Articles

Cyclic and Linear Polyamides from Polycondensations of Hexamethylenediamine and *m*-Xylylenediamine with Adipic, Isophthalic, and Terephthalic Acids

Nancy Singletary,*,† Robert B. Bates,*,‡ Neil Jacobsen,‡ Albert K. Lee,‡ Guangxin Lin,‡ Arpad Somogyi,‡ Matthew J. Streeter,‡ and H. K. Hall, Jr.*,‡

Solvay Advanced Polymers, 4500 McGinnis Ferry Road, Alpharetta, Georgia 30005, and the C. S. Marvel Laboratories, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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ABSTRACT: Cyclic and linear oligoamides were extracted with methanol in 0.1−0.9% yield from condensation polymers of hexamethylenediamine or *m*-xylylenediamine with mixtures of adipic, isophthalic, and terephthalic acids. The parent polymers and methanol extracts were analyzed using mass spectrometry, and the extracts, in which the smaller molecules were concentrated by a factor of about 200, were studied by nuclear magnetic resonance (NMR) spectroscopy. Small cyclic oligoamides dominated all of the extract spectra. Cyclic monomers were observed with adipic acid but not with the aromatic acids. Cyclic dimers and trimers predominated and yields of higher cyclics decreased rapidly with increasing ring size, especially in the extracts. The degree of incorporation of the acids into small cyclics was adipic > isophthalic > terephthalic. NMR spectra of extracts from all polymers containing terephthalic and/or isophthalic acid units showed linear oligomers with benzoyl end groups, which presumably arose from thermal decarboxylation during polymerization, lowering the polymer molecular weight and affecting other polymer properties.

Introduction

In recent years Professor H. R. Kricheldorf and his colleagues at Hamburg have given a remarkable new perspective on polycondensation. Making use of the powerful MALDI−TOF mass spectral technique, they have shown that for both thermodynamically[1,2] and kinetically[3−5] controlled polymerizations, large rings constitute a much larger portion of condensation polymers than was previously recognized. This has been found for a wide variety of polymers, including polyamides, polyesters, and polysulfones.

Cyclic oligomers have long been known to accompany high polymers during polycondensation. They cause technical problems in melt processes such as fiber spinning, film extrusion, and injection molding, and in dyeing.[6] Cyclic oligoamides have been encountered in both AB ring opening[7] and condensation polymerizations.[8,9]

Herman Stetter and Helmut Zahn pioneered the stepwise synthesis of well-defined caprolactam cyclic AB oligomers and linear 66 nylon AABB oligomers.[10−22] Stetter later used interfacial polycondensation at high dilution to synthesize AABB cyclic oligomers.[23]

Experimental Section

Extraction Procedure. Approximately 100 g of each of six milled polymer samples was charged to a thimble which was placed in a Soxhlet extractor. The extractor was attached to a flask containing 500 mL of methanol which was then heated in a 108 °C bath to allow 24 h of siphon cycles. At the end of each extraction, solid was removed by filtration and solvent was removed using a rotary evaporator to provide the extracts.

Mass Spectra. Matrix assisted laser desorption ionization (MALDI) was used to generate ions that were analyzed by time-of-flight (TOF) analyzers on Bruker Reflex III MALDI−TOF and Ultraflex III MALDI−TOF/TOF instruments (Bruker Daltonics, Billerica, MA), equipped with N2 (357 nm) and Nb/Yag lasers (332 nm), respectively. Samples were dissolved in hexafluoroisopropanol (HFIP) in a concentration of ca. 0.01 M. Two matrices were used: 2-(4-hydroxyphenylazo)benzoic acid (HABA, used in the excellent mass spectral study of nylon 66 by Weidner[24]) and 4,4′-dihydroxyoctofluoroazobenzene (DOF[25]). These matrices were dissolved in tetrahydrofuran (THF) in a concentration of about 0.1 M. The matrix:analyte ratio was varied in the region 10−50. Cationic spectra were obtained in both the reflectron mode (up to *m*/*z* 5000) for its better resolution and mass accuracy and the linear mode for its greater range (up to *m*/*z* 10 000).

NMR Spectra. Run on Bruker DRX-500 and −600 spectrometers. ^{1}H, COSY, and TOCSY spectra were run in dimethyl-d_6 sulfoxide (DMSO) with the solvent peak set at δ2.49. HSQC spectra were run in DMSO with the ^{13}C solvent peak set at δ39.5. ^{13}C spectra were run in hexafluoro-2-propanol-d_2 (HFIP) with the solvent peak set at δ70.0. TOCSY spectra used the MLEV-17 mixing sequence with a spin-lock power of 8.3 kHz.[26]

Results and Discussion

The present work examines further polyamides in the light of these discoveries. Methanol extraction of the polyamides enabled us to obtain extracts sufficiently enriched in low cyclic and linear oligomers that they could be identified by a combination of mass and NMR spectroscopies and quantified by NMR spectroscopy; these mixtures of low molecular weight

* To whom correspondence should be addressed.
† Solvay Advanced Polymers.
‡ C. S. Marvel Laboratories, Department of Chemistry, University of Arizona.

