# Preparation, Characterization, and Copolymerization of the 12-Membered Cyclic Diamide 1,6-Diazacyclododecane-2,5-dione

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**ABSTRACT:** A 12-membered cyclic diamide monomer for nylon 64 was successfully synthesized in fairly high yield (~45%). The synthesis conditions were varied to see the effect of the diamine and succinyl chloride reactants on yield. Threefold excess of 1,6-hexamethylenediamine (HDA) gave the highest yield, while further increasing the amount of HDA decreased the yield. Using *N*,*N*-diisopropylethylamine as acid scavenger resulted in the formation of two different cyclic amides, which were fully analyzed by <sup>1</sup>H and <sup>13</sup>C solution nuclear magnetic resonance spectrometry and mass spectrometry. Copolymerization of cyclic amides with  $\varepsilon$ -

**INTRODUCTION** Cyclic amides are continuing research topics of polymer science for two main reasons. They are either used as monomers for ring-opening polymerization, or they are generated by normal step-growth polymerization and ring-opening polymerization processes as minor components.<sup>1</sup> Cyclic diamides can be obtained in several ways including by direct cyclization of dicarboxylic acid derivatives with a diamine,<sup>2–4</sup> depolymerization of polyamides,<sup>5</sup> and rearrangement of another cyclic species.<sup>6</sup> One of the complications of homopolymerization of cyclic diamides are that they usually have high melting points, especially those with small rings; the actual melting points may be very close to molecular degradation temperatures.<sup>7</sup>

Polyamide 6, or nylon 6, is generally prepared by ringopening polymerization of  $\varepsilon$ -caprolactam (CLA). CLA is most widely polymerized via hydrolytic<sup>8</sup> or anionic<sup>9,10</sup> polymerization methods. Although it is not commercially used, cationic ring-opening homo- and copolymerization is also of research interest.<sup>11</sup> Polyamide 6 is a semicrystalline thermoplastic material with a relatively high melting point. Due to its good mechanical strength, impact resistance, rigidity, and low density, it is widely used as an engineering material. Although polyamide 6 shows outstanding thermal and mechanical properties, copolymerization of CLA with various monomers are of industrial and academic interest, caprolactam via an anionic route gave a block copolyamide with a two distinct endotherms in the differential scanning calorimetry analysis. However, copolymerization by the hydrolytic route gave only nylon 6 with terminal 64 units. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 96–103

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because this allows tailoring of properties for specific applications.  $^{\rm 12-15}$ 

Nylon 64 is of interest because of its higher melting point when compared with commercial nylon 66. Unlike nylon 46, which has been commercialized by DSM under the trade name Stanyl<sup>®</sup>,<sup>16</sup> nylon 64 has not yet been commercialized, possibly due to the side reactions which inhibit obtaining high molecular weight polymer via polycondensation reaction. Therefore, an alternate route to high molecular nylon 64 is still needed. Ring-opening polymerization of the 12-membered cyclic monomer of nylon 64 may offer an alternative way to obtain a high molecular weight homo- or copolymers of nylon 64.

Herein, we report the synthesis and characterization of the 12-membered cyclic diamide, 1,6-diazacyclododecane-2,5dione. The effects of the reactants on yield and products were studied. Ring-opening reactivity of this cyclic diamide was also explored. For this purpose, copolymerization of the 12-membered cyclic diamide with CLA was investigated with different polymerization methods and conditions.

### **EXPERIMENTAL**

### Materials

All reagents were used as received. Succinyl chloride, *N*,*N*-diisopropylethylamine (DPEA), 4-dimethylaminopyridine

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**SCHEME 1** Synthesis of 1,6-diazacyclododecane-2,5-dione.

(DMAP), succinic anhydride, *N*-acetylcaprolactam, 2,2,2-tri-fluoroethanol (TFE), and chloroform d were purchased from Aldrich Chemical Company. 1,6-Hexamethylenediamine (HDA) and chloroform were purchased from Fluka. CLA was purchased from ACROS and recrystallized from acetone; the crystals were dried at 70  $^\circ$ C under reduced pressure overnight before use.

# Instrumentation and Techniques

Routine solution <sup>13</sup>C nuclear magnetic resonance spectrometry (NMR) was performed on Varian *Mercury*<sup>*PLUS*</sup> 200 and 500 MHz spectrometers. Transmission infrared measurements were carried out on a Mattson Galaxy Series FTIR 5000 using KBr pellets and 256 transients. Differential scanning calorimetry (DSC) experiments were performed on a TA Instruments 2920. The temperature was ramped at a heating rate of 10 °C/min under nitrogen.

