**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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H. R. Kricheldorf[a]; M. Al Masri[a]; G. Schwarz[a]
[a] Institut für Technische und Makromolekulare Chemie, Hamburg, Germany

**To cite this Article** Kricheldorf, H. R. , Masri, M. Al and Schwarz, G.(2006) 'Syntheses of Cyclic Polyamides from Cyclic Dicarboxylic Anhydrides', Journal of Macromolecular Science, Part A, 43: 1, 1 — 9

**To link to this Article: DOI:** 10.1080/10601320500405745

**URL:** http://dx.doi.org/10.1080/10601320500405745

*Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry*, 43:1–9, 2006

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320500405745

# Syntheses of Cyclic Polyamides from Cyclic Dicarboxylic Anhydrides

H. R. KRICHELDORF, M. AL MASRI, AND G. SCHWARZ

Institut für Technische und Makromolekulare Chemie, Hamburg, Germany

*Two secondary diamines, namely 1,6-bis(methylamino)hexane and 4,4′-trimethylene-bispiperidine, TMBP, were polycondensed with cyclic aliphatic anhydrides. All polycondensations were conducted in the melt at a final reaction temperature of 240°C and high molar mass polyamides were obtained. The MALDI-TOF mass spectra displayed, almost exclusively, peaks of cyclic polyamides in the mass range below 5,000 Da (technical limit). The DSC measurements revealed that the polyamides derived from succinic acid were crystalline despite the lack of H-bonds. The solubility in chloroform enabled SEC measurements of all polyamides, which proved broad molar mass distributions (with polydispersities around 3) which is characteristic for polymers containing high fractions of cycles.*

**Keywords** macrocycles, cyclic anhydrides, polycondensation, polyamides, MALDI-TOF

## Introduction

The classical theory of polycondensation, as presented in all polymer science textbooks, goes back to the work of Carothers (1, 2) and Flory (3, 4). In this theory, (and in the underlying experiments) linear, difunctional monomers react with each other yielding linear difunctional oligomers, which at high conversions, finally yield linear, difunctional polymers. The dependence of the degree of polymerization on the conversion is described by the so-called Carothers equation (1).

The present work had the purpose of elaborating a complementary type of polycondensation in the field of polyamides, namely the synthesis of cyclic polyamides from cyclic monomers. In the textbooks, cyclic monomers are almost exclusively discussed in connection with ring-opening polymerization. However, cyclic dicarboxylic anhydrides were used six decades ago by Kienle and coworkers (5, 6) as reaction partners of glycerol in "$a_2 + b_3$"-type polycondensations. Depending on the conversion, either low molar mass branched resins or intractable gels were obtained. More recently, we have demonstrated (7) that a broad variety of difunctional heterocycles may be used as monomers for ring-opening polycondensation. Furthermore, we have recently hypothesized that in thermodynamically controlled polycondensations (as studied in this work), the fraction of cycles increases with the conversion, so that all reaction products are cycles at 100%

Received and Accepted 1 May 2005.

Address correspondence to H. R. Kricheldorf, Institut für Technische und Makromolekulare Chemie, Bundesstr. 45, D-20146, Hamburg, Germany. E-mail: kricheld@chemie.uni-hamburg.de

conversion. In the case of Nylon-6 prepared in the melt at 250°C, the fraction of cycles detected by MALDI-TOF mass spectrometry was certainly far above 30 wt%. This is in contrast with the Jacobson and Stockmayer (8) theory, which predicted around 2.5 wt%. The polycondensations studied in this work were based on cyclic aliphatic anhydrides, and on two secondary diamines. Primary diamines were not useful because they yield imide endgroups when reacted with cyclic anhydrides.

The monomers used in this work, and the resulting polyamides, are presented in Schemes 1 and 2. Finally, it should be mentioned that polyamides derived from trimethylene bispiperidine, TMBP, were reported by several research groups (9–13). However, the synthetic methods used for their preparation were quite different from that described in the present work, and in most cases, the structure was also quite different.