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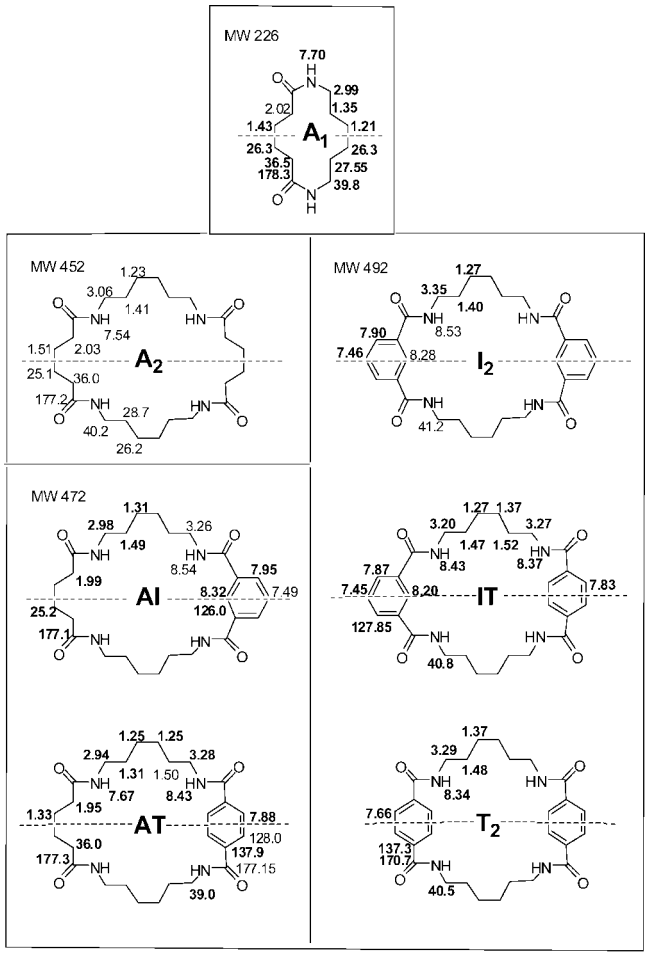

Figure 1. Structures and NMR shifts of cyclic monomer and dimers. Proton shifts (DMSO) are on the upper halves and carbon shifts (HFIP) are on the lower halves of the structures. Boldface numbers are shifts notably different from polymer values.

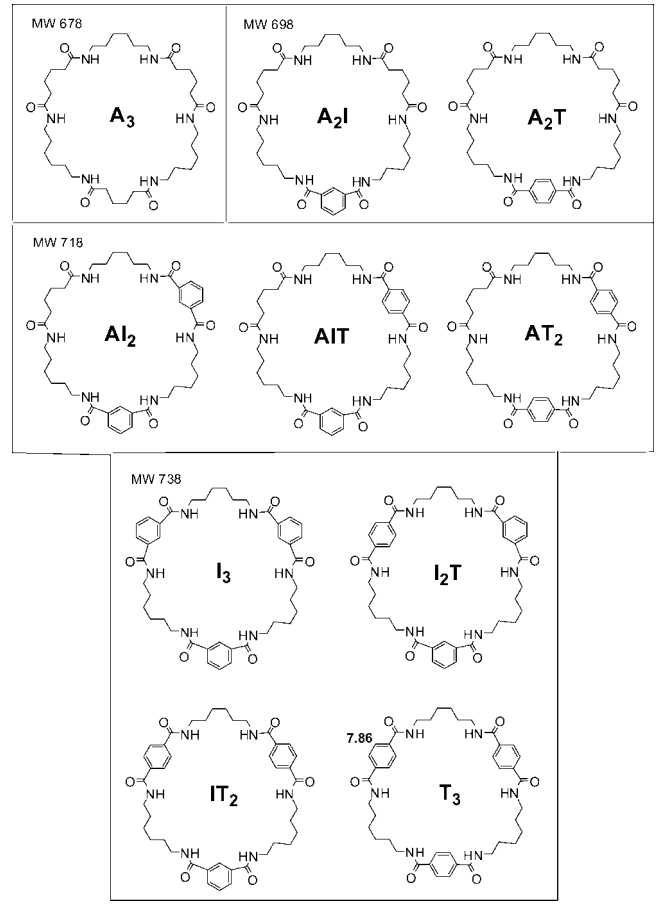

Figure 2. Structures and a $\mathbf{T_3}$ NMR shift of cyclic trimers (see Figure 1 title). Their other NMR shifts are very close to those of the linear oligomers in Figure 3.

linear and cyclic oligomers are referred to as "extracts" below. We also observed these low molecular weight oligomers directly in the polymers by mass spectroscopy, but not by NMR due to their low concentrations.

