A Novel Method for the Preparation of Monocarboxyl-End-Grouped Polycaprolactam with an Adjustable Molecular Weight

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ABSTRACT: A novel method was used to synthesize adjustable-molecular-weight polycaprolactams with monocarboxyl end groups. The reaction device and conditions are discussed. The products were characterized by Fourier transform infrared spectroscopy, ^{1}H-NMR spectroscopy, high-resolution pyrolysis gas chromatography–mass spectrometry, and wide-angle X-ray diffraction. The thermal properties were studied by differential scanning calorimetry and thermogravimetric analysis. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 722–727, 2004

Key words: catalysis; synthesis; thermal properties

INTRODUCTION

Although the effects of reinforcing fibers and fillers on the mechanical properties of polymeric composites are well documented,[1–3] these still have adverse effects on the processability of the resultant materials, such as the increase in melting viscosity, which in some instances, is too high for the material to be processed. A new concept called *molecular composites* was developed by Takayanagi[4,5] with which the basic principle providing a macrofiber-reinforced composite with excellent properties can be extended to the molecular level when the reinforcing molecules retain their rigidities and are dispersed uniformly in the ductile matrix polymers. Considerable efforts have been taken by many researchers[6–10] to explore this principle to prepare a new category of high-performance polymeric materials. One of the most important approaches is the design and synthesis of suitable reinforcing components, which are generally block, graft, or multipode copolymers.[11–17] Thus, the synthesis of prepolymers with proper molecular weights and reactive functional end groups has become more important in matching the requested properties of the desired copolymers.

A novel approach for the preparation of so-called melt-processable molecular composites was recently developed by Xu et al.,[18] of which a series of model block copolymers with different rigid and flexible blocks were designed and synthesized, and the most important consideration for the design was the optimization and harmonization of the length of the rigid and flexible blocks of the copolymers. So the design and synthesis of some suitable block segments (with certain molecular weights and some expected reactive functional end groups) for further polymerization has become more and more important, and this may be a stream in the field of polymer modification as the use of functional polymers grows. In this study, we set a practical example with polycaprolactam (PA6). A series of low-molecular-weight polycaprolactams with reactive functional end groups as the flexible blocks were synthesized before the copolymerization of the triblock copolymers.

The synthetic methods and studies on the industry production of nylon 6 by ε-caprolactam can be ubiquitously found in the literature, including solid-phase polymerization[19] and anionic polymerization.[20] However, little work has been done on the preparation of low-molecular-weight polycaprolactam, as most of the reports concern industrial uses, such as fiber or plastics, which generally require high molecular weights. Wang et al.[21] and Koch[22] once reported the polymerization of polycaprolactam with 6-aminphexenoic acid as a catalyst and discussed the mechanism of polymerization in detail. However, as a difunctional compound, 6-aminohexenoic acid is not practical for the synthesis of mono-end-group polycaprolactam, and the reaction equipment used was also complex and quite dangerous for laboratory use. Thus, a new approach for the preparation of such a low-molecular-

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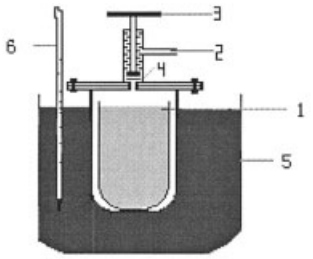


1 reaction vessel 2 gas piping 3 cock 4 PTFE seal
5 salt bath 6 thermometer

Figure 1 Schematic diagram of the reaction device designed for ε-caprolactam polymerization.

weight prepolymer needed to be developed. In this work, a simple and expedient method with a self-designed equipment is reported, which was used to prepare monocarboxyl-end-grouped polycaprolactam with an adjustable molecular weight. Additionally, the choice of catalyst system and the control of the reaction conditions are discussed. The structures of the products obtained by these means were characterized, and the thermal properties were studied.