Wide angle X-ray diffraction (WAXD) measurements were obtained with a Rigaku Ultima III diffractometer operated at 40 kV and 44 mA. Powder samples were run with a scan speed of  $2^{\circ}$  per minute from  $2^{\circ}$  to  $45^{\circ}$ .

The molecular weight of cyclic diamide and cyclic tetramide (structures below) were determined by a ThermoFisher LXQ Ion-Trap instrument running in positive mode. The samples were prepared by placing  ${\sim}10$  mg of cyclic diamide or cyclic tetramide in an Eppendorf tube, then adding 1 mL of 1:1 THF:MeOH with NaCl. The sample was vortexed for 1 min to ensure a homogenous solution. 100 µL of this sample was then diluted to 1 mL with 900  $\mu L$  of the 1:1 THF:MeOH NaCl solution (the NaCl concentration in the THF:MeOH is approximately 1  $\mu$ M). The diluted sample was then infused into the spectrometer at a rate of 10  $\mu$ L/min until a stable spectrum was observed. The spectrum was then collected and optimized on the sodium adduct of cyclic diamide or cyclic tetramide using the autotune function in the XCalibur software, which controls the instrument. The final spectra are the average of several such collected spectra.

### Synthesis of 1,6-Diazacyclododecane-2,5-dione

The procedures for synthesis of the cyclic monomers are given for sample 4. All other samples were synthesized using the same procedure except the ratio of reactants or the amounts of solvent were varied. HDA (16.9 mmol), DPEA (33.9 mmol), and 4-dimethylaminopyridine (DMAP) (1.6 mmol) were dissolved in 50 mL chloroform and charged to a syringe. A second syringe was charged with succinyl chloride (16.9 mmol) in 50 mL chloroform. These two syringes were placed in a syringe pump and their contents added very slowly (addition rate 0.5 mL/min) to 500 mL of chloroform

in a three-necked round-bottomed flask under nitrogen. After the reaction was complete, the precipitant was removed by filtration. Solvent was removed from the filtrate under reduced pressure at 50 °C and the remaining solid was washed with acetone several times. The final product was obtained as white powder. It was recrystallized from acetonitrile. The melting point of the 12-membered cyclic diamide was obtained as 290 °C using DSC.

## Synthesis of HAD-bisimide

HDA (34 mmol) and succinic anhydride (72 mmol) were dissolved in 20 mL of deionized water. The mixture was refluxed for 2 h and then vacuum was applied to remove water while the temperature was increased to 150 °C. The reaction was carried out for another 2 h. After completion, the crude product was allowed to cool down to room temperature and washed with water several times. After filtration, the crude product was recrystallized from water twice, which gave the final product as white crystals in 70% yield. <sup>13</sup>C NMR (200 MHz, TFE:CDCl<sub>3</sub>): 179.1, 38.2, 27.5, 26.6, 25.7 ppm.

### Synthesis of HAD-bisamide Acid

HDA (34 mmol) and succinic anhydride (136 mmol) were dissolved in 100 mL of deionized water. The mixture was stirred at room temperature for 6 h. After the reaction was complete, the precipitant was removed by filtration, and washed with hot water several times. After washing with acetone one more time, the final product was allowed to dry in a vacuum oven overnight. The product was obtained as white powder in 50% yield. <sup>13</sup>C NMR (200 MHz, TFE:CDCl<sub>3</sub>): 176.8, 174.4, 39.8, 30.3, 29.5, 28.6, 26.1 ppm.

# Synthesis of Copolymer Nylon (6-*co*-64) via the Anionic Polymerization Method

CLA (2 g) and 10 w % cyclic diamide (0.2 g) were charged to a test tube. Another test tube was charged with CLA (0.3 g) and dry sodium hydride (0.02 g). Nitrogen was bubbled through both test tubes for 15 min before heating. Both test tubes were placed in a previously heated oil bath at 140 °C. After melting, 0.3 mL of N-acetylcaprolactam was added to the CLA/cyclic diamide mixture by a syringe and the mixture was allowed to stir for another 10 min. The caprolactam/ sodium hydride mixture was then added to this mixture, and the polymerization was carried out at 145 °C until the mixture solidified after 15 min. The product was allowed to cool down to room temperature under nitrogen, and was then powdered and washed with refluxing ethanol overnight to remove unreacted monomers. After washing with ethanol one more time, the final product was dried in a vacuum oven for 12 h at 100 °C (yield  $\sim$ 34%).



