers are similar but the coordinated atom pairs could be altered with the increase of  $\text{AlEt}_3$  component in the  $\text{Nd}(\text{vers})_3$  solution. When the chlorine source  $\text{Al}(i\text{Bu})_2\text{Cl}$  was added further into the mixture solution of  $\text{AlEt}_3$  and  $\text{Nd}(\text{vers})_3$ , the X-ray absorption spectral features have an obvious change mainly in the height of the white line and the position of coordination peak. For Sample A1, A2, and A3, the dominate coordination peak locates at about  $1.95 \text{ \AA}$ , which almost coincides with the main peak position of  $\text{Nd}(\text{vers})_3$ . But the intensity decrease of their coordination peak with the content increase of the  $\text{AlEt}_3$  component could imply that there have been partial Nd-C bonds <sup>[s5]</sup> formed in the Sample A1, A2, and A3. After  $\text{Al}(i\text{Bu})_2\text{Cl}$  was added into the mixture solution of  $\text{Nd}(\text{vers})_3$  and  $\text{AlEt}_3$ , the peak position (Sample A4) shifts dramatically towards high- $R$  end about  $0.39 \text{ \AA}$ . Such a large position shift of the coordination peak cannot be simply attributed to the distortion of local atomic structures but the replacement of backscattering atoms, meaning that larger bond-lengths of atom-pairs were formed in the neighborhood of Nd centers. A possible reason is that Nd-Cl and/or Nd-Al bonds have been formed in Sample A4.



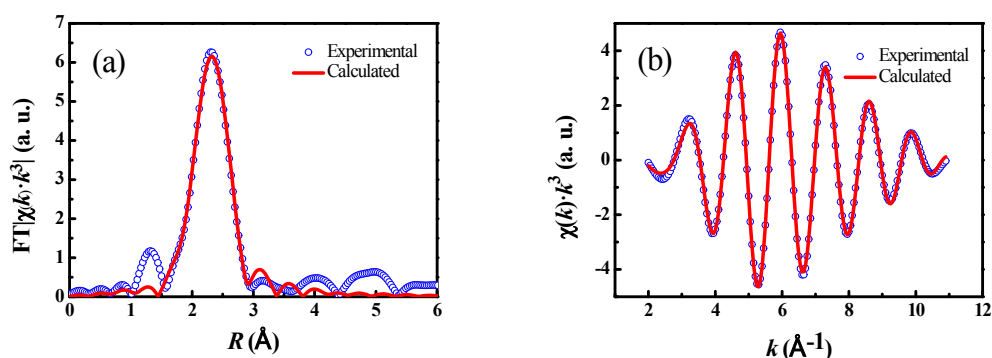
**Figure S1.** (a) Normalized Nd  $L_{III}$ -edge X-ray absorption spectra. (b)  $k^3$ -weight Fourier transform spectra of Nd  $L_{III}$ -edge EXAFS data. The dash lines indicate the peak positions at 1.95 and 2.34 Å.

**Alkylation Step:** Samples A1-A3 stand for the alkylation process of the Nd-based ternary catalyst containing  $Nd(vers)_3$ ,  $AlEt_3$ , and  $Al(iBu)_2Cl$ . Before further XAFS analysis, multielectron effect<sup>[S6]</sup> located at about  $6.5 \text{ \AA}^{-1}$  in the  $k$ -space was removed from the Nd  $L_{III}$ -edge XAFS spectra by improving the backgrounds. The Fourier filter region is approximately from 1.3 to 2.7 Å. Two sub-shells involved Nd-O and Nd-C bonds were used for the best fitting of the XAFS signals. Due to the serious distortion of the structure in Sample A3, the third cumulant  $C_3$  had to be used for the best and reasonable fitting. The fitting curves are shown in Fig. S2.



**Figure S2.** Fourier transform spectra and  $k^3$ -weight XAFS functions of Nd  $L_{III}$ -edge for Samples A1 (a, a'), A2 (b, b'), and A3 (c, c').

**Chlorination Step:** Samples A4 stands for the chlorination process of the Nd-based ternary catalyst containing  $\text{Nd}(\text{vers})_3$ ,  $\text{AlEt}_3$ , and  $\text{Al}(i\text{Bu})_2\text{Cl}$ . The FT spectrum and the isolated EXAFS function of Sample A4 are shown in Fig. S3. Three sub-shells including Nd-C, Nd-Cl and Nd-Al have to be used for the EXAFS fitting after testing various fitting strategies. The fitting result demonstrates that the original Nd-O coordination is completely disappeared after  $\text{Al}(i\text{Bu})_2\text{Cl}$  was added into the mixture solution of  $\text{Nd}(\text{vers})_3$  and  $\text{AlEt}_3$ , but two new bondings of Nd-Cl and Nd-Al are formed.



**Figure S3.** Fourier transform spectra and  $k^3$ -weight EXAFS function of Nd  $L_{III}$ -edge for Sample A4. Open circles represent the experimental values and solid lines represent the fitting curves.

## 2. Fitting parameters for Catalyst-II

The XAFS fitting parameters for Sample A1-A4 are shown in Table SI. For convenient comparison, the structural parameters of the Nd(vers)<sub>3</sub> hexane solution are also listed in Table SI.

**Table SI.** Nd L<sub>III</sub>-edge EXAFS fitting parameters of the Nd-based ternary catalyst containing Nd(vers)<sub>3</sub>, AlEt<sub>3</sub>, and Al(<sup>i</sup>Bu)<sub>2</sub>Cl. *N* is the coordination number, *R* is the interatomic distance,  $\sigma^2$  is the Debye-Waller factor, and *C*<sub>3</sub> is the third cumulant which denotes an asymmetrical atom-pair distribution. [Nd] denotes Nd(vers)<sub>3</sub>, [Al] denotes AlEt<sub>3</sub>, and [Cl] denotes Al(<sup>i</sup>Bu)<sub>2</sub>Cl.