EXPERIMENTAL

Materials

The ε-caprolactam used was polymerization grade, the benzoic acid (BA) and formic acid were analytical reagents, and potassium acid phthalate was of spectral purity. All were used as received. Benzyl alcohol was chemically pure and was purified by vacuum distillation.

Preparation of monocarboxyl-end-grouped polycaprolactam with varied molecular weights

ε-caprolactam, BA, and water were mixed completely, put into a reactor designed by our laboratory, vacuumed for half an hour, and then sealed up. The reaction was carried out in a salt bath at 250°C for 5 h.

Characterization

The molecular weights of polymers were mensurated by terminal analysis with KOH solution according to the method reported in ref. 23. The viscosity measurement was performed at 25°C with formic acid as a solvent. Fourier transform infrared (FTIR) spectroscopy (Nicolet 205FT-IR), ^{1}H-NMR (Jeol FX-90Q, Japan), wide-angle X-ray diffraction (WAXD; Rigaku D/MAX-3A, Japan), and high-resolution pyrolysis gas chromatography–mass spectrometry (HRPyGC–MS, Japan) were used to determine the chemical structure. Differential scanning calorimetry (DSC; PerkinElmer DSC-7, Japan) measurements was carried out at a heating rate of 20°C/min under N_2. A thermogravimetric analyzer (Shimadzu TGA-50, Japan) was used to carry out the thermogravimetric analysis (TGA) under N_2 at a heating rate of 20°C/min up to 700°C.

RESULTS AND DISCUSSION

Synthesis

Reaction device designed for laboratory use

As is well known, polyamide is easily oxidized and changes color at high temperatures. So it is important to maintain an anaerobic atmosphere during the polymerization process. Normally, there are two ways to achieve this in the laboratory. One of them is to carry out the polymerization in a sealed glass tube, but it is actually dangerous sometimes. Another method is to aerate deoxidized, highly purified N_2 into the reaction system, but the deoxidation process is a complex and miscellaneous task in the laboratory. After a number of trials, a stainless steel reaction device was designed on the basis of the sealed polymerization, as shown in Figure 1. The mixed reacting substance was first put into the vessel (1); the cock (3) was opened. The mixture was then vacuumed for half an hour through the gas piping (2). Last, the cock was closed, and the system was sealed by polytetrafluoroethylene (PTFE) (4). The device was then embedded in a salt bath (5). An anaerobic atmosphere was thus achieved expediently and simply.

TABLE I
Effects of Water Content on the Polymerization of ε-Caprolactam Catalyzed by Benzoic Acid

Sample	ε-Caprolactam (g)	Benzoic acid (g)	Water (g)	Temperature (°C)	Time (h)	Product status	Yield[a] (%)
1	120	10	0	250	5	White wax	34.6
2	120	10	0.05	250	5	White wax	51.5
3	120	10	2	250	5	White stick	76.9

[a] The primary product was dissolved in formic acid, precipitated by water, washed by hot water, and then dried.

TABLE II
Effects of Water–Benzoic Acid Catalyst on the Polymerization of ε-Caprolactam and the Properties of the Low-Molecular Polycaprolactam

Name	Monomer (g)	BA (g)	I	Yield (%)	$[\eta]$[a]	M_m	(M_c)	P_n[b]
N1	120	15	7.5	70.4	0.11	1460	(1000)	12
N2	120	10	5	76.9	0.14	1830	(1500)	15
N3	120	7.2	3.6	81.0	0.17	2200	(2000)	18
N4	120	5	2.5	85.6	0.20	2980	(3000)	25
N5	120	3	1.5	89.4	0.29	4370	(5000)	38

Reaction temperature-250°C; reaction time = 5 h. The primary product was dissolved in formic acid, precipitated by water, washed by hot water, and then dried.
[a] $[\eta]$: intrinsic viscosity.
[b] P_n: degree of polymerization.