We examined commercial polymers of hexamethylenediamine (**HMDA**) and *m*-xylylenediamine with adipic (**A**), isophthalic (**IPA**), and terephthalic (**TPA**) acids. Since the diamine in all but one case was HMDA, this diamine will be assumed, and its cyclic monomer with adipic acid will simply be represented as "$\mathbf{A_1}$", the cyclic trimer from one adipic acid and two terephthalic acids as "$\mathbf{AT_2}$", etc. (Figures 1 and 2). The repeating units and end groups of linear oligomers containing HMDA are shown in Figure 3. The cyclic monomer from *m*-xylylenediamine and adipic acid will be represented by "$\mathbf{X_1}$", the cyclic dimer by $\mathbf{X_2}$, etc.; the cyclic monomer and dimer and repeating unit in products from *m*-xylylenediamine are shown in Figure 4.

Inspection of the literature found many references to the $\mathbf{A}_n$ series of cyclic oligomers accompanying nylon 66, a reference to $\mathbf{I_1}$ and $\mathbf{T_1}$,[27] and a reference to $\mathbf{X_1}$.[28] No references were found to the other cyclic oligoamides in this paper.

The polymers examined are shown in Table 1. The diamine was HMDA for samples 1−5 and *m*-xylylenediamine for sample 6. Before extraction, the polymers were characterized by gel permeation chromatography (GPC); the resulting M_n values, given in the table, are based on comparisons with a standard polymer of known molecular weight. Methanol extraction was done with a Soxhlet apparatus for 24 h. Filtration and evaporation gave residual extracts in yields ranging from 0.1− 0.9% as shown.

Mass Spectra of Extracts and Polymers. MALDI−TOF mass spectra were used to distinguish many cyclic oligoamides and various linear oligoamides with different end groups, since many of the compounds of interest had different masses. Sample 6 (a simple case) and sample 3 will be used for illustration.

Figure 5 shows the HABA spectra of extract 6 (below) and polymer 6 (above), an uncapped polymer with adipic acid as the only acid component. The spectra of both polymer and extract are dominated by the labeled peaks for low molecular cyclics $\mathbf{X}_n$, which start with an $\mathbf{X_1}$ peak at mass 269 (not shown; about 1/4 as tall as the 515 peak from $\mathbf{X_2}$). The peaks from the extract cyclics decrease more rapidly with increasing molecular weight than those from the polymer cyclics, indicating that as expected, the smaller cyclics are extracted by methanol more efficiently than the larger ones. The polymer spectrum shows peaks for cyclics with the maximum at 761 for $\mathbf{X_3}$ and continuing up to mass 4697 for $\mathbf{X_{19}}$; ms/ms experiments indicated that these higher mass cyclics fragment in the same ways as the lower mass cyclics and thus presumably have very large rings (up to 247 members). The extract spectrum shows a maximum at mass 515 for $\mathbf{X_2}$ rather than 761 for $\mathbf{X_3}$, again indicating that smaller rings are extracted more efficiently than larger ones; peaks for cyclics through $\mathbf{X_{16}}$ (mass 3960) were above noise when the spectral data were collected for a long time.

Figure 5 (especially the insert) also shows peaks due to the linear oligomers which accompany the cyclic oligomers, and that methanol extraction removes linear oligomers less well than