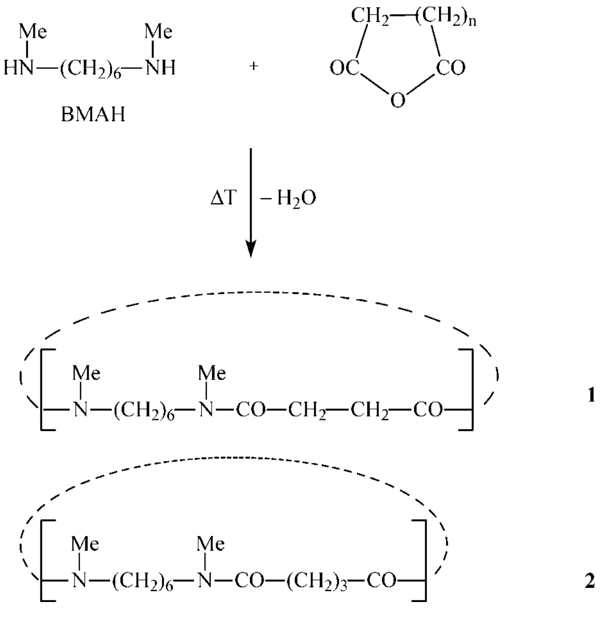
## Experimental

### Materials

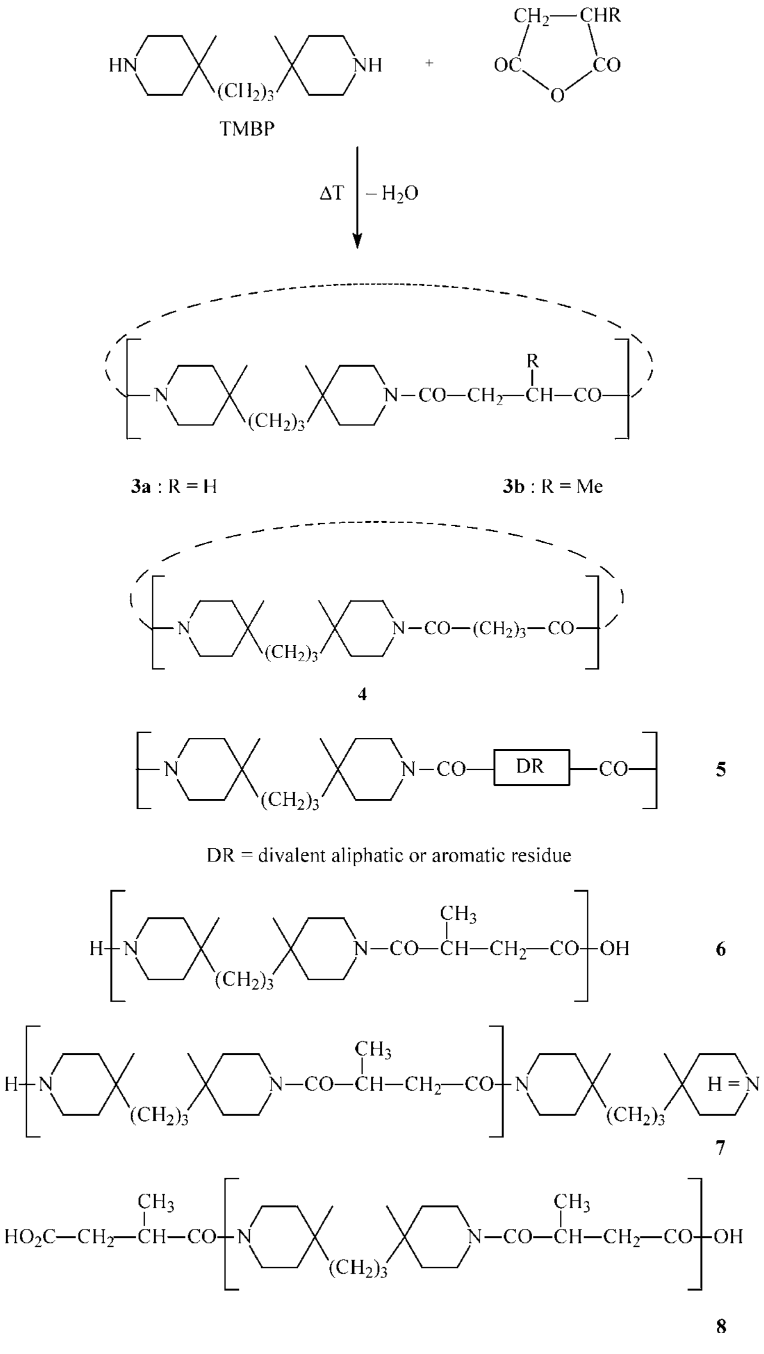
1,6-Bis(methylamino)hexane, BMAH, and 4,4′-trimethylenebispiperidine, TMBP, were purchased from Aldrich Co. (Milwaukee, WI) and distilled *in vacuo*. Succinic anhydride, methylsuccinic anhydride, and glutaric anhydride were also purchased from Aldrich. They were recrystallized from toluene with the addition of 10 mol% of acetic anhydride. Succinic anhydride was finally sublimed and the other anhydrides distilled *in vacuo*.