Choice of the catalyst

As ε-caprolactam is a very stable seven-heterocyclic ring, the monomer can be polymerized only at high temperatures in the presence of a catalyst, such as water; inorganic acids such as phosphoric acid and sulfuric acid; organic acids such as formic acid, acetic acid, and BA; or other anionic polymerization catalysts.[3,8–10] Most of the catalysts used for industrial purposes, however, were not applicable to our aim. To obtain a monocarboxyl-end-grouped polycaprolactam to be used at high temperature, a monofunctional-group organic acid with a high boiling point had to be chosen. In this study, BA was an ideal catalyst for its high melting point and low volatility. Additionally, BA acted here not only as a catalyst but also a molecular control agent. It could react with the terminal amino group of the growing polycaprolactam, and the polymerization could be ended to adjust the molecular weight. Monocarboxyl-end-grouped polycaprolactam with an adjustable low molecular weight could thus be obtained through the control of the amount of catalyst.

Effects of BA–water system on the polymerization

Table I compares the effects of water content on the polymerization of ε-caprolactam catalyzed by BA. The experimental results showed that if there was no water in the reaction system, the polymerization did not occur completely, and the obtained reactant was a white wax-like product without any mechanical strength even, when an extended reaction time was used. When the water content was too low (<0.5%), the same reactant was obtained because of the evaporation of water at high temperatures. However, when the water content in the system was suitable, polycaprolactam was obtained at a high yield. It was obvious that the water content had to be properly controlled to achieve the polymerization.

Thus, a complex catalyst system, BA–water, was used in the polymerization of ε-caprolactam. The results in Table II show that the ratio of BA and water had a strong effect on the molecular weight of the products. M_c is a theoretical value of molecular weight calculated by the molar ratio of ε-caprolac-

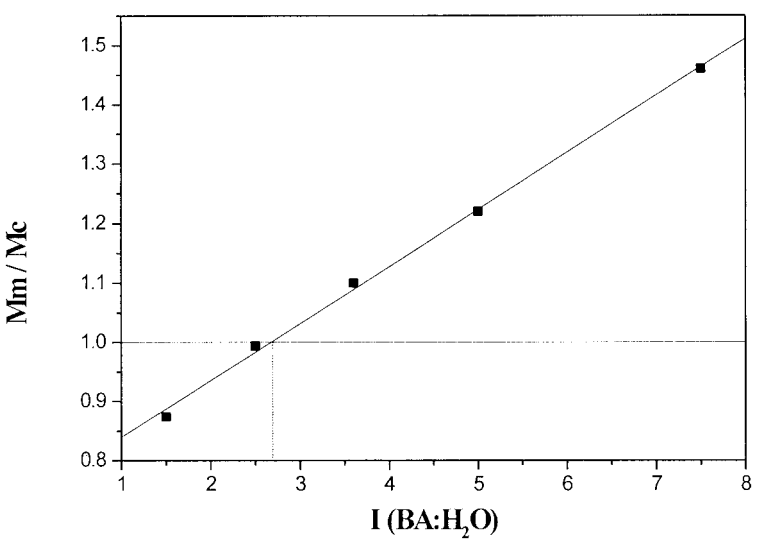


Figure 2 Plot of I versus M_m/M_c.

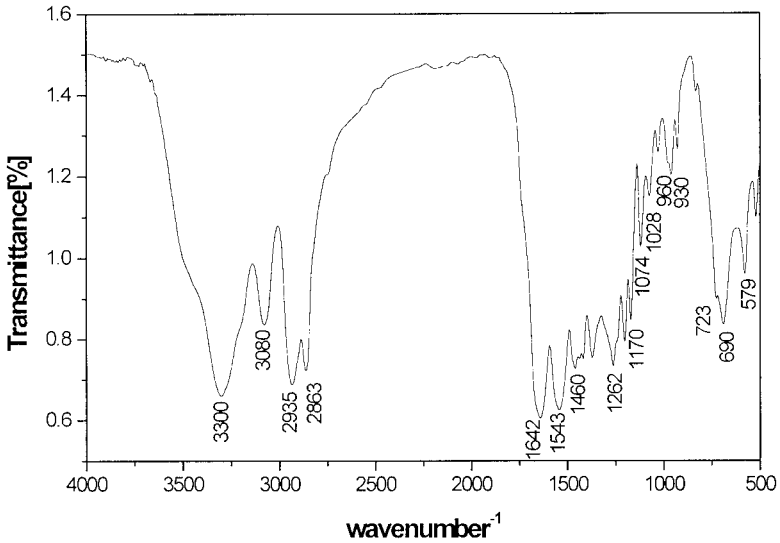
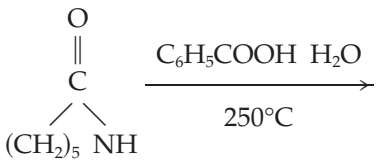