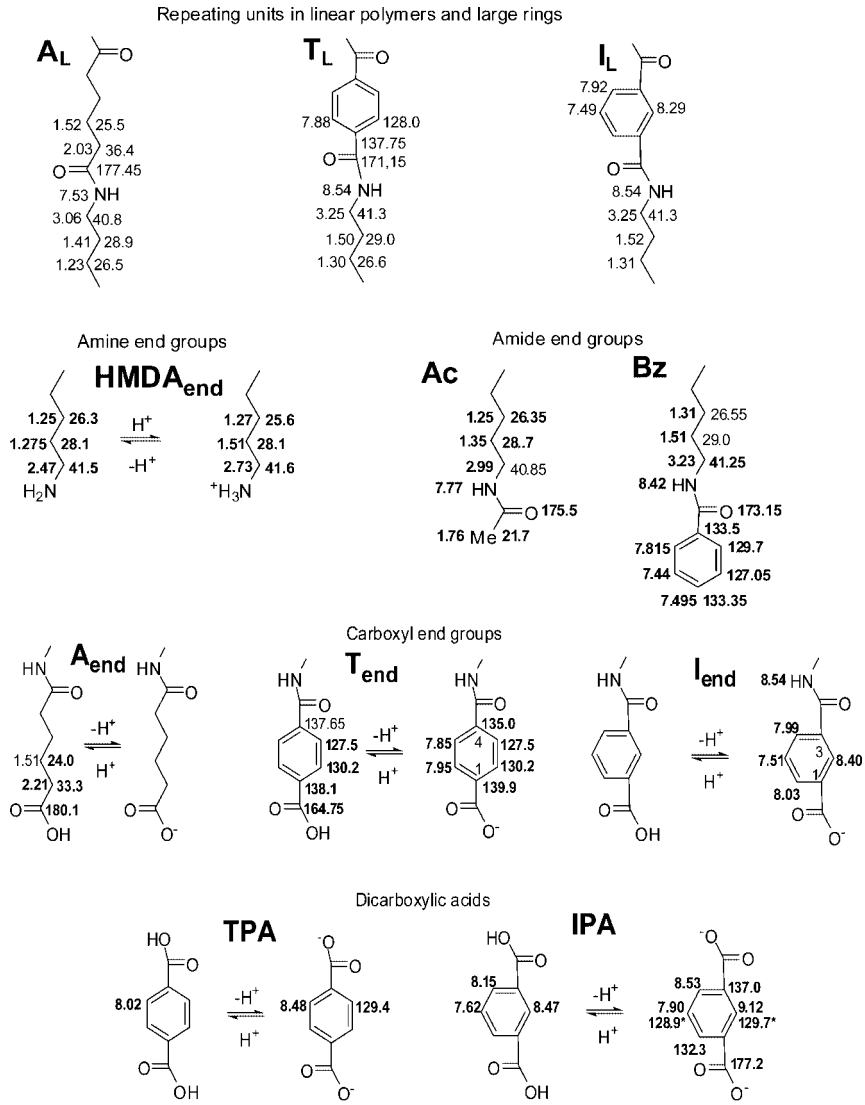

Figure 3. Proton (left side, DMSO) and carbon (right side, HFIP) NMR shifts in linear oligomers and polymers. Boldface numbers are shifts notably different from polymer values. *may be reversed.

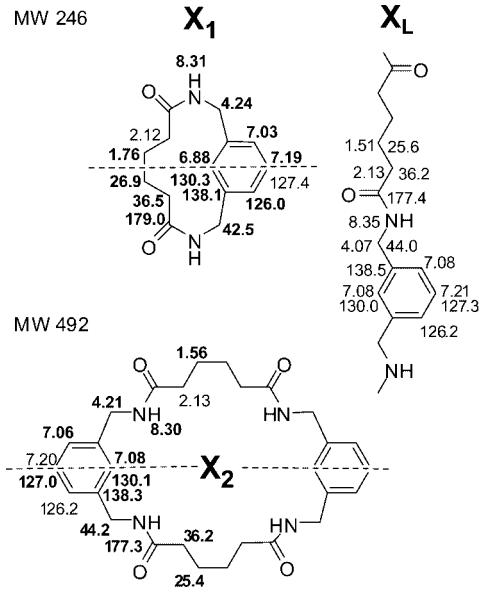

Figure 4. Structures and NMR shifts of **X**-containing species from extract 6 (see Figure 1 title).

cyclics. The two expected end groups (carboxyl and amino) gave three types of linear molecules, with amino acid peaks dominating early, diacid peaks later, and much weaker peaks for diamines. Polymer spectra showed linear oligomers up to about mass 16000 (65 monomer units), and extract spectra run for long times showed that linear oligomers up to mass 5500 (22 monomer units) are extracted by methanol.

Figures 6 and 7 show MALDI−TOF mass spectra of polymer 3 and extract 3 with the DOF matrix, and Table 2 lists peaks expected for monomeric through tetrameric sodiated species (M − Na^+), which were the major peaks. In cases of strong peaks for complexes with Na^+, it was often possible to see a peak 22 mass units lower for the complex with H^+ and/or a peak 16 mass units higher for the complex with K^+, increasing confidence that the large peaks were due to Na^+ complexes; some peaks for potassiated ions are marked "K" in Figures 6 and 7. **TPA** and **IPA** are 20 mass units heavier than adipic acid, making it easy to tell how many aromatic acid units are present in molecules containing acid-derived groupings.