### Polycondensation

In an atmosphere of dry nitrogen, an anhydride (24.25 mmol), the corresponding dicarboxylic acid (0.75 mmol) and a diamine (25.75 mmol) were weighed into a cylindrical



**Scheme 1.** Syntheses of polyamides from 1,6-bis(methylamino)hexane.



**Scheme 2.** Syntheses of polyamides from trimethylene bispiperidine.

glass reactor, which was equipped with a mechanical stirrer, gas-inlet, and gas-outlet tubes. Chlorobenzene (10 mL) was added, and the reactor was placed into an oil bath preheated to 120°C. After 0.5 h, the temperature was raised to 140°C for 0.5 h, then to 160°C for 0.5 h, to 220°C for 0.5 h and, finally, to 240°C for 17 h. The chlorobenzene and eliminated water were removed with a slow stream of nitrogen. The cold polyamides were dissolved in dichloromethane, precipitated into cold diethyl ether (all polyamides are soluble in methanol) and dried at 20°C *in vacuo*.

### *Measurements*

The inherent viscosities were measured in dichloromethane by means of an automated Ubbelohde viscometer thermostated at 20°C.

The IR spectra were recorded on a Nicolet using KBr pellets. The 400 MHz $^1$H-NMR spectra were recorded on a Bruker Avance 400 spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent and shift reference. The MALDI-TOF mass spectra were measured with a Bruker Biflex III equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were recorded in the reflection mode using an acceleration voltage of 20 kV. The irradiation targets were prepared from a chloroform solution using dithranol as matrices and potassium trifluoroacetate as a dopant. The DSC measurements were conducted with a Mettlar Toledo apparatus "DSC 821e" in aluminum pans under nitrogen with a heating rate of 20°C/min.

A series of SEC measurements was conducted at 25°C with an apparatus of Polymer Laboratories equipped with the pump PL-LC 1120 and a RI detector Shodex RI 101. A combination of three PL mixed-bed columns was used with chloroform as eluent at a flow rate of 1.0 mL/min. The elution curves were calibrated with commercial polystyrene standards. Three more SEC measurements were performed at 35°C on a homemade SEC apparatus equipped with a Shodex RI detector and a combination of two Polymer Laboratories column "HFiP-Gel" and "100 Å PL-Gel". HFiP was used as eluent with a flow rate of 0.7 mL/min. Polyamide-6 standards of Bayer AG was used for calibration.