Sample #	HDA	Succinyl Chloride	Chloroform (mL)	DPEA	DMAP	Yield (%)
1	<b>3</b> ×	Х	500	-	-	45
2	5×	×	500	-	-	26
3	×	×	500	<b>2</b> ×	-	42
4	×	×	500	<b>2</b> ×	0.1×	12
5	<b>3</b> ×	×	1000	-	-	40
6	×	X	1000	<b>2</b> ×	-	32

TABLE 1 Synthesis of 1,6-Diazacyclododecane-2,5-dione

# Attempted Synthesis of Copolymer Nylon (6-co-64) via Hydrolytic Polymerization Method

CLA (2 g), 10 w % cyclic diamide (0.2 g), 10 mol % aminocaproic acid, and 1 mL deionized water were charged to a test tube. Nitrogen was bubbled through the mixture for 15 min before heating. The temperature was then maintained at 250 °C for 4 h in a sand bath. The product was allowed to cool down to room temperature under nitrogen, and was then powdered and washed with refluxing ethanol overnight to remove unreacted CLA and cyclic diamide. After washing with ethanol one more time, the final product was dried in a vacuum oven for 12 h at 100 °C.

## **RESULTS AND DISCUSSION**

The overall synthetic procedure for the 12-membered cyclic diamide is given in Scheme 1. The synthesis of cyclic diamides of diamines and diacid chlorides is usually carried out with high-dilution methods or slow addition of reactants into a solvent to decrease the possibility of linear oligomer or polymer formation.<sup>3</sup>

It was of interest here to explore the effects of reactants, ratio of reactants, and amount of solvent used for synthesis of the 12-membered cyclic diamide on yield. For this purpose, the amount of succinyl chloride was kept almost constant ( $\sim X = 17$  mmol) and the amounts of the other

 $\begin{array}{c} O & a & O \\ HN & P & NH \\ b & c & d \\ \\ e & b & a \\ c & d \\ \\ e & b & b \\ \\ e & b & a \\ c & d \\ \\ e & b & b \\ \\ e$ 

**FIGURE 1** <sup>13</sup>C solution NMR spectrum of 1,6-diazacyclododecane-2,5-dione. The sample was dissolved in TFE:CDCl<sub>3</sub>. reactants were changed with respect to the succinyl chloride. The data are given in Table 1. The best yield was obtained for the samples numbered 1 and 3. The catalyst, DMAP, somehow inhibited the cyclization. Threefold-excess of HDA gave the best yield. Increasing HDA concentration even further decreased the yield of the cyclic diamide, possibly due to increasing probability that one succinyl chloride could react with two HDA leading to a linear monomer.

The 12-membered ring cyclic diamide obtained as a white powder was not soluble in chloroform, and a TFE: $CDCl_3$  mixture was used for NMR analysis. The <sup>13</sup>C solution NMR spectrum of 1,6-diazacyclododecane-2,5-dione in TFE: $CDCl_3$  is shown in Figure 1. The carbonyl carbon peak of the cyclic amide appears at 173.3 ppm. This peak and the peak assigned as "a" are strong indicators of the absence of linear compounds in the final product.

The <sup>1</sup>H solution NMR spectrum of 1,6-diazacyclododecane-2,5-dione is shown in Figure 2. All peaks are assigned based on the molecular structure expected for the cyclic diamide. The amide NH can be seen around 6.6 ppm and there is a small shoulder on this peak at 6.9 ppm. The protons  $\alpha$  to the amide NH can be observed at 3.3 ppm, and this peak also has a small shoulder around 3.2 ppm. The shoulder may be related to higher order macrocycle formation, which cannot be observed easily with <sup>13</sup>C solution NMR. No free acid or amine end-groups were observed, confirming macrocycle formation.



FIGURE 2  $^{1}$ H solution NMR of 1,6-diazacyclododecane-2,5-dione. The sample was dissolved in TFE:CDCl<sub>3</sub>.



FIGURE 3 FTIR spectrum 1,6-diazacyclododecane-2,5-dione.

