

Supporting Information

Microwave-Assisted In-Situ Ring-Opening Polymerization of ϵ -Caprolactone in the Presence of Modified Halloysite Nanotubes Loaded with Stannous Chloride

Gang Yang, Rui Ma*, Shifan Zhang, Ziyang Liu, Dexuan Pei, Hongyun Jin*, Jiaqi Liu, Wenjie Du

1. Comparison of earlier reported catalysts for the ROP of ϵ -CL with the composite catalytic system of APTES-P-h-HNTs-SnCl₂

To study the advantages of composite catalytic system, a series of work had been carried out. In our earlier work, the catalytic activity of HNTs and SnCl₂, which were two important components of the composite catalytic system, on the ROP of ϵ -CL were studied respectively as the control groups. Subsequently, as the experimental groups, the ROP of ϵ -CL catalyzed by the composite catalytic system of APTES-P-h-HNTs-SnCl₂ were studied.

As shown in Table S1, HNTs, which had been purified, calcined, and activated by acid or base, had certain catalytic activity for the ROP of ϵ -CL. The polymerization process was that chain initiation occurred on hydroxyl groups on the surface of HNTs, and the active hydrogen on the hydroxyl group attacked C-O bond of ϵ -CL to make the chain grow.^{1, 2} The mechanism of the ROP was cationic polymerization. However, the ROP of ϵ -CL catalyzed solely by HNTs led to the low conversion rate (CR) of ϵ -CL and PCL products of low molecular weights. In comparison, SnCl₂, which was one of the traditional tin-based catalysts for the ROP of ϵ -CL, significantly increased the conversion rate of ϵ -CL and the molecular weights of PCL products. The mechanism of these ROP was coordination-insertion polymerization. Finally, the composite catalytic system of APTES-P-h-HNTs-SnCl₂ was used as the catalyst. The mechanism of corresponding ROP included cationic polymerization and coordination-insertion polymerization. Specifically, hydroxyl groups and physically supported SnCl₂ on the surface of modified HNTs, and alkoxy-tin generated by the above two active sites reacting with each other led to the ROP of ϵ -CL.³ Because of the synergistic catalysis of HNTs and SnCl₂, as well as the new groups of alkoxy-tin, the catalytic effect of the composite catalytic system on the ROP of ϵ -CL was better than that of pure HNTs or SnCl₂, in terms of the conversion rate of ϵ -CL, molecular weights and physicochemical properties of PCL products.

Table S1 ROP of ϵ -CL with different catalysts (APHS represents APTES-P-h-HNTs-SnCl₂)

n	catalyst	I/M	synthesis process	T(°C)	t(h)	CR(%)	M _n (g·mol ⁻¹)
1	HNTs	1wt%	HROP	140	24	11.1	-
2	HNTs	1wt%	HROP	140	36	27.3	-
3	HNTs	1wt%	HROP	140	48	75.7	12094
4	SnCl ₂	0.1mol%	HROP	150	24	85.8	17124
5	SnCl ₂	0.1mol%	HROP	150	36	85.4	30054
6	SnCl ₂	0.1mol%	HROP	150	48	83.2	21947
7	APHS	1wt%	HROP	150	24	92.4	28190
8	APHS	1wt%	HROP	150	36	89.8	33417
9	APHS	1wt%	HROP	150	48	88.5	25466
10	HNTs	1wt%	MROP(400W)	250	1	9.8	13935
11	SnCl ₂	0.1mol%	MROP(400W)	250	1	88.8	28669
12	APHS	1wt%	MROP(400W)	250	1	93.9	52088