## Results and Discussion

All polycondensations performed in this work were conducted in such a way that the diamine and a cyclic anhydride were mixed in an inert solvent and heated to 250°C in a stepwise manner, so that the last stage of the polycondensation occurred in the melts. The procedure presented in the experimental part is the result of an optimization process, which will be mentioned presently. Polycondensations based on an exact 1 : 1 feed ratio were not as successful as expected because apparently, the reaction of diamine and dianhydride was not rapid enough, so that a small fraction of the diamine distilled off causing an imbalance of the stoichiometry. The addition of potential catalysts, such as 4-toluene sulfonic acid or 4-(N,N-dimethylamino)pyridine slightly improved the molecular weights. However, the best results (presented in Tables 1 and 2) were obtained when a few mol% (typically 3%) of the cyclic anhydride was replaced by the free dicarboxylic acid. Unfortunately, a simple reaction mechanism explaining the unexpected result cannot be presented at this time.

The success of this procedure is documented by the relatively high inherent viscosities and by the molecular weights (number average: $M_n$, and weight average: $M_w$) listed in Table 2. The absence of H-bonds rendered the polyamides of this work soluble in a variety of organic solvents, including methanol, dichloromethane, and chloroform (but not in tetrahydrofuran or diethyl ether). Therefore, it was feasible to perform SEC measurements in chloroform and dichloromethane. The measurements conducted in chloroform were calibrated with commercial polystyrene standards and $M_n$s up to 50,000 Da with $M_w$s up to 150,000 Da were found (Table 2). However, it is known

**Table 1**

Properties of polyamides prepared by polycondensation of cyclic anhydrides in bulk

| Polymer no. | Diamine | Anhydride of | Yield % | $\eta_{inh}{}^{a,b}$ (dL/g) | Elemental analyses[b] | | | | $T_g{}^{b,c}$ °C | $T_m{}^{b,c}$ °C |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | | |
| **1** | 1,6-Bis(methylamino) hexane | Succinic a. | 92 | 0.97 | Calcd. | 63.68 | 9.80 | 12.38 | 7.5 | 63.0 |
| | | | | | Found | 63.30 | 9.74 | 12.16 | | |
| **2** | 1,6-Bis(methylamino) hexane | Glutaric a. | 93 | 0.74 | Calcd. | 64.97 | 10.06 | 11.65 | 3.0 | — |
| | | | | | Found | 64.71 | 10.05 | 11.55 | | |
| **3a** | 4,4′-Trimethylene diperidine | Succinic a. | 98 | 1.50 | Calcd. | 69.83 | 9.65 | 9.58 | 99.0 | 215.5 |
| | | | | | Found | 69.65 | 9.69 | 9.26 | | |
| **3b** | 4,4′-Trimethylene diperidine | Methylsuccinic a. | 91 | 1.25 | Calcd. | 70.55 | 9.87 | 9.14 | 72.0 | — |
| | | | | | Found | 70.22 | 9.61 | 9.06 | | |
| **4** | 4,4′-Trimethylene diperidine | Glutaric a. | 96 | 1.05 | Calcd. | 70.55 | 9.87 | 9.14 | 58.0 | — |
| | | | | | Found | 70.49 | 9.63 | 9.14 | | |

[a] Measured at 20°C with c = 2 g/L in dichloromethane.
[b] Determined from virgin reaction products.
[c] From DSC measurements with a heating rate of 10°C/min.