The infrared spectra for the 12-membered cyclic diamide displayed the characteristic peaks of amide groups and methylene groups, as shown in Figure 3. Peaks were found at 3313 cm<sup>-1</sup> (N—H stretching), 3095 cm<sup>-1</sup> (overtone of N—H in-plane bending), 2834–3000 cm<sup>-1</sup> (C—H stretching), 1644 cm<sup>-1</sup> (C=O stretch), and 1538 cm<sup>-1</sup> (C—N stretch and CO—N—H bend).<sup>17</sup>

For the reaction of HDA with succinyl chloride, only one kind of cyclic product was obtained (samples 1, 2, 5 in Table 1). The second product, which gives a peak around 6.9 ppm in the  $^{1}$ H NMR spectrum, was speculated as being due to

higher order cyclic formation. However, the same reaction with DPEA gives a 50/50 mixture of cyclic diamide and cyclic tetramide. Cyclic diamide is the same 12-membered cyclic compound obtained without DPEA. Cyclic tetramide, on the other hand, can be obtained nearly pure as a white powder with a melting point of 250 °C after recrystallization of the 50/50 mixture from acetonitrile. Using mass spectrometry, the molecular weight of cyclic diamide and cyclic tetramide were determined to be 198.18 and 396.41 g/mol, respectively, corresponding to mono- and biscyclic amides. Triethylamine, which is commonly used in synthesis to obtain cyclic diamides<sup>18</sup> instead of DPEA, gives negligible yield of cyclic product with the monomers used here. This may be due to higher reactivity of succinyl chloride when compared with other aliphatic diacid chlorides evaluated previously.<sup>3</sup>

Figure 4 shows the <sup>13</sup>C solution NMR spectra of the macrocycle mixture and of cyclic tetramide in TFE:CDCl<sub>3</sub> solvent mixture. All peaks are assigned based on the expected structures of the cyclic monomers from molecular weight determination by mass spectrometry. It can be seen that there are two set of peaks with the same number of peaks of roughly equal intensities. However, the peak intensities of the carbonyl carbons are not the same, perhaps due to different relaxation times for these carbons. The peaks associated with cyclic diamide appear exactly at the same chemical shifts as for the cyclic monomer obtained without DPEA and are assigned with the same letters. The carbonyl carbon peak of cyclic tetramide appears at 173.5 ppm. When compared to the cyclic diamide, peaks related to cyclic tetramide are shifted significantly. The peak  $\alpha$  to the amide groups of cyclic diamide assigned as "b" (observed at 36.7 ppm) shifts to 38.4 ppm for the cyclic tetramide. An upfield shift is observed for the methylene group  $\alpha$  to the carbonyl which moves from 34.5 to 31.4 ppm. The significant difference in



FIGURE 4 <sup>13</sup>C solution NMR of the 50/50 mixture (top) and cyclic tetramide (bottom). Each sample was dissolved in TFE:CDCl<sub>3</sub>.



**FIGURE 5** <sup>1</sup>H solution NMR of a 50/50 mixture (top) and purified tetramide (bottom). The sample was dissolved in  $TFE:CDCI_3$ .

chemical shifts for these two cyclic amides is consistent with different ring strains and/or conformational mobility for these two monomers.

The solution <sup>1</sup>H NMR spectra of the mixture and of cyclic tetramide are shown in Figure 5. Two sets of peaks with the same number and roughly equal intensities are also observed in the <sup>1</sup>H NMR spectra. All peaks are assigned based on the molecular structure of cyclic amides. The peaks associated with the protons  $\alpha$  to the amide NH, which are hardly observed in Figure 2, are of equal intensities. Splitting of the peaks associated the same protons of cyclic diamide is seen at 3.3 ppm. The amide NH, which can be observed around 6.6 ppm for cyclic diamide, shifts downfield to 6.9 ppm for cyclic tetramide. Similar downfield shifts were observed for various ring size cyclic oligo(undecanamide)s.<sup>1</sup> However, the shifts are not as pronounced for cyclic oligo(undecanamide)s of different sizes. This may be due to the fact that the ring strain is more crucial for the cyclic amides in this study. The exchangeable hydrogen peak at 4.39 ppm

for TFE broaden and shifted in the bottom spectra probably due to a trace amount of water.

