DOI: 10.1021/ma102696y

Macromolecules
ARTICLE

Synthesis of High Molecular Weight Nylon 46 in Supercritical Carbon Dioxide

Ziyong Zhang,* Kaijin Huang, and Zonghua Liu

Department of Materials Science and Engineering, Jinan University, Guangzhou 510632, China

Received November 28, 2010

ABSTRACT: Nylon 46 with high molecular weight was successfully synthesized in supercritical carbon dioxide (sc-CO_2) by one-step three-stage polymerization using the salt prepared from 1,4-diaminobutane and 1,6-adipic acid as a monomer. The polymerization process was divided into three reaction stages: precondensation, postcondensation, and vacuum. To prepare high molecular weight nylon 46, the precondensation of the salts with pH over 7.23 was first carried out at 190 °C under 30 MPa for 2 h. Then CO_2 in the reactor was exhausted along with removing byproduct water, and the reactor was refilled with dry liquid CO_2. Subsequently, the prepolymer formed was subjected to the postcondensation at 280 °C for 3 h under 15 MPa. Finally, the reactor was heated in vacuum at 270−280 °C for 30−45 min. The highest viscosity-average molecular weight of the nylon 46 sample synthesized from the above process is 48 200 g/mol. The chemical structure and thermal properties of the nylon 46 were characterized by Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The nylon 46 sample, as an example, has melting point of 310 °C, glass transition temperature of 67 °C, starting decomposition temperature of 400 °C, and maximum decomposition rate at 450 °C.

1. Introduction

Polyamides (nylons) are important commercial polymer materials used widely in a variety of applications. Among aliphatic nylons, polytetramethylene adipamide, nylon 46, is particularly suitable for maintaining strength in elevated temperature environments because of its high melting point and good strength, all of which thermally related properties exceed those of other commercially available nylons. Nylon 46 exhibits increasing mechanical strength with increasing molecular weight. Therefore, seeking methods by which higher molecular weight nylons 46 can be obtained are of utility and commercial importance.

As early as 1938, Carothers[1] mentioned nylon 46, which had very low molecular weight and pale color. This work was confirmed by Coffman[2] 10 years later. Beamen[3] synthesized nylon 46 by a two-step melt polymerization and obtained a product with an inherent viscosity of 0.84 (0.5 g/100 mL in *m*-cresol at 30 °C). During the melt polycondensation process, certain side reactions such as oxidation, thermal degradation, and 1,4-diaminobutane cyclization to pyrrolidine may occur due to higher polymerization temperatures[4] and thus result in low molecular weight and discoloration of the product. An interfacial polymerization was also reported to prepare nylon 46 by using 1,6-adipoyl chloride in chloroform and 1,4-diaminobutane in water.[5] However, this method had some problems such as the cost and toxicity of 1,6-adipoyl chloride, and still low molecular weight of the product, and thus had no importance.

One route to prepare high molecular weight nylon 46 has been developed through solid state polymerization (SSP). The prepolymers obtained from the monomer by precondensation are heated to a temperature between glass transition temperature and melting point so as to make the end groups mobile enough to react each other,[6−8] and the byproducts are removed by passing an inert gas through the reacting mass or by maintaining reduced pressure.[7,9,10] In 1977, Gaymans[4] reported synthesis of nylon 46 with high molecular weight by SSP, which had inherent viscosity of 2.09 (0.5 g/100 mL in 98% formic acid at 30 °C). The advantage of SSP is mainly low operating temperature, which restrains side reactions and thermal degradation of the polymer with high melting point. Its disadvantages focus on the low reaction rate comparing to melt polymerization. DSM Co. developed the manufacture technologies of nylon 46 and marketed under the trade name Stanyl.[11−15]