The largest peaks by far in all the extract spectra were for cyclic monomers, dimers, and trimers. The only cyclic monomers observed were $\mathbf{A_1}$ from adipic acid with HMDA and $\mathbf{X_1}$ from adipic acid with *m*-xylylenediamine; the strained cyclic monomers involving **TPA** and **IPA** were not formed in

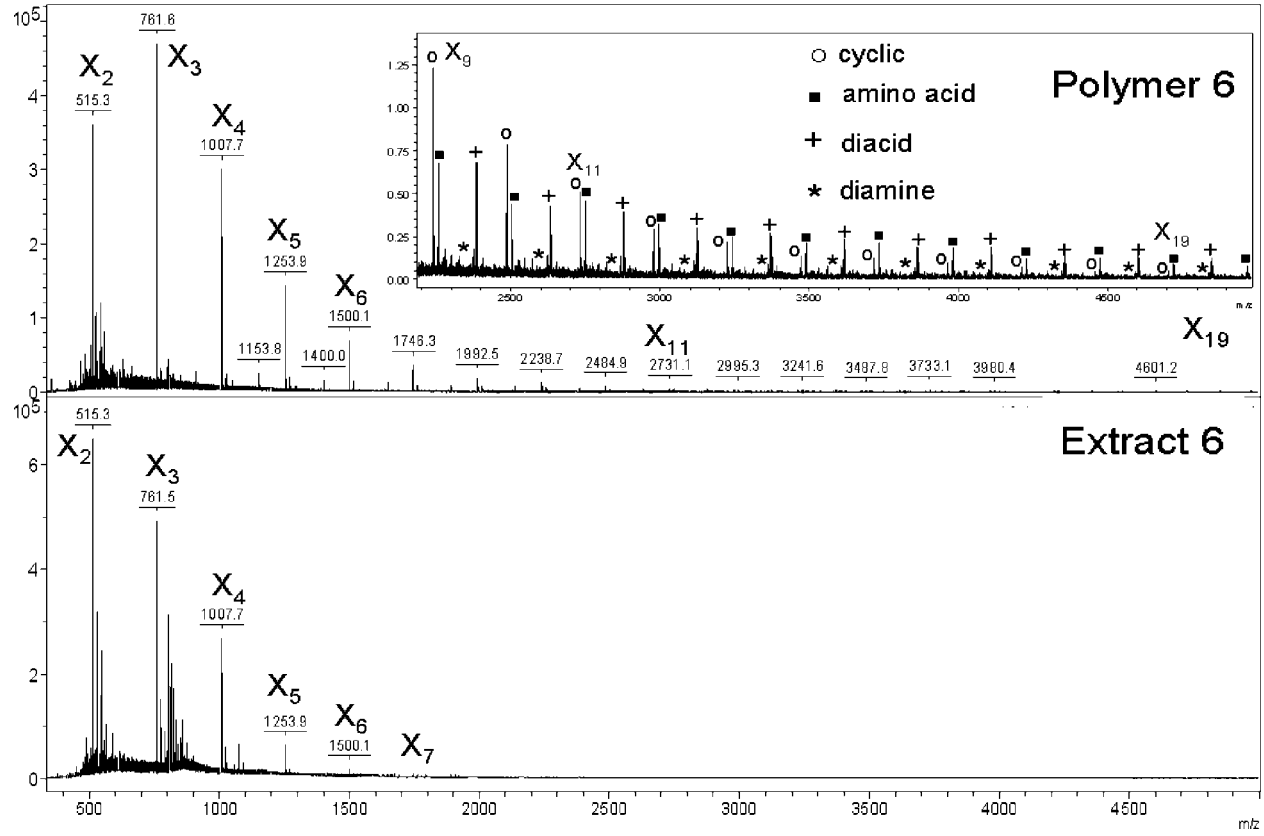

Figure 5. MALDI−TOF mass spectra of polymer 6 and extract 6 with the DOF matrix.

Table 1. Polymer Compositions and Extraction Yields[a]

				composition						
sample no.	product	grade	M_n (GPC)	% **A**	% **T**	% **I**	cap	polymer wt, g	extract wt, mg	% yield
1	Zytel 101	Nylon 66	14900	100	−	−	none	94	800	0.85
2	Amodel	A-6000	13700	40	60	−	Ac	97	249	0.26
3	Amodel	A-4000	11300	30	70	−	Ac	95	195	0.21
4	Amodel	A-1004	11000	10	70	20	Ac	100	110	0.11
5	Arlen	A3000	9200	−	70	30	Bz	98	106	0.11
6	PArA	PArA0012	13600	100	−	−	none	99	400	0.40

[a] Ac = acetyl. Bz = benzoyl

detectable amounts. Table 2 lists some sodiated peaks for cyclics and for linear species with the expected end groups. Without capping (samples 1 and 6), linear molecules have three expected end group combinations, giving amino acids, diacids, and diamines. The polymers capped in their preparation by adding acetic acid (samples 2−4) or benzoic acid (sample 5) should give molecules of three additional types: amido acids, amino amides, and diamides. Peaks for all six of these types were present in some spectra, but the peaks for diacids and diamines were not above noise in Figure 7. The spectra of products containing carboxyl groups had the further complication of extra peaks for carboxylic acid Na and K salts. Monocarboxylic acids can give Na or K salts, and dicarboxylic acids can give Na, K, 2Na, 2K, or Na/K salts. Extra peaks of these types sometimes complicated the spectra.