Sample	Ingredient	Bond	<i>N</i>	<i>R</i> (Å)	$\sigma^2(\text{Å}^2)$	<i>C</i> <sub>3</sub> (Å <sup>3</sup> )
Nd(vers) <sub>3</sub>	[Nd]=100%	Nd-O	4.9	2.39	0.0011	
		Nd-O	4.8	2.54	0.0016	
A1	[Al]/[Nd]=1:1	Nd-O	4.9	2.38	0.0042	
		Nd-C	3.8	2.58	0.0015	
A2	[Al]/[Nd]=2.5:1	Nd-O	4.4	2.38	0.0042	
		Nd-C	4.3	2.58	0.0036	
A3	[Al]/[Nd]=10:1	Nd-O	1.5	2.37	0.0047	0.004093
		Nd-C	4.0	2.58	0.0033	0.003074
A4	[Cl]/[Al]/[Nd]=3:10:1	Nd-C	4.5	2.58	0.0025	
		Nd-Cl	3.0	2.88	0.0048	
		Nd-Al	2.2	3.15	0.0046	

## 3. Theoretical calculation

**Table SII.** Nd-O and Nd-C bondlengths of the Nd complexes at the B3LYP/6-31G(d)/SMD/RECP level of theory in hexane solution. The binding energies (*E*<sub>binding</sub>, kcal/mol) of the complexes are listed at the same level of theory

Complex	Bond	Bond length (Å)						Average	<i>E</i> <sub>binding</sub>
Complex A	Nd-O	2.240	2.269	2.479	2.489	2.507		2.397	-1104.09
	Nd-O	2.509	2.525	2.593	2.590	2.640		2.571	
Complex B	Nd-O	2.345	2.326	2.382	2.343	2.752	2.660	2.468	-1159.83
	Nd-C	2.574	2.570					2.572	
Complex C	Nd-O	2.306	2.312	2.508	2.506			2.408	-1091.48
	Nd-C	2.544	2.594	2.600				2.580	

Complex D	Nd-O	2.352	2.334		2.343	-1167.55
	Nd-C	2.859	2.894	2.596	2.657	

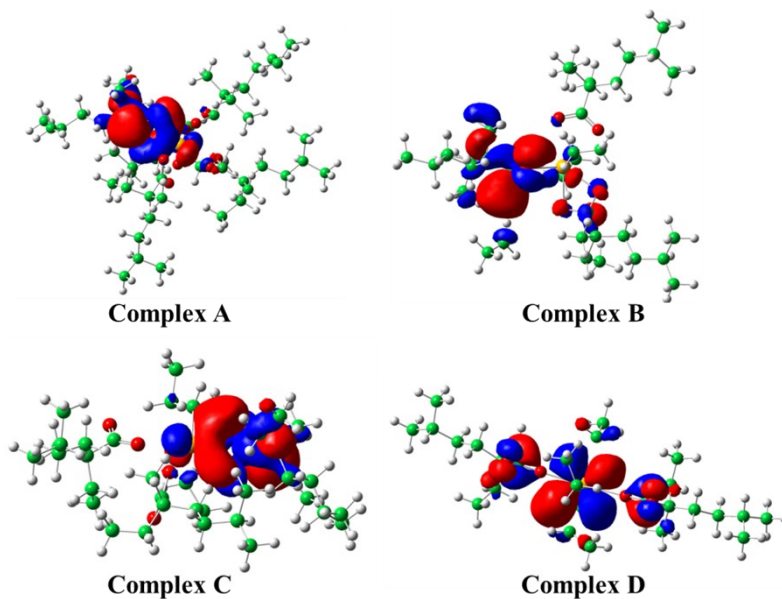
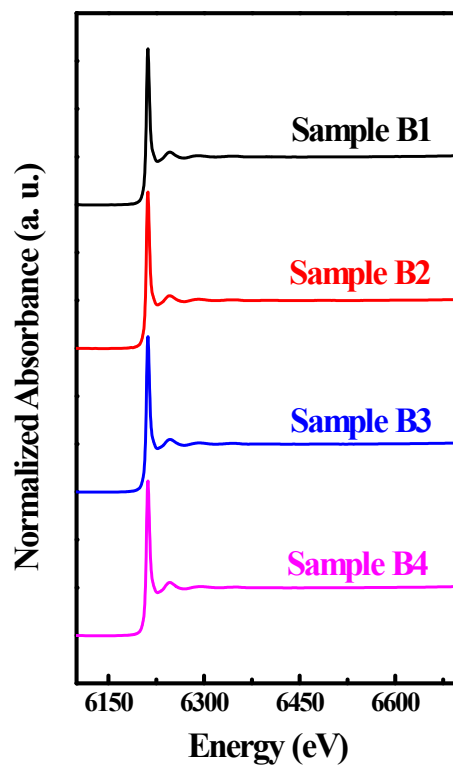


Figure S4. The SOMO diagrams of complexes A-D.

#### 4. X-ray absorption spectra of Samples B1-B4



**Figure S5.** Normalized Nd L<sub>III</sub>-edge X-ray absorption spectra of four Nd-based ternary catalysts with different alkylaluminums {AlEt<sub>3</sub>, Al(<sup>n</sup>Oct)<sub>3</sub>, Al(<sup>i</sup>Bu)<sub>3</sub>, and Al(<sup>i</sup>Bu)<sub>2</sub>H} in the polymerization processes of isoprene (Samples B1-B4).

## References

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