The use of the inert gas in SSP systems serves three principal objectives: to remove the condensate, to inhibit polymer oxidation, and to heat the reacting mass. The inert gases used most often in SSP processes are nitrogen (N_2), helium (He),[16] carbon dioxide (CO_2), superheated steam, and sc-CO_2.[17,18] The sc-CO_2 is a green medium due to its inert, nontoxic, nonflammable, and environmentally friendly properties. Since 1992, DeSimone[19] successfully synthesized fluoropolymers in sc-CO_2, and the polymerization in sc-CO_2 has become a hot research area. Except anionic polymerization, almost all polymerizations such as radical polymerizations and step polymerizations have been investigated in sc-CO_2.[20] Only fluoropolymers and silicon-containing polymers can be dissolved in sc-CO_2, carbon-chain polymers, and heterochain polymers are indissoluble but can be swelled and plastified. Thereby, sc-CO_2 becomes a plasticizing agent and swelling agent which can enhance the free volume of carbon-chain or heterochain polymers. The byproduct formed from polycondensation may diffuse and separate from melting mass or solid phase to sc-CO_2 phase to favor shifting the reaction equilibrium to the right. sc-CO_2 has been used as the reaction medium in polycondensation to prepare polycarbonate, poly(ethylene terephtalate), and nylon-66.[21,22] The number-average molecular weight of nylon-66 prepared in sc-CO_2 is only 24 500 g/mol. This result indicates that high molecular weight product is confined to some extent in a closed system of sc-CO_2.

In this paper, high molecular weight nylon 46 has been prepared in sc-CO_2 by using nylon 46 salt formed from 1,4-diaminobutane

*Corresponding author. E-mail: tzhangzy@163.com.

 Published on Web 01/20/2011

and 1,6-adipic acid as a monomer by one-step three-stage polymerization method. The nylon 46 sample prepared is white and the highest molecular weight measured by viscometry is near 50 000 g/mol. The chemical structure and thermal properties of the samples were characterized by means of FT-IR, DSC, and TGA. The polymerization process, some effect factors on the molecular weight such as pH of the salts, reaction temperatures, and time are discussed.

2. Experimental Section

2.1. Materials. 1,4-Diaminobutane (99%) and formic acid (95%) were purchased from J&K Chemical Ltd. and used without further purification. 1,6-Adipic acid was kindly supplied by Shenma Industrial Co., Ltd., China, and purified by recrystallization. CO_2 (99.99%) was obtained from Guangdan Gas Co. Ltd., China.

2.2. Preparation of Nylon 46 Salt. Nylon 46 salts were prepared by mixing the ethanol solution of 1,4-diaminobutone with the ethanol solution of 1,6-adipic acid according to different molar ratios to obtain a white precipitate. The precipitate was filtrated and then dried in a vacuum oven. The pH values of nylon 46 salts in aqueous solution with a concentration of 1 wt % were determined by using a pH meter.[3]

2.3. Synthesis of Nylon 46. Nylon 46 samples were synthesized by using certain quantity of nylon 46 salts as a monomer in sc-CO_2. A stainless steel reactor of 50 mL was used and fixed with a manometer and a temperature regulating device but without stirrer. The polymerization process is called one-step method but divided into three stages according to the difference in reaction temperatures. The precondensation of nylon 46 salts were carried out at a temperature of about 190 °C for 2 h at sc-CO_2 pressure of 30 MPa. Then CO_2 gas in the reactor was exhausted and liquid CO_2 refilled. The temperature was elevated to about 280 °C, and the postcondensation was carried out for 1−5 h at 15 MPa. Finally, the system was evacuated at 270−280 °C for 0.5−1 h. The nylon 46 samples were obtained.