As seen in Figures 5−7, peaks from linear oligomers were much smaller than those from low molecular weight cyclic oligomers, but as the masses increase, the linear molecules dominate. The peaks for linear oligomers are observed to much higher masses. Figure 7 and the insert in Figure 5 are blowups of spectral regions in Figures 5 and 6 which show linear molecules with various end groups. The possibility of overlapping peaks is illustrated in Table 2 and Figure 7 at masses 987 and 1007. The latter peak is partly from the cyclic $\mathbf{T_4}$ and partly from the linear tetramer with four adipic acids capped with acetic acid. The relative amounts of these two contributing species can be estimated by assuming that the related molecules in the groups concerned (e.g., cyclics $\mathbf{A_4}$ to $\mathbf{T_4}$) occur in roughly the same relative amounts as occur in the groups giving peaks nearby.

A consistent difference between the extract and polymer spectra was that the peaks for diamines were smaller in the extract spectra, suggesting that diamines are largely protonated in the polymer and the resulting diammonium ions are not very soluble in methanol.

NMR Spectra of Extracts. Although the above mass spectra showed which linear and cyclic species were present, the results are only semiquantitative since some types of molecules give ions much more readily than others. Also, the mass spectra were very sensitive to the attenuation setting, which drastically affected the relative amounts shown for various molecules. The methanol extraction procedure concentrated the smaller molecules by a factor of about 200, enough that NMR could easily be used to study them. ^{1}H, ^{13}C, COSY, TOCSY, and HSQC NMR spectra were obtained for more quantitative information, and also to distinguish **TPA** from**IPA** derived units in extracts 4 and 5 which contained both aromatic acids. Although the