**Table 2**
Results of SEC measurements

| Polymer no. | $\eta_{inh}$[a] (dL/g) | SEC in $CHCl_3$[b] | | SEC in HFiP[c] | | $M_w$ (HFiP)[d] |
|---|---|---|---|---|---|---|
| | | $M_n$ (Da) | $M_w$ (Da) | $M_n$ (Da) | $M_w$ (Da) | |
| **1** | 0.97 | 31,500 | 100,000 | — | — | — |
| **2** | 0.74 | 24,000 | 70,000 | — | — | — |
| **3a** | 1.50 | 50,000 | 155,000 | 20,500 | 70,000 | 65,000 |
| **3b** | 1.25 | 40,000 | 140,000 | 19,000 | 65,000 | 58,000 |
| **4** | 1.05 | 36,000 | 115,000 | 18,000 | 61,000 | 55,000 |

[a] Measured at 20°C with $c = 2\,g/L$ in $CH_2Cl_2$.
[b] Calibrated with polystyrene.
[c] Calibrated with polyamide-6.
[d] Determined by triple detection including light-scattering.

(14–18) from aliphatic polyesters that calibration with polystyrene over estimates the real molecular weights by 50–60% for $M_n$s above 10,000 Da and up to 80% for $M_n$s below 10,000 Da. Therefore, the three polyamides with the highest molar masses were also subjected to SEC measurements in hexafluoroisopropanol (HFiP). This solvent has the advantage that it prevents any association between the polyamide chains. The elution curves were calibrated with polyamide-6 (poly-ε-caprolactam). The second set of $M_n$ and $M_w$ data (listed in Table 3) was much lower than those obtained by calibration with polystyrene. In order to decide which set of molecular weight data is closer to reality,

**Table 3**
IR and $^1$H-NMR spectroscopic data

| Polymer no. | IR spectra[a] $V_{CO}$ ($cm^{-1}$) | $^1$H-NMR chemical shifts measured in $CDCl_3$ relative to TMS[b] |
|---|---|---|
| **1** | 1650 | 1.25 (s, 4H), 1.44 (s, 2H), 1.53 (s, 2H), 2.60 (s, 4H) |
| | 1455 | 2.84, 2.95 (d) |
| **2** | 1650 | 1.25 (s, 4H), 1.46 (s, 4H), 1.90 (s, 4), 2.35 (s, 4H), 2.84 + 2.92 (s, 6H) |
| | 1455 | 3.21 —, 3.27 (m, 4H) |
| **3a** | 1652 | 1.05 (m, 4H), 1.22 (s, 4H), 1.30 (s, 2H), 1.44 (s, 2H), 1.70 (t, 4H) |
| | 1455 | 2.53 (t, 2H), 2.66 (s, 4H), 2.98 (t, 2H), 2.95 (d, 2H), 4.57 (d, 2H) |
| **3b** | 1651 | — — — — — — |
| | 1455 | |
| **4** | 1651 | 1.05 (m, 4H), 1.22 (s, 4H), 1.30 (s, 2H), 1.44 (s, 2H), 1.71 (t, 4H) |
| | 1455 | 1.93 (s, 2H), 2.41 (s, 4H), 2.51 (t, 2H), 2.96 (t, 2H), 3.90 (d, 2H), 4.57 (d, 2H) |

[a] Measured with KBr disks.
[b] Several signals display a splitting due to cis-transisomerism of the amide groups.

the SEC measurements performed in HFiP were also evaluated by means of a triple detector including light scattering, so that absolute $M_w$ values were obtained. These $M_w$ values were even slightly lower than those resulting from calibration with polyamide-6. In other words, the calibration with polystyrene in chloroform overestimated the real molecular weights by more than 100%. Regardless of the calibration, the $M_n$ and $M_w$ data indicate polydispersities in the range of 3.0–4.0. The classical theory of polycondensations formulated by Flory (3, 4) predicts polydispersities around 2.0, but it did not account for the formation of cyclic oligomers and polymers. However, a high extent of cyclization occurred, which is characteristic for all clean polycondensations with high conversions (>99.9%). Therefore, the high polydispersities found for the polyamides **1–4** suggest a considerable content of cycles.