2.4. Characterizations. *2.4.1. Viscosity-Average Molecular Weight.* The relative viscosity of the nylon 46 samples in a solution of 0.6 g of polymer in 100 mL of 90% formic acid was measured at 25 °C by using an Ubbelohde viscometer. The intrinsic viscosity and the viscosity-average molecular weight of the nylon 46 samples were calculated from eqs 1 and 2, respectively. The latter is the Mark−Houwink equation for nylon 46, of which the corresponding values of K and α are 0.0464 cm^3/g and 0.76, respectively.[23]

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{c} \quad (1)$$

$$[\eta] = KM^{\alpha} \quad (2)$$

2.4.2. Measurements by DSC, TGA, and FT-IR. DSC measurements for nylon 46 salt and nylon 46 samples were carried out by using a Netzsch SQL600 DSC instrument at a heating rate of 10 °C/min and under a N_2 atmosphere. The weights of all samples were about 8 mg. The peak temperatures on the DSC curves were taken as the melting points of the samples. The relative crystallinity of the samples (X_c) was calculated from eq 3:

$$X_c = \Delta H_f / \Delta H_f^{\circ} \quad (3)$$

where ΔH_f and ΔH_f° are the fusion enthalpy for the sample detected by DSC and the fusion enthalpy for the complete crystal of nylon 46, respectively; $\Delta H_f^{\circ} = 270$ J/g.[24]

TGA measurement of the nylon 46 sample was carried out by using a Netzsch SQL600 TGA instrument at a heating rate of 20 °C/min and under a N_2 atmosphere.

FT-IR spectrals of the nylon 46 samples were measured by using a Bruker EQUINX 55 spectrometer. The KBr tabletting specimens were prepared by using KBr and the nylon 46 powder which were precipitated from a solution of the nylon 46 sample in formic acid by adding ethanol as a precipitator.

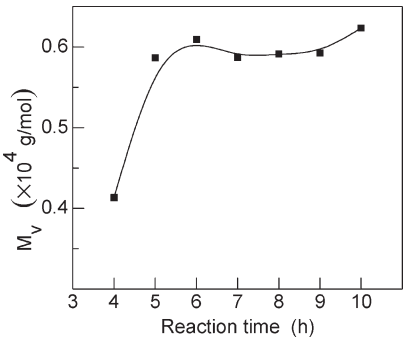

Figure 1. Influence of polymerization time on the molecular weight of the samples prepared by a one-step method.

3. Results and Discussion

3.1. Polymerization Method and Process. Melt condensation polymerization is inapplicable to nylon 46 due to its high melting point of over 300 °C. To obtain nylon 46 with high molecular weight, the polymerization method and process in sc-CO_2 were investigated. After the nylon 46 salt prepared from equimolar diamine and diacid was continuously heated to a temperature of 280 °C in sc-CO_2, below melting point of nylon 46, polymerization process was further carried out at this temperature for 5−8 h. The nylon 46 sample obtained has the viscosity-average molecular weights of around 6000 g/mol. This polymerization process is attributed to one-step method because of no opening of the reactor. Since the by-product water could not be removed from the closed reaction system of sc-CO_2, the molecular weight of the sample could not be increased. Figure 1 shows that the polymerization time ranged from 5 to 10 h, but the molecular weights of the samples were still around 6000 g/mol. To increase the molecular weight of the product, we improved the condensation process and divided it into three stages: precondensation, postcondensation, and vacuum according to different reaction temperature and time. The precondensation was carried out at a temperature of 190 °C near the melting point of nylon 46 salt for 2−3 h, which could be melted at this temperature under action of sc-CO_2. The process commenced as a melt condensation and then became a SSP along with converting the salt to a prepolymer, of which the melt temperature increased gradually from 200 to 290 °C. To remove water formed in the precondensation, CO_2 gas in the reactor was exhausted and liquid CO_2 refilled in the end of the process. The postcondensation process was the second stage, and the SSP of the prepolymer was carried out in sc-CO_2 for 3−5 h at a temperature of 280 °C below the melting point of nylon 46. Finally, the vacuum was the third stage. The system was evacuated for 0.5−1 h to increase further the molecular weight of the samples by removing water and shifting the reaction equilibrium to the right. The molecular weight of the sample obtained by this improved method was increased to about 14 000 g/mol, but a further increase was baffled.