2. The recyclability of APTES-P-h-HNTs-SnCl₂

Homogeneous catalyst had high activity and selectivity, but it was difficult to separate from the reaction system and reuse, so the catalyst cost was high. In contrast, heterogeneous catalysts had the advantage of being easily separated from the reaction system and could be reused. As a heterogeneous catalyst, the active component of APTES-P-h-HNTs-SnCl₂ is SnCl₂, and the cocatalyst and support both were modified HNTs. The recyclability of APTES-P-h-HNTs-SnCl₂ was studied. The sample used was PCL-HNTs (1wt%), and the specific research process was to dissolve appropriate amount of PCL-HNTs (1wt%) in dichloromethane and centrifuge them at 10000r/min. The solid component obtained by centrifugation was dissolved in dichloromethane for the second time and centrifuged at 10000r/min. Then the solid component obtained by the second centrifugation was then dried and ground. It was tested by XRD and compared with APTES-P-h-HNTs-SnCl₂. As shown in Figure S1, they were the same substance, that was, the recycled solid component was APTES-P-h-HNTs-SnCl₂ (cycle 2). The recycle rate (RR) of APHS obtained by this method was 78.0% (Table S2). Because part of APTES-P-h-HNTs-SnCl₂ generated alkoxy-tin in the reaction, and PCL catalyzed by alkoxy-tin was grafted to HNTs, resulting in the failure of recycling part of APTES-P-h-HNTs-SnCl₂ (cycle 1).

As shown in Table S2, using APTES-P-h-HNTs-SnCl₂ (cycle 2) as the catalyst, the conversion rate of ε-CL and the molecular weight of PCL products were similar to the ROP of ε-CL using APTES-P-h-HNTs-SnCl₂ (cycle 1) as the catalyst, which proved the excellent recyclability of the heterogeneous catalyst of APTES-P-h-HNTs-SnCl₂.

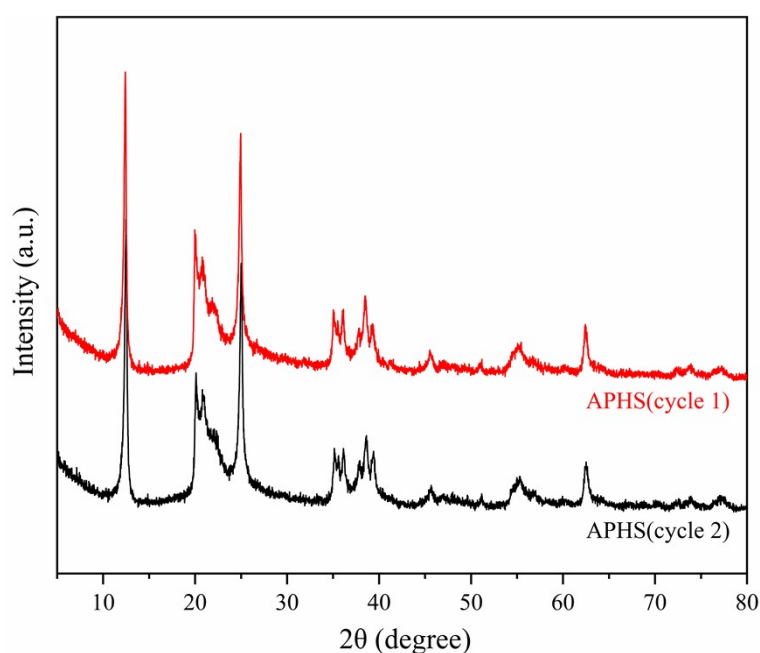


Figure S1 XRD spectra of APHS(cycle 1,cycle 2) (APHS represents APTES-P-h-HNTs-SnCl₂)

Table S2 The recyclability of APTES-P-h-HNTs-SnCl₂ (APHS represents APTES-P-h-HNTs-SnCl₂)

cycle	catalyst	I/M	synthesis process	T(°C)	t(h)	CR(%)	M _n (g·mol ⁻¹)	RR(%)
1	APHS	1wt%	MROP(400W)	250	1	93.9	52088	78.0
2	APHS	1wt%	MROP(400W)	250	1	90.5	56728	72.7

Reference

1. R. Ma, P. Hu, J. Fan, W. Tang, T. Chen and L. Shi, *Polymer Plastics Technology & Engineering*, 2018, 1-13.
2. G. Wang, R. Ma, T. Chen, C. Yan, J. Gao and F. Bao, *Polymer-Plastics Technology and Engineering*, 2013, **52**, 1193-1199.
3. M. Lahcini, S. Elhakioui, D. Szopinski, B. Neuer, A. El Kadib, F. Scheliga, M. Raihane, F. B. Calleja and G. Luinstra, *Eur. Polym. J.*, 2016, **81**, 1-11.