The chemical structure and purity of all polyamides were characterized by elemental analyses (Table 1) and by IR- and $^1$H-NMR spectroscopy (Table 3). All analytical data agreed with the expected structures. Characteristic for these $^1$H-NMR spectra is the splitting of several signals (mainly of $CH_2$-N or $CH_3$-N protons) due to cis-transisomerism of the amide groups. This phenomenon, which is typical for polyamides or polypeptides of secondary amino groups has, for instance, been described for polyamides of piperazine (19–20). However, in the field of polycondensates the most informative analytical method is MALDI-TOF mass spectrometry. This method proved that all polyamides of this work contain a high molar fraction of cyclic oligo- and polyamides. Unfortunately, MALDI-TOF mass spectra of polyamides are relatively difficult to measure and most mass spectra obtained in this work did not exceed the mass range of 5,000 Da. However, within this mass range, only peaks of cyclic polyamides were detectable as illustrated in Figures 1 and 2. In a high molar mass range, these polyamides may, of course, contain linear chains. Nonetheless, these mass spectra indicated that the reaction conditions were close to those of an ideal polycondensation. In an ideal polycondensation (no side reaction, ideal stoichiometry), 100% cycles are formed at 100% conversion, regardless whether the polycondensation is kinetically or thermodynamically

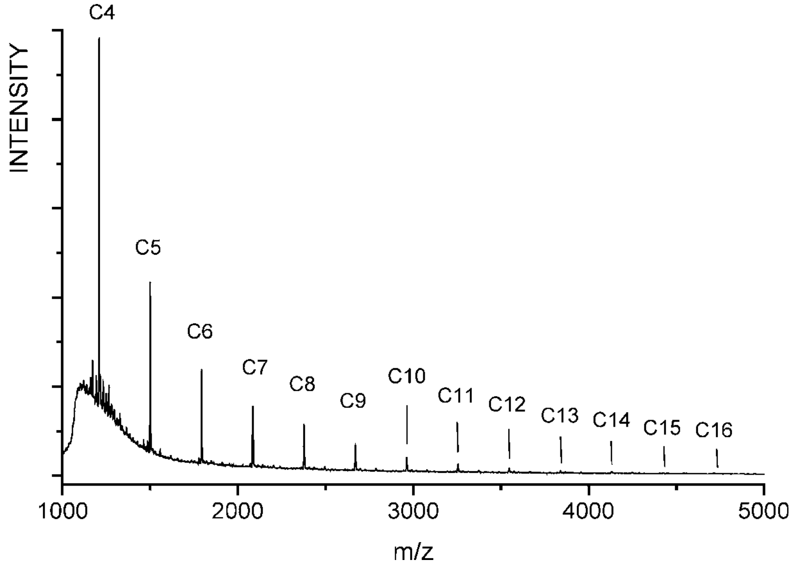


**Figure 1.** MALDI-TOF mass spectrum of polyamide **3a**.

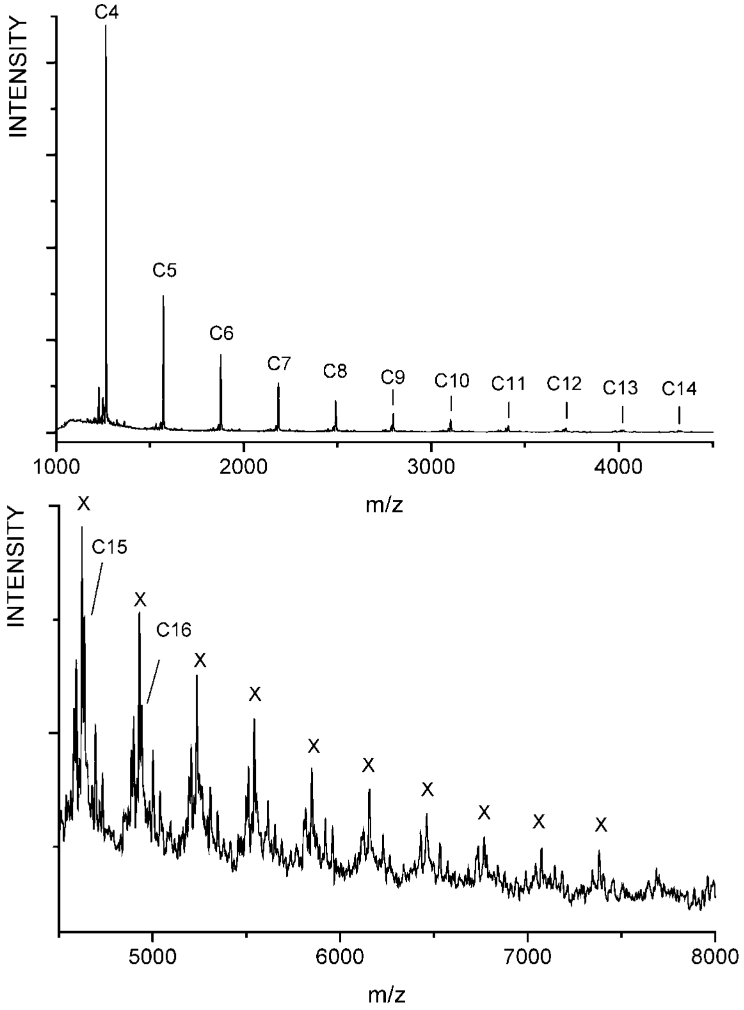


**Figure 2.** MALDI-TOF mass spectrum of polyamide **3b**.

controlled (7, 21). Therefore, the cycles content is a reliable indicator of the perfection of a polycondensation. In the case of polyamide **3b**, the mass spectrum was measurable up to 8,000 Da. Above 4,000 Da, numerous small mass peaks of linear chains became detectable having masses of 60, 98, 264 or 294 Da in addition to the mass of a cycle. However, in a clean polycondensation, only three kinds of linear chains should exist, corresponding to the three combinations outlined for **3b** in