It is worth notice that 1,4-diaminobutane is unstable at a high temperature. It could cyclize to pyrrolidine,[4] volatilize to sc-CO_2 phase, and escape along with water in exhaust to impair the quality of the reactant and product, i.e., decrease the amount of amino groups. Therefore, the amine end groups should be in excess in order to compensate for the loss and to maintain near stoichiometric equivalence during the polymerization. Several nylon salts with different excess of the diamine were prepared to synthesize high molecular weight nylon 46.

3.2. pH of the Nylon 46 Salt. In order to investigate the influence of the excess of 1,4-diaminobutane in the salt on the molecular weight of the nylon 46 samples, a series of salts were prepared and their pH values of 1 wt % solution in water were determined, as listed in Table 1. It is clear that the pH values of the salts increase along with the excess molar accounts of 1,4-diaminobutane added in preparing nylon 46 salt, especially in the range from 0 to 4 mol %, and then is near constant. It shows that the excess of the diamine presented in the salts is not directly proportional to its molar amount added and the excessive part should be left in the ethanol solution.

The nylon 46 samples were prepared in sc-CO_2 by using the above salts with different pH by one-step three-stage method under the same conditions as the sample II (see Table 2), and their molecular weights are shown in Figure 2. It can be seen that the viscosity-average molecular weights of the samples are obviously increased, for example, from 14 600 to 36 200 g/mol, as the pH of the salts ranges from 7.01 to 7.23. While the pH value is larger than 7.23, this molecular weight increase trend is slow. The highest molecular weight, 39 600 g/mol, was obtained by using the salt with the pH of 7.26. This indicates that an appropriate excess of the amino end groups in the salts plays an important role in enhancing the molecular weight of nylon 46 samples.

3.3. Effect of Reaction Conditions. The reaction condition mainly involves the pressure of sc-CO_2, reaction temperature, and resident time of each stage in condensation. Generally, the higher the pressure of sc-CO_2 is, the stronger the swelling and plasticing abilities of the polymer are. Since the highest compression resistance of the reactor used is 30 MPa, thus all precondensation processes were carried out under this pressure. After the precondensation, CO_2 was expelled from the reactor, and the reactor was refilled with liquid CO_2 at the temperature of 190 °C. The pressure in the reactor produced by injecting CO_2 was not high enough and could only achieve about 15 MPa as the temperature in the system was elevated from 190 to 280 °C. Thus, the postcondensation pressures were controlled to 15 MPa for all processes.

The molecular weights of the nylon 46 samples obtained by polymerization under various conditions are presented in Table 2. It can be found that there is a distinct difference in molecular weights for the samples I−IV due to different temperatures of the precondensations. For example, the sample II has the highest molecular weight of 39 600 g/mol, while the sample I shows the lowest molecular weight of 12 700 g/mol. If the postcondensations were not carried out, the prepolymer of sample I is a wax solid and obvious different from a hard solid of the sample II despite its precondensation temperature is only 10 °C lower. This indicates that the precondensation temperature can not only affect its prepolymer molecular weight but also results in distinct difference in the molecular weight of the final product.

The molecular weights of the samples III and IV decrease with every 10 °C increment of the precondensation temperature and are 34 600 and 26 800 g/mol, respectively. In the case of the latter, the molecular weight decreased significantly, possibly due to the fact that the reaction temperature is near or over the melting point and the decomposition temperature of the diamine monomer. DSC and TGA curves of the nylon 46 salt are shown in Figures 3 and 4, respectively. The melting point of the salts is 201 °C, and it has been decomposed below 200 °C. There are two peaks in DTG curve, which are the maximum decomposition rates of 1,4-diaminobutane and 1,6-adipic acid, respectively. Although sc-CO_2 fluid has certain protection action for the monomer and may decrease its melting point temperature in a way, the precondensation temperature should not be near or over the decomposition temperature of the salt. In fact, the salt has been melted at 190 °C under the action of the sc-CO_2 system pressure due to the fact that the prepolymer was found to be a melting bulk. Therefore, the precondensation temperature for the salt monomer must be high enough to facilitate chain growth but could not be so high that it leads to decomposition and cyclization side reactions. This result revealed that the preferred prepolymerization temperature should be below 200 °C,

