

Notes

POLYMERIZATION OF γ -STEARYL- α , L -GLUTAMATE
N-CARBOXYANHYDRIDE USING RARE EARTH COORDINATION CATALYSTS*Xiao-ping Hu^a, Jian Wu^{b**}, Zhi-kang Xu^a and Lin-xian Feng^a^a Institute of Polymer Science, Zhejiang University, Hangzhou 310027, China^b Department of Chemistry, Zhejiang University, Hangzhou 310027, China

Abstract A rare earth coordination system was first investigated as a new type of catalyst for the ring-opening polymerization of α -amino acid *N*-carboxyanhydrides (NCAs). The results for the polymerization of γ -stearyl- α , L -glutamate (SLG) NCA using neodymium acetylacetonate (Nd(acac)₃)- or neodymium tris(2-ethylhexylphosphonate) (Nd(P₂₀₄)₃)-triethylaluminum-water as catalysts were compared with those using conventional catalysts. It was found that the helical poly(γ -stearyl- L -glutamate) with high molecular weight as well as narrow molecular weight distribution can be obtained in the presence of Nd(acac)₃/AlEt₃-1/2H₂O. The polymer obtained was characterized by IR and NMR spectroscopy.

Keyword Rare earth coordination catalyst, Ring-opening polymerization, Polypeptide, Poly(γ -stearyl- α , L -glutamate)

INTRODUCTION

Poly(γ -stearyl- α , L -glutamate) (PSLG) is an appealing model for the fundamental study of rod-like polymer, which exhibits not only the stiffness arising from its helical backbone but also high solubility in common organic solvents due to its long aliphatic side chain. PSLG has been prepared by transesterification of poly(γ -methyl- α , L -glutamate) or poly(γ -benzyl- α , L -glutamate) with stearyl alcohol^[1, 2], but incomplete transesterification yields copolymers that are likely to be unsuitable for many fundamental studies. Recently, Daly *et al.*^[3] reported the polymerization of γ -stearyl- α , L -glutamate *N*-carboxyanhydride (SLGNCA) initiated by benzylamine or sodium methoxide, leading to pure PSLG in a range of molecular weights. However, the physical properties of the resulting polydisperse PSLG fall short of what is necessary for most applications.

It has been found that rare earth coordination catalysts are effective catalysts for the ring-opening polymerization of epoxides and lactones to produce polymers with high molecular weight and narrow molecular weight distribution^[4, 5]. In the present study, the coordination systems of neodymium acetylacetonate or naphthanate with partially hydrolyzed alkylaluminum were used for the polymerization of SLGNCA. This note describes some characteristics of the polymerization and the result of investigations on the helical structure of the PSLG obtained.

EXPERIMENTAL

Materials

All solvents and reactants were reagent grade. Tetrahydrofuran (THF) and *n*-hexane were refluxed over sodium and distilled before use. Dichloromethane (DCM) and toluene were dried over 0.4 nm molecular sieves at least overnight prior to use. Bis(trichloromethyl)carbonate (triphosgene) was purchased from Aldrich Chemical Co.. SLG and SLGNCA were synthesized according to the literature^[6, 7]. Nd(acac)₃ and Nd(P₂₀₄)₃ were prepared by

* This work was supported by National Natural Science Foundation of China (No. 29504029).

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Received October 26, 1999

the method described in reference^[8].

Catalyst Preparation and Polymerization

Pre-prepared AlEt_3 -1/2 H_2O toluene solution^[4] was transferred into a bottle in which a prescribed amount of $\text{Nd}(\text{acac})_3$ or $\text{Nd}(\text{P}_{204})_3$ had been put. The resultant catalyst solution was aged at 70°C for 3 h, and then added to the DCM solution of SLGNCA in a bottle under a nitrogen atmosphere with a certain monomer/catalyst molar ratio. Polymerization reaction was carried out at 30°C and terminated by precipitation with acetone. The product was recovered by gravity filtration and dried under vacuum at room temperature.