FTIR spectra of the 50/50 mixture and purified cyclic tetramide are shown in Figure 6. As expected, the two spectra are almost identical with only minor differences when compared with cyclic diamide. Most changes are observed for the stretching vibration of NH groups, as seen by comparing the FTIR spectrum of cyclic diamide (Fig. 3) with the spectrum of cyclic tetramide. For diamide, this band is narrower and shows only one peak at 3313  $\mbox{cm}^{-1}$  with a small shoulder, while two peaks at 3301 and 3334 cm<sup>-1</sup> are observed for the tetramide. This band is very sensitive to hydrogen bonding and generally enhanced vibration is a result of conformational disorder, which leads to a broader peak, while an ordered structure will show a narrower band.<sup>19,20</sup> Based on the shape and frequency of this band, it appears that cyclic diamide is more ordered in the solid state when compared with cyclic tetramide. Alternatively, the difference may also be related to the types of inter- and intramolecular hydrogen bonding of the different cyclic structures.<sup>2</sup>

Crystallinities of these cyclic diamides were investigated using WAXD and found to be completely different for each cyclic monomer when compared to the mixture. WAXD patterns recorded at room temperature of the 50/50 mixture, and purified cyclic diamide and cyclic tetramide, are shown in Figure 7. Cyclic tetramide was purified by recrystallization from the 50/50 mixture. The WAXD pattern for each of the diamides is different from each other and both are very different when compared to the 50/50 mixture. This may indicate that the mixture crystallizes as a 1:1 molecular complex rather than into separate crystallites for each of the two cyclic structures. Further work is needed to clarify and understand this behavior.

Homopolymerizations of these cyclic diamides in the molten state were difficult due to the fact that the melting points of these monomers are so high, especially for the 12-membered cyclic diamide, which melts at about 290 °C, in the range of nylon 64. For this reason, we first explored the copolymerization of CLA with these cyclic monomers to investigate



FIGURE 6 Partial FTIR spectra of the 50/50 mixture (solid line) and cyclic tetramide (dashed line).



FIGURE 7 WAXD patterns of 50/50 mixture (bottom), cyclic tetramide (middle), and cyclic diamide (top).

ring-opening capabilities and the effect of nylon 64 repeat units on possible improvement of thermal and mechanical properties of nylon 6. Polymerizations of monomer mixtures could be carried out at temperatures lower than those required for pure monomers, offering a pathway to nondegraded and more easily processed products.

Copolymerization of 1,6-diazacyclododecane-2,5-dione with CLA was attempted with both anionic and hydrolytic polymerization methods to investigate the effect of the reaction mechanism on final properties. The details of the copolymerization are described in the experimental section. As anionic polymerization is faster and carried out at lower temperature, it was expected to give fewer side products. Cyclic amides used for polymerization mostly contained a single type of cyclic diamide.

The <sup>13</sup>C solution NMR spectrum of a typical copolymer synthesized by anionic polymerization is shown in Figure 8. The spectrum of homopolymer nylon 6 is included for comparison. The carbonyl carbon peak of the cyclic amide observed at 173.3-173.5 ppm shifts downfield to 174 ppm in the polymer backbone. The peaks assigned as a and c of cyclic diamide are observed at 34.05 and 25.4 ppm, respectively, while these peaks appear at 31.5 and 28.8 ppm, respectively, in the copolymer. These chemical shift values are very close to those of these same carbons of the cyclic tetramide. This is a good indication that cyclic tetramide possesses lower ring strain when compared with diamide, as would be expected for larger cycle size. Based on the intensity of the carbonyl carbon peak, the incorporation of nylon 64 segments is calculated as being 12 mol %. The actual intensity of the carbonyl carbon of nylon 64 units is divided by two based on the assumption that there are two carbonyl carbons for nylon 64 units while there is only one for nylon 6 units. The copolymer number-average molecular weight was calculated to be 8927 g/mol using NMR data with the application of previously published equations,<sup>21,22</sup> and peak assignments.23

As expected, copolymerization using the hydrolytic polymerization method is more complicated and results in several side products. To identify the peaks of such copolymers, two novel model compounds were synthesized and the chemical shifts of copolymers analyzed based on the chemical shift of these compounds in the same solvent system (3:1



FIGURE 8 <sup>13</sup>C solution NMR of neat nylon 6 (top) and nylon (6-*co*-64) (bottom) by anionic polymerization method; 3:1 TFE:CDCl<sub>3</sub> NMR solvent.