Table 1. pH of the Salts by Adding Different Excess Moles of 1,4-Diaminobutane

	added excess moles of 1,4-diaminobutane (%)								
	0	1	2	3	4	5	6	7	8
pH of nylon 46 salt	7.01	7.06	7.12	7.16	7.23	7.24	7.25	7.26	7.26

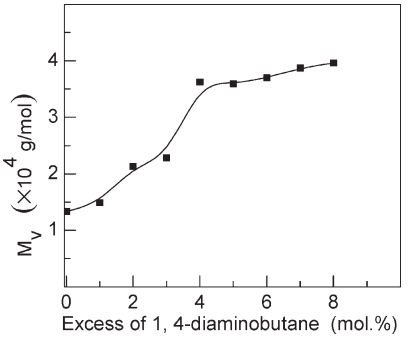

Figure 2. Correlation between the molecular weight of the samples and excess molar amount of 1,4-diaminobutane added in preparing nylon 46 salt.

Table 2. Reaction Conditions and Molecular Weights of the Nylon 46 Samples

	precondensation			postcondensation					
sample	temp (°C)	time (h)	pressure (MPa)	temp (°C)	time (h)	pressure (MPa)	time in vacuum (min)	$\overline{M}_v \times 10^4$	color
I	180	2	30	280	3	15	30	1.27	white
II	190	2	30	280	3	15	30	3.96	white
III	200	2	30	280	3	15	30	3.46	white
IV	210	2	30	280	3	15	30	2.68	white
V	190	2	30	270	3	15	30	2.96	white
VI	190	2	30	290	3	15	30	2.50	white
VII	190	2	30	280	1	15	30	2.96	white
VIII	190	2	30	280	2	15	30	3.57	white
IX	190	2	30	280	4	15	30	3.15	white
X	190	2	30	280	5	15	30	2.32	white
XI	190	2	30	280	3	15	0	2.59	white
XII	190	2	30	280	3	15	40	4.30	white
XIII	190	2	30	280	3	15	45	4.82	white
XIV	190	2	30	280	3	15	60	4.17	white

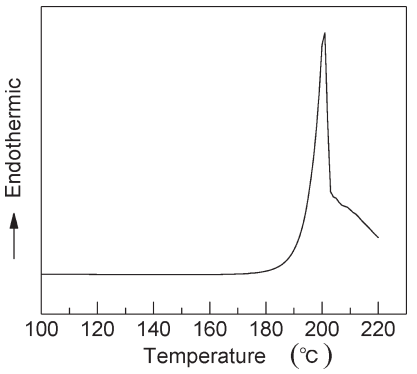

Figure 3. DSC curve of the nylon 46 salt.

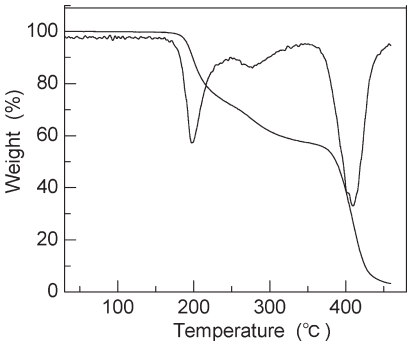

Figure 4. TGA and DTG curves of the nylon 46 salt.

preferably 190 °C. In a word, the precondensation temperature is probably one of the most important factors for the polymerization process and plays a significant role in determining the molecular weight of the nylon 46.