Measurements

IR spectra were recorded on a Bruker Vector-22 spectrometer. NMR spectra were run in deuterated chloroform on a Advance-DCM 500 MHz instrument, using TMS as the internal reference. GPC data were collected on a Waters Associates-208 gel permeation chromatograph. The inherent viscosity of PSLG was measured at 30°C in THF using an Ubbelohde capillary viscometer. M_w was calculated according to the equation^[3]:

$$[\eta] = 1.26 \times 10^{-7} M_w^{1.290}$$

RESULTS AND DISCUSSION

NCA polymerizations are usually initiated by nucleophiles and bases^[9]. It is generally accepted that primary amine initiations lead to polymers with comparatively narrow molecular weight distributions (MWD) and low molecular weights. Strong bases such as sodium alkoxides can yield much higher molecular weight polymers with very broad MWD. SLGNCA polymerizations were performed using rare earth coordination catalysts and other conventional catalysts, the results are given in Table 1. It was found that the rare earth coordination catalysts can initiate the ring-opening polymerization of SLGNCA monomer, leading to PSLG with relatively high molecular weight and narrow molecular weight distribution in high yield compared with those using conventional catalysts. Furthermore, the polymerization result with the AlEt_3 -1/2 H_2O catalyst system is also listed in Table 1 for comparison. It was shown that the molecular weight of PSLG increased and the MWD became narrower with the addition of neodymium compounds, and $\text{Nd}(\text{acac})_3/\text{AlEt}_3$ -1/2 H_2O is more effective than $\text{Nd}(\text{P}_{204})_3/\text{AlEt}_3$ -1/2 H_2O for the polymerization of SLGNCA, which is similar to that in the polymerization of propylene oxide^[10].

Table 1. Polymerization of SLGNCA by different catalysts at 30°C in DCM^a

Catalyst	NCA conc. (W/V)%	[M]/[I]	time (days)	Yield (%)	$[\eta]$ (dL/g)	$M_w \times 10^{-4}$ ^[3]	M_w/M_n
$\text{Nd}(\text{acac})_3/\text{AlEt}_3$ -1/2 H_2O	5	200 ^a	6	82.4	0.146	5.02	
$\text{Nd}(\text{acac})_3/\text{AlEt}_3$ -1/2 H_2O	5	100 ^a	6	87.2	0.159	5.36	1.26
$\text{Nd}(\text{acac})_3/\text{AlEt}_3$ -1/2 H_2O	5	100 ^a	3	86.2	0.130	4.59	
$\text{Nd}(\text{acac})_3/\text{AlEt}_3$ -1/2 H_2O	2	100 ^a	15	87.4	0.285	8.43	1.22
$\text{Nd}(\text{P}_{204})_3/\text{AlEt}_3$ -1/2 H_2O	2	200 ^a	15	80.1	0.209	6.63	1.31
$\text{Nd}(\text{P}_{204})_3/\text{AlEt}_3$ -1/2 H_2O	5	100 ^a	6	80.4	0.118	3.56	
AlEt_3 -1/2 H_2O	5	100	6	83.6	0.103	3.83	1.53
RONa^b	5	100	5	90.4	0.830	19.3	4.71
BzNH_2	5	100	5	92.6	0.106	3.92	2.43

^a [I] = [Nd], Al/Nd = 6

^b R = Alkyl groups

In the experiment we found that the initial NCA concentration and the NCA/Nd molar ratio greatly influenced the SLGNCA polymerization with the rare earth coordination catalyst. The 5% monomer concentration and the NCA/Nd ratio of 100 appear to be optimal; a high activity of $\text{Nd}(\text{acac})_3/\text{AlEt}_3$ -1/2 H_2O and a high molecular weight of PSLG were obtained. The Al/Nd molar ratio is also an important factor to influence both the molecular weight and the yield of PSLG produced by the $\text{Nd}(\text{acac})_3/\text{AlEt}_3$ -1/2 H_2O system, as shown in Table 2. It was notable that the yield of PSLG increased slightly with increasing Al concentration while keeping NCA/Nd = 100, but the molecular weight of PSLG increased to a large degree with the addition of $\text{Nd}(\text{acac})_3$.