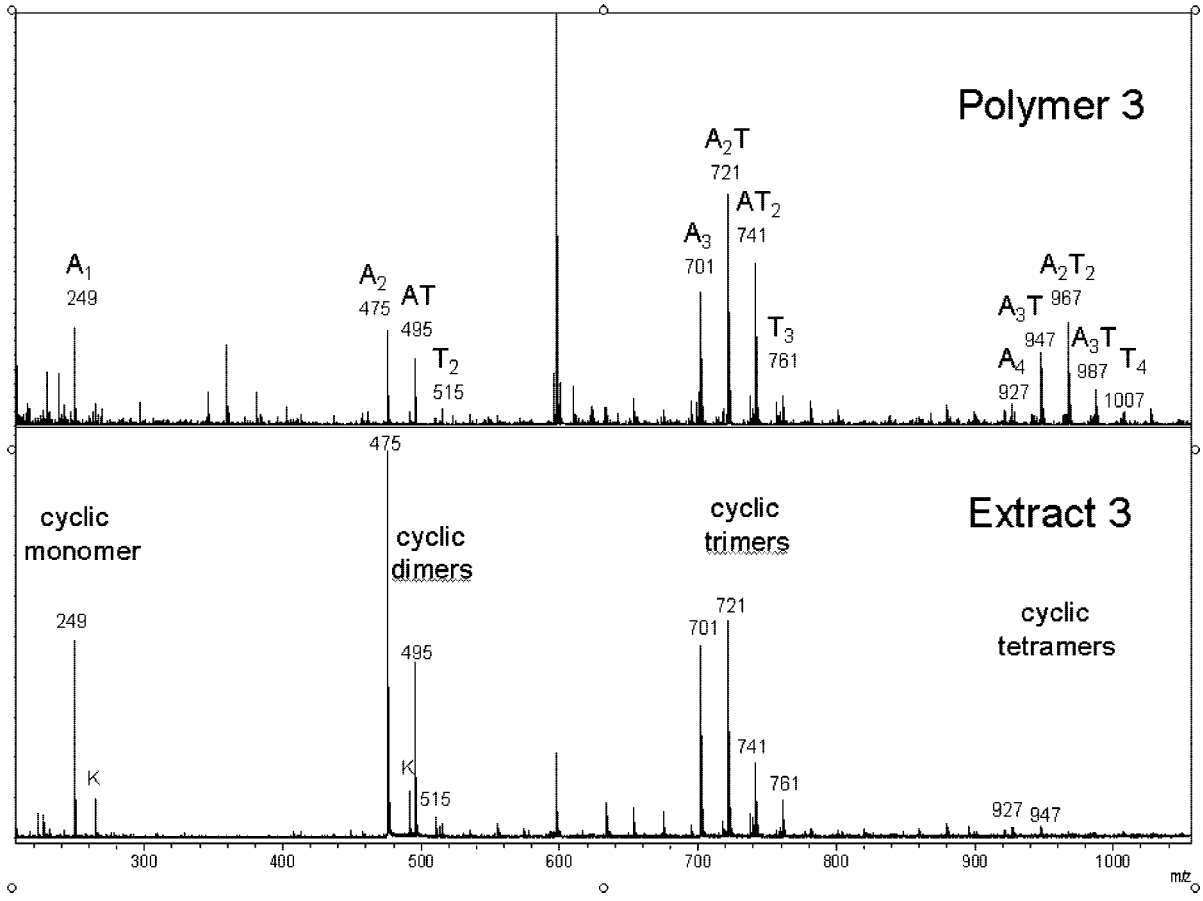

Figure 6. MALDI−TOF mass spectra of polymer 3 and extract 3 with the DOF matrix.

Table 2. Masses of Expected Sodiated Ions from Cyclic and Linear Monomers, Dimers, Trimers and Tetramers from HMDA and Adipic, Terephthalic, and Isophthalic Acids, Capped with Acetic Acid

no. of units	no. of **A** units	no. of **T/I** units	cyclic C	amino acid C + 18	amido acid C + 60	diamine C + 116	diacid **A** C + 146	amino amide C + 158	diacid **T/I** C + 166	diamide C + 200
1	1	0	**249**[a]	267	309	365	395	407	415	449
	0	1	269	287	329	385	415	427	435	469
2	2	0	**475**	493	535	591	621	633	641	675
	1	1	**495**	513	555	611	641	653	661	695
	0	2	**515**	533	575	631	661	673	681	715
3	3	0	**701**	719	761	817	847	859	867	901
	2	1	**721**	739	781	837	867	879	887	921
	1	2	**741**	759	801	857	887	899	907	**941**
	0	3	**761**	779	821	877	907	919	927	961
4	4	0	**927**	945	987	1043	1073	**1085**	1093	**1127**
	3	1	**947**	965	1007	1063	1093	**1105**	1113	**1147**
	2	2	**967**	985	1027	1083	1113	**1125**	1133	**1167**
	1	3	**987**	1005	1047	1103	1133	**1145**	1153	1187
	0	4	**1007**	1025	1067	1123	1153	1165	1173	1207

[a] Boldface numbers indicate masses seen in Figures 5−7.

mixtures of cyclic and small linear oligomers in the extracts were not separated, with the mass spectra showing what species were present and giving an idea of their relative amounts, and with comparisons with NMRs from other extracts and from model compounds, it was possible to assign the NMR peaks for many components of the mixtures as shown on the structures in Figures 1−4. The TOCSY spectra were especially useful since they showed chains of protons which were in the same molecule.[26]

^{1}H NMR spectra were run on the extracts in dimethyl-d_6 sulfoxide (DMSO) at 600 MHz. This solvent has no exchangeable hydrogens and slows the exchange of amide NH protons enough that their peaks appear separately and provide additional information. COSY, TOCSY, and HSQC spectra were also run in DMSO on samples 4 and 5 to aid in making the assignments. ^{13}C NMR spectra were measured on all the extracts in HFIP for comparison with previously obtained spectra of polymers in this solvent.

Figure 3 gives chemical shifts derived from spectra of polymers for the repeating units and simple model compounds such as HMPA, diacetyl-HMPA, and dibenzoyl-HMPA for the end groups in linear oligomers and polymers. The excellent ^{13}C NMR studies on nylon 66 in 2,2,2-trifluoroethanol/chloroform-*d* by Mathias et al.[27] were very helpful in assigning peaks in the present work. The amine and carboxyl end group shifts vary with pH,[27] and at the end of these polymerizations, the shifts indicated that the amine end groups were almost entirely protonated, whereas there was an excess of free carboxyl end groups. This might be expected since acetic or benzoic acid was added for capping in most cases (see cap column in Table