The samples V and VI show the effect of the postcondensation temperature on the product molecular weight. Compared with the sample II, the molecular weights of both samples decrease and are 29 600 and 25 000 g/mol, respectively.

The samples II and VII−X show the effects of different reaction times in the postcondensations on the molecular weights under the same reaction conditions. It shows that the sample II carried out the postcondensation for 3 h has the highest molecular weight of 39 600 g/mol. Either to shorten or to extend the resident time in the postcondensation will decrease the molecular weights of the products.

3.4. Effect of the Vacuum. For most of the samples I−IX in Table 2, the time of the vacuum is 0.5 h in the end of the postcondensation. The vacuum process is also an importance factor to enhance the molecular weights of the nylon 46 samples. Without the vacuum process in whole polycondensation, the sample X has only the molecular weight of 25 900 g/mol. The samples II and XI−XIII exhibit the effect of the vacuum time on increasing the molecular weight. When other polymerization conditions were the same as sample II, with the vacuum time extending from 30 to 45 min, the molecular weights of the samples are increased from 39 600 to 48 200 g/mol, respectively. The latter is the highest molecular weight of the sample obtained from our experiments. However, the molecular weights of the sample XIII decreased to some degree when the vacuum time was extended to 60 min. It could be relate to the crystallinity of the product and the lengthening in duration at higher temperatures of about 280 °C.

Generally, the crystallinity of a polymer product increases with the polymerization process, in which the molecular weight rises gradually and the molecular weight distribution becomes more uniform. But high crystallinity can also

Table 3. Molecular Weight or Intrinsic Viscosity (η_{inh}) of Nylon 46 Obtained under Different Reaction Conditions by One-Step or Two-Step Polymerization Methods

polymerization methods	starting material	reaction conditions	measurement conditions	η_{inh} or MW
one-step polymerization	nylon 46 salt	heated to 280 °C, 5−8 h, sc-CO_2 (30 MPa)	0.6% solution in 90% formic acid at 25 °C	6000
one-step three-stage polymerization	nylon 46 salt	190 °C, 2 h, sc-CO_2(30 MPa); 280 °C, 3 h, sc-CO_2 (15 MPa) 280 °C,45 min, in vacuum	0.6% solution in 90% formic acid at 25 °C	2.37 (48 200)
two-step melt polymerization	nylon 46 salt	220 °C, 1−2 h, N_2; >283 °C, 1−2 h, in vacuum	0.5% solution in *m*-cresol at 30 °C	0.84 [3]
two-step solid-state polymerization	nylon 46 salt	215 °C, 2 h, N_2 (4 MPa); 290 °C, 1 h, in vacuum	0.5% solution in 98% formic acid at 30 °C	2.09 [4]
	nylon 46 salt in water (90%)	155−200 °C, 160 min; 260 °C, 6 h, N_2/H_2O	1% solution in 96% sulfuric at 20°%	4.90 (34 700) [11]
	nylon 46 salt in *N*-methylpyrrolidone (40%)	heated to 300 °C in 15 min, N_2; 260 °C, 3.5 h, N_2/H_2O	1% solution in 96% sulfuric at 20°%	4.13 [15]
	nylon-66 salt[a]	220 °C, 2 h, CO_2(3000 psi); 270 °C, 3 h, CO_2 (3000 psi)		24 500 [21]

[a] As a control.

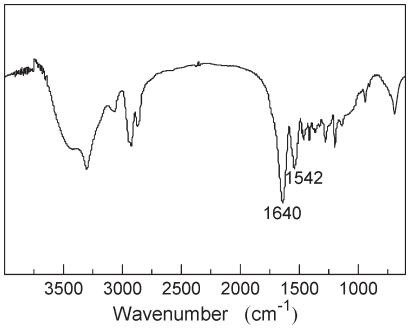

Figure 5. FT-IR spectrum of the nylon 46 sample.