Figure 3 FTIR spectra of the monocarboxyl-end-grouped polycaprolactam.

tam and BA used in the reaction, and M_m is the average molecular weight as measured by viscometry. The value of BA:H_2O (I) versus M_m/M_c are plotted as shown in Figure 2; there was a linear relationship between them. At the intersection point where $I = 2.7$, M_m was equal to M_c, suggesting that the desired molecular weight could be obtained accurately by the adjustment of the dosage of BA and water in the reaction system. Further study is needed to understand the mechanism of these two components in the control of the molecular weight of the products. The approach for the preparation of the monocarboxyl-end-grouped polycaprolactam with an adjustable molecular weight can be expressed as



$$\times C_6H_5COO\text{-}[\text{-}NH(CH_2)_5CO\text{-}]_m OH \quad (1)$$

Characterization

Chemical structure

Figure 3 shows the FTIR spectra of the monocarboxyl-end-grouped polycaprolactam. The peaks at 1642,

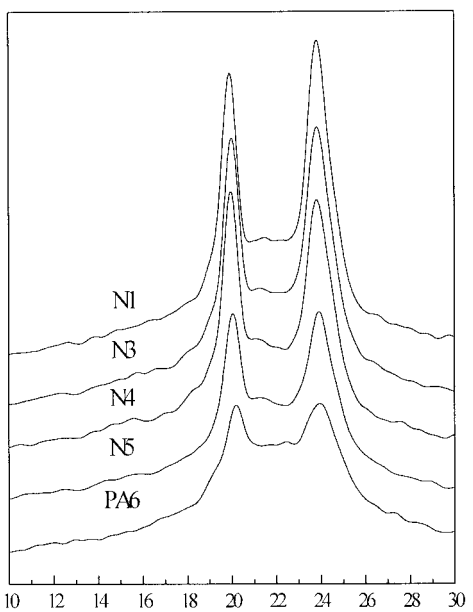


Figure 4 WAXD curves of polycaprolactams with different molecular weights.

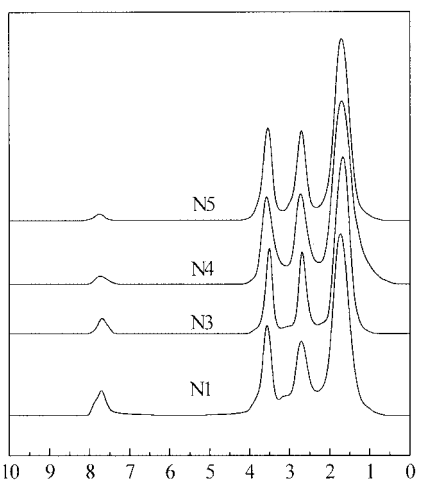
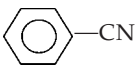
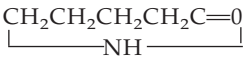
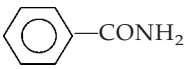


Figure 5 ^{1}H-NMR spectra of polycaprolactams with different molecular weights.