The optimum Al/Nd molar ratio for high $[\eta]$ is about 6.

Table 2. Effect of Al/Nd molar ratio on SLGNCA polymerization^a

Al/Nd (mol/mol)	PSLG[Nd(acac) ₃ /AlEt ₃ -1/2H ₂ O system] ^b		PSLG[AlEt ₃ -1/2H ₂ O system] ^b	
	Yield (%)	$[\eta]$ (dL/g)	Yield (%)	$[\eta]$ (dL/g)
4	81.8	0.096	78.8	0.0820
5	84.7	0.122	78.4	0.0807
6	87.9	0.146	77.8	0.0790
7	91.6	0.135	77.6	0.0777
8	91.2	0.117	75.3	0.0773
12	90.6	0.109	72.7	0.0700

^a NCA conc. (W/V)% = 5%. NCA/Nd = 100, 30°C, 5 days in DCM

^b AlEt₃-1/2H₂O system with the corresponding Al concentration

PSLG prepared with Nd(acac)₃/AlEt₃-1/2H₂O were characterized by IR and NMR spectroscopy. The IR spectra of PSLG displayed bands typical of an α -helical conformation (CONH bands at 1660 and 1550 cm⁻¹)^[11]. The ¹H-NMR spectrum of PSLG (Fig. 1a) shows considerable overlap of peaks since the backbone of PSLG is in the helical conformation. Note that the peaks in the ¹H-NMR spectrum become more clearly resolved when the helix is broken after the addition of TFA (Fig. 1b). The α -CH peak in the ¹H-NMR spectrum of PSLG shifts also from δ = 3.9 for the α -helix conformation to δ = 4.6 for the random coil conformation^[12]. A similar result was also obtained from ¹³C-NMR of PSLG.

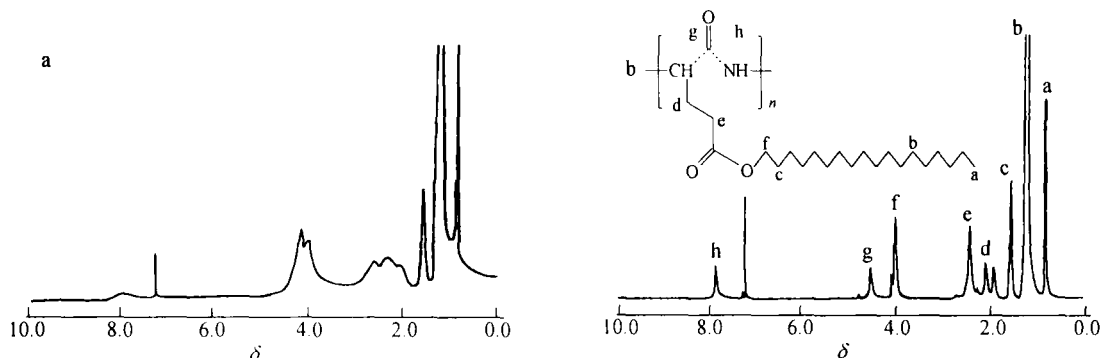


Fig. 1 ¹H-NMR spectra of PSLG run in CDCl₃ with TMS standard

a) 500-MHz ¹H-NMR without trifluoroacetic acid (TFA)

b) 500-MHz ¹H-NMR with 10% TFA

In summary, our study confirmed that Nd(acac)₃/AlEt₃-1/2H₂O is a novel effective catalyst for the ring-opening polymerization of SLGNCA, producing PSLG with high molecular weight and narrow molecular weight distribution.

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