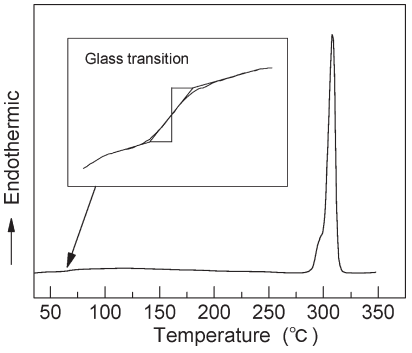

Figure 6. DSC curve of the nylon 46 sample.

synchronously decrease the amorphous area, the concentration, and mobility of the polymer chain end groups in this area as well as the diffusion rate of the condensate. These factors are unfavorable for enhancing molecular weight. In addition, the vacuum was carried out at 280 °C and a longer duration at this higher temperature could give rise to degradation of the polymers. Korshak[25] affirmed that the highest polymer molecules are easier to degrade. In fact, there are two competitive reactions: a step-growth reaction and a degradation reaction. When the latter predominates, the molecular weight of the product could be decreased.

Finally, we summarized the synthesis methods and reaction conditions of nylon 46 from our work and the ones reported in the literature, as shown in Table 3. It indicates that synthesizing nylon 46 with high molecular weight in sc-CO_2 is predominant.

3.5. Characterizations of the Nylon 46. *3.5.1. FT-IR Analysis.* FT-IR spectra of the nylon 46 sample are shown in Figure 5. It can be found that there are two strong absorptions at 1640 and 1542 cm^{-1} on the curve. The first absorption peak is for an amide I band (stretching of C═O), and the other one is for amide II band (twisting of N−H and stretching of C−N). The two characteristic absorptions prove that nylon 46 salt has been successfully reacted to nylon 46. The other important absorption bands listed as follows: 3302 (N−H stretching), 2924 and 2872 (C−H bonding), 1280 (amide III), 941 (amide IV), and 692 (amide V).

3.5.2. Thermal Properties. The melting points of the nylon 46 samples were determined by DSC. As an example, DSC curve of the sample II is shown in Figure 6. There is only a strong single endothermic peak on the curve in the range of determining temperatures. The peak temperature, as the melting point of the sample, is at 310 °C, and the melting range is from 295 °C to near 320 °C. High melting point of the nylon 46 sample results from its symmetrical structure and synthesis environment in sc-CO_2. The melting enthalpy of the sample determined from Figure 6 is 172.4 J/g, and its

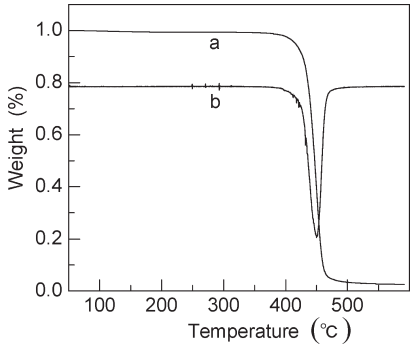

Figure 7. Curves of TGA and DTG of the nylon 46 sample.

relative crystallinity calculated from eq 3 is 63.9%. The glass transition temperature is 67 °C, and the change of heat capacity is 0.152 J/(g K).

Figure 7 shows the TGA and DTG curves for the sample II. It shows that the sample starts to decompose at about 400 °C, and the maximum decomposition rate is at about 450 °C. The results reveal that the nylon 46 exhibited a higher melting temperature and quite good thermal stability. Thus, these excellent heat-resistance properties allow nylon 46 to be used as a high-performance engineering plastic in some application areas.