the formulas **6**, **7**, and **8**. Interestingly, the mass peaks of **6**, **7**, and **8** were absent, suggesting that stoichiometry and conversion were close to the optimum, whereas unidentified endgroups were formed by thermal degradation. The formation of relatively large amounts of cyclic oligomers and polymers is in good agreement with the high polydispersities mentioned above.

Finally, it should be mentioned that all polyamides were characterized by DSC measurements. Melting endotherms indicating crystallinity were only observed for polyamides derived from succinic acid (**1** and **5a**). This finding agrees with the results of Preston and Smith (9), who also reported crystallinity for polyamide **3a**. This result is noteworthy because it is a widespread prejudice that the NH-bonds favor crystallization of polyamides. However, when polyesters and polyamides of analogous structure are compared, the polyesters crystallize faster and generate higher degrees of crystallinity, because the H-bonds of the polyamides hinder the segmental motion of the polyamide chains. The glass-transition temperatures listed in Table 1 display the expected trend. The polyamides derived from TMBP possess the higher $T_g$s.

## Conclusions

Polycondensations of cyclic dicarboxylic anhydrides with secondary diamines conducted in bulk at temperatures up to 240°C gave high yields of high molar mass polyamides. By light-scattering, weight average molecular weights up to 65,000 Da were found, whereas calibration of SEC elution curves with polystyrene gave $M_w$ values up to 100,000 Da, thus overestimating the real $M_w$s by more than 100%. The MALDI-TOF m.s. proved a high extent of cyclization, and is in agreement with the formation of cyclic oligo- and polyamides, relatively high polydispersities (3, 4) were found. Therefore, these results prove that cyclic anhydrides may be used in normal polycondensation processes for syntheses of cyclic polymers.

## Acknowledgement

We wish to thank Dr. Claus-Ludolf Schultz (Bayer AG, Uerdingen) for the SEC measurements in hexafluoroisopropanol.

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