TABLE III
Pyrolysate Yields of Monocarboxyl-End-Grouped Polycaprolactam

m/z	Structure	*m/z*	Structure
42	$CH_2{=}CHCH_3$	94	$CNCH_2CH_2CH_2CN$
53	$NCCH{=}CH_2$	101	$H_2NCOCH_2CH_2CH_2CH_3$
54	$CH_2{=}CHCH{=}CH_2$	103	
55	$NCCH_2CH_3$	*113	
69	$CH_3CH_2CH_2CN$	*121	
73	$CH_3CONHCH_3$	*129	$CH_3CH_2CH_2CONHCH_2CH_2CH_3$
*78		*177	

* The characteristic fragments that confirm the chemical structure of the polymer.

1543, and 1262 cm^{-1} were the three characteristic absorptions of the amino linkage. The peak at 723 cm^{-1} was the special absorption for $(CH_2)_4$. The absorptions at 1170, 1074, and 1460 cm^{-1} were intrinsic for the benzene ring, which indicated that the amine chain end was terminated by a benzyl acid, thus leading to a single terminal function end group for the polycaprolactam. The peaks at 1028, 960, 930, and 579 cm^{-1} were specific for the α crystalline form of polycaprolactam, which was also confirmed by the WADX studies, as seen in Figure 4. All of the products exhibited two reflections at $2\theta = 20$ and 23°, which were related to the α form of the nylon 6 crystal.

The ^{1}H-NMR measurements (CF_3COOD was used as a solvent) were also helpful for proving the chemical structure of the products. In Figure 5, the peaks at $\delta = 3.6$ (—NCH_2—), 2.8 (—$COCH_2$—), and 1.1–2.0 (—C—CH_2—C—) were all intrinsic for nylon 6. Similarly, chemical shift of the benzene ring was detected at $\delta = 7.6$–7.9.

The HRPyGC–MS results gave more intuitive evidence for the structures of the products. The fragments listed in Table III were from the pyrolysate of the resultant polycaprolactam. Obviously, the common feature of the nylon 6 spectra was the presence of an ion signal at $m/z = 113$, corresponding to the ε-caprolactam monomer. Those signals, such as $m/z = 94$ and $m/z = 129$, came from the degradation of the nylon 6 main chain. Other characteristic ions confirming the termination of amine end by benzyl acid were fragments at $m/z = 78$, 103, 121, and 177.

Thermal properties

Table IV lists the results of TGA and DSC studies on the low-molecular-weight polycaprolactam. As

TABLE IV
TGA and DSC Results of Low-Molecular-Weight Polycaprolactam

Sample	M_n[a]	Temperature (°C)		Residual weight at 700°C (%)	T_m[b] (°C)	T_c[c] (°C)
		5% loss	10% loss			
N1	1460	345.8	362.2	0.83	205.2	172.1
N2	1830	353.4	368.6	0.89	209.8	176.4
N3	2200	361.0	377.4	0.62	212.0	180.3
N4	2980	367.3	383.7	0.65	214.6	182.0
N5	4370	376.1	395.1	0.76	216.8	183.7

[a] M_n: number-average molecular weight.
[b] T_m: peak melting temperature by DSC.
[c] T_c: peak crystallization temperature by DSC.

shown, the melting and crystallization temperatures were elevated as the molecular weight increased, which matched very well with the relationship between the properties and the molecular weight of the polymer. The TGA results also showed that all of the samples maintained their thermal stability, and the residual weight at 700°C could be attributed to the carbonification other than decomposition of the terminal benzene ring at high temperatures.

CONCLUSIONS

A new reaction device was designed in this study to perform the polymerization of polycaprolactam in the laboratory more simply and safely. A BA–water system was used as the catalyst, and the ratio between BA and water strongly affected the molecular weight of the products. The polycaprolactam obtained by this method had the same chemical structure as nylon 6, and it preferred to form α crystals, which is a more stable crystalline form of nylon 6.[25] The exhibition of the benzene ring in the structural characterization indicated a reaction between BA and the terminal amino group. Meanwhile, the molecular weight of the polymer could be adjusted expediently by a change in the ratio of BA to water.

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