4. Conclusions

High molecular weight nylon 46 has been successfully prepared by SSP in sc-CO_2. This polymerization process is called one-step three-stage method which can operate continuously, and the overall polymerization time is about 5−6 h. The highest molecular weight of the sample obtained is 48 200 g/mol. The precondition to achieve high molecular weight nylon 46 is to use the nylon 46 salt with excess amine groups, which has a pH of over 7.23. The polymerization temperatures for the precondensation and the postcondensation are the most important factor based on a consideration for increasing molecular weight. During the polymerization process the preferable reaction conditions are at 190 °C for 2 h for the precondensation, at 280 °C for 3 h for the postcondensation, and at 280−270 °C for 30−45 min for the vacuum. The pressures of sc-CO_2 adopted in the system are the highest ones the reactor can achieve. The chemical structure and thermal properties of the nylon 46 samples have been characterized.

Acknowledgment. We thank the National Natural Science Foundation of China (50873046) and Guangdong Province Science Foundation of China (8151063201000055) for financial support of this work.

References and Notes

(1) Carothers, W. H. U.S. Patent 2,130,948, 1938.
(2) Coffman, D. D.; Berchet, G. J.; Peterson, W. R.; Spanagel, E. W. *J. Polym. Sci.* **1947**, *2* (3), 306–313.
(3) Beaman, R. G.; Cramer, F. B. *J. Polym. Sci.* **1956**, *XXI*, 223–235.
(4) Gaymans, R. J.; Vanutteren, T. E. C.; Vandenberg, J. W. A. *J. Polym. Sci.* **1977**, *15*, 537–545.
(5) Ke, B.; Sisko, A. W. *J. Polym. Sci.* **1961**, *50*, 87–98.
(6) Chang, T. *Polym. Eng. Sci.* **1970**, *10* (6), 364–368.
(7) Ravindranath, K.; Mashelkar, R. *J. Appl. Polym. Sci.* **1990**, *39*, 1325–1345.
(8) Shi, C.; DeSimone, J.; Kiserow, D.; Roberts, G. *Macromolecules* **2001**, *34*, 7744–7750.
(9) Weger, F.; Hagen, R. U.S. Patent 5,773,555, 1998.
(10) Fakirov, S.; Avramova, N. *Acta Polym.* **1982**, *33*, 271–275.
(11) Gaymans, R. J.; Edmond, H. J. P. U.S. Patent 4,480,036, 1983.
(12) Gaymans, R. J.; Bour, E. H. J. P. U.S. Patent 4,460,762, 1984.

(13) Gaymans, R. J.; Bongers, A. J. P. U.S. Patent 4,716,214, 1987.
(14) Bongers, A. J.; Roerdink, E. U.S. Patent 4,814,356, 1989.
(15) Warnier, J. M. M.; Knape, P. M. U.S. Patent 5,371,174, 1994.
(16) Mallon, F.; Beers, K.; Ives, A.; Ray, W. *J. Appl. Polym. Sci.* **1998**, *69*, 1789–1791.
(17) Gross, S.; Flowers, D.; Robers, G.; Kiserow, D.; DeSimone, J. M. *Macromolecules* **1999**, *32*, 3167–3169.
(18) Shi, C.; Gross, S.; DeSimone, J. M.; Kiserow, D.; Robers, G. *Macromolecules* **2001**, *34*, 2062–2064.
(19) Desimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945–947.
(20) Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999**, *99*, 543–563.
(21) Bruke, A. L. C.; Givens, R. D.; Likei, M.; DeSimone, J. M. *Polym. Prepr.* **1997**, *38*, 387–388.
(22) Givens, R. D.; Likei, M.; DeSimone, J. M. *Polym. Prepr.* **1997**, *38*, 468–469.
(23) Srinivasan, R.; Almonacil, C.; Desal, P.; Narayan, S.; Abhiraman, A. S. *Macromolecules* **1998**, *31*, 6813–6821.
(24) Schmack, G.; Schreiber, R.; Veeman, W. S. *J. Appl. Polym. Sci.* **1997**, *66*, 377–385.
(25) Korshak, V.; Frunze, T. *Synthetic Hetero-Chain Polyamides*; Israel Program for Scientific Translations: Jerusalem, 1964; pp 87, 442.