FIGURE 9 Chemical structures of (a) HAD-bisimide and (b) HAD-bisamide acid.

TFE:CDCl<sub>3</sub>). The structures of these compounds are shown in Figure 9.

The <sup>13</sup>C solution NMR spectrum of the copolymer with 10 wt % feed of cyclic diamide monomer synthesized by hydrolytic polymerization is shown in Figure 10. All peaks are assigned based on the chemical shifts of model compounds and nylon (6-co-64) obtained by anionic polymerization. Four distinct carbonyl peaks are observed including the carbonyl carbon of nylon 6. The carbonyl peak of acid endgroups appears at 178 ppm, while the carbonyl peak of imide-end groups appear at 179.8 ppm. The peak associated with nylon 64 carbonyl is observed at 173.9 and split into two; one probably in the backbone, and the other the carbonyl carbon close to the carboxylic acid end-group. The splitting can be observed easily for the methyl carbon  $\alpha$  to the carbonyl assigned as a. There are three peaks observed for this carbon in which one is associated with the carbon  $\alpha$ to carboxylic acid end-groups and the others are associated with carbons  $\alpha$  to backbone amides and amides close to carboxylic acid end-groups. Considering the intensities of the peaks, the cyclic diamide appears to have reacted only once with nylon 6 units to form either imide or carboxylic acid terminal units.

The DSC heating thermograms of Nylon (6-*co*-64) prepared by hydrolytic polymerization and anionic polymerization is shown in Figure 11. The latter shows two distinct peaks at 217 °C and 280 °C indicating two different crystal populations. The lower endotherm is similar to that of nylon  $6^{24}$ 



**FIGURE 10**  $^{13}$ C solution NMR of nylon (6-*co*-64) by hydrolytic polymerization method. The sample was dissolved in 3:1 TFE:CDCl<sub>3</sub>.

while the higher endotherm is almost the same as the melting point of nylon 64, which was reported as 278  $^{\circ}C.^{1}$  The two melting endotherms were still observed even after several washing and reprecipitation processes.

In addition to <sup>13</sup>C solution NMR spectrum of the copolymer synthesized by the anionic method, which shows one peak and no splitting for nylon 64 repeat units, two distinct peaks in the DSC similar to each homopolymer strongly suggests that the copolymer is a block copolyamide, and that the reactivity of 1,6-diazacyclododecane-2,5-dione and CLA are sufficiently different to minimize alternating monomer incorporation. Similar results were reported by Roda et al.,<sup>25,26</sup> for the copolymerization of CLA and  $\omega$ -laurolactam by different initiator systems. The copolymer prepared by sodium salt of caprolactam in combination with N-benzoyl-*e*-caprolactam initiator system showed a random character with a single melting endotherm and one crystalline form, while the copolymer prepared by  $\varepsilon$ -caprolactam magnesium bromide initiator showed two melting endotherms and two crystalline forms ( $\alpha$  and  $\gamma$ ). Unlike nylon (6-*co*-64) reported here showing two distinct blocks, the copolymer of CLA and  $\omega$ laurolactam shows a melting endotherm around 140 °C corresponding to the melting of a random copolymer of CLA and  $\omega$ -laurolactam, whereas the second endotherm around 214 °C corresponds to the melting of nylon 6.

Two distinct peaks at 195 °C and 218 °C are also observed in the DSC heating thermogram of nylon (6-co-64) obtained by hydrolytic polymerization. No endotherm is observed at a



**FIGURE 11** DSC heating thermograms of nylon (6-*co*-64) by hydrolytic polymerization (dashed line) and anionic polymerization (solid line).

temperature higher than the melting point of nylon 6. The higher endotherm is presumed to be the melting point of nylon 6 segments, while the lower endotherm appears to be related to the melting of terminal nylon 64 units at the surface of nylon 6 crystallites, or of very short nylon 6 chains with acid and/or imide terminal units.

## CONCLUSIONS

The 12-membered cyclic diamide has been successfully synthesized in a reasonable yield. The yield and the ring size of cyclic diamide were found to depend on the reactants used and their feed ratios. The synthesis of cyclic diamide with DPEA gave two different cyclic structures, which were easily separated by recrystallization. The crystal packing as well as the melting points of each diamide is very different. These cyclic diamides were shown to copolymerize with  $\varepsilon$ -caprolactam, resulting in block copolymers of nylon 6 and 64.

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