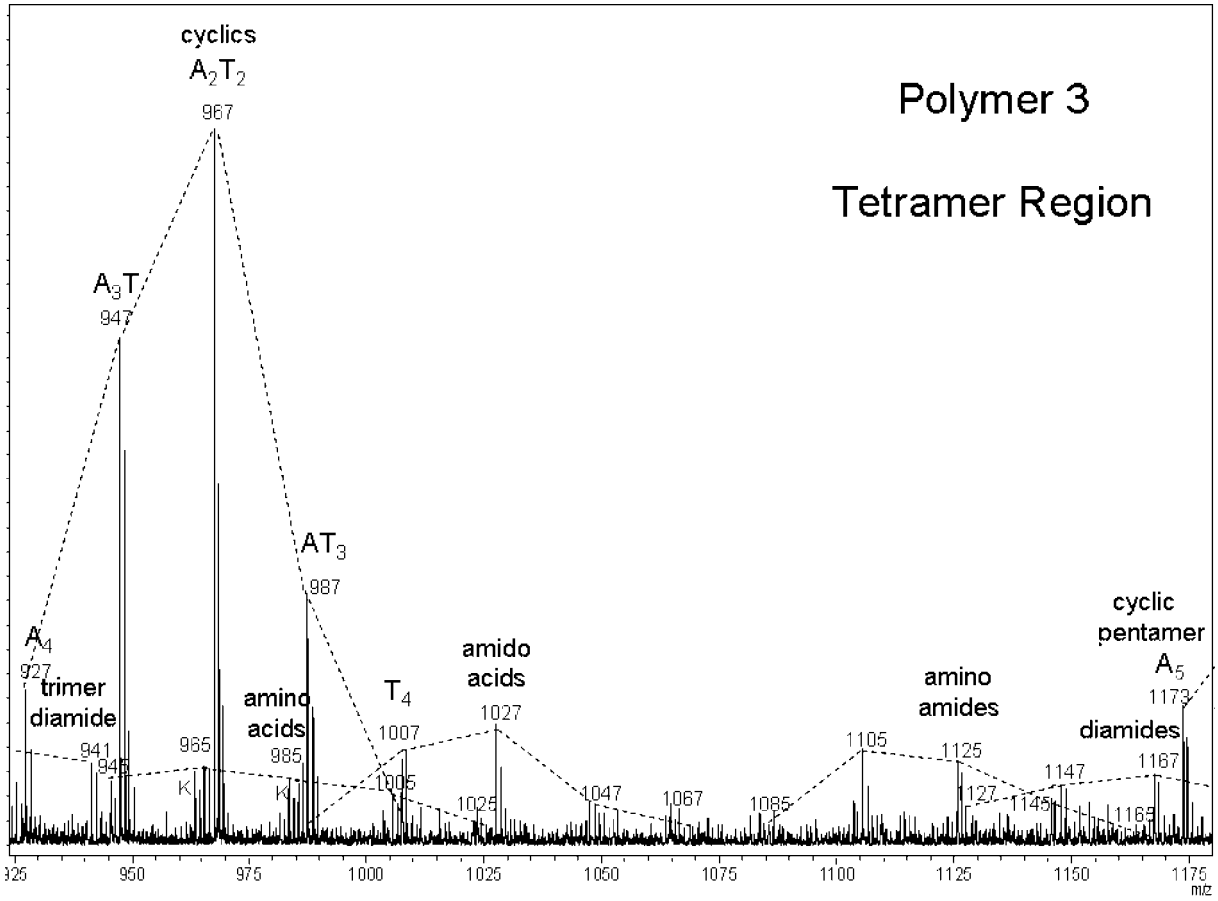

Figure 7. MALDI−TOF mass spectrum of polymer 3 with the DOF matrix, tetramer region.

Table 3. Mole Percents of Extract Components from ^{1}H NMR Spectra in DMSO-d_6[a]

				small cyclic oligomers																
	input %			monomers	dimers						trimer	internal units			end groups in linear oligomers					
nos.	**A**	**I**	**T**	$\mathbf{A_1}$	$\mathbf{A_2}$	**AI**	**AT**	$\mathbf{I_2}$	**IT**	$\mathbf{T_2}$	$\mathbf{T_3}$	$\mathbf{A_L}$	$\mathbf{I_L}$	$\mathbf{T_L}$	**Ac**	**Bz**	$\mathbf{A_{end}}$	$\mathbf{I_{end}}$	$\mathbf{T_{end}}$	$\mathbf{HMDA_{end}}$
1	100	0	0	25	*	-	-	-	-	-	-	75	-	-	-	-	0	-	-	0
2	40	0	60	17	*	-	13	-	-	3	1	48	-	7	10	tr	tr	-	1	tr
3	30	0	70	17	*	-	8	-	-	3	1	32	-	9	11	tr	2	-	11	5
4	10	20	70	7	*	7	3	3	7	4	1	16	6	6	19	tr	tr	1	10	10
5	0	30	70	-	-	-	-	2	8	4	8	-	16	12	-	16	-	12	16	4
6	100	0	0	58 ($\mathbf{X_1}$)	16($\mathbf{X_2}$)	-	-	-	-	-	-	26 ($\mathbf{X_L}$)	-	-	-	-	0	-	-	-

[a] Key (*) = lumped with $\mathbf{A_L}$; (-) not possible; (tr) present, but less than 0.5%.

1). A complicating factor which would reduce the excess of carboxylic acid over amine was the decarboxylation of terephthalic and isophthalic end units to give benzamide end groups (discussed below), which occurred to a small extent in all cases in which these aromatic diacids were used.

It was easy to identify $\mathbf{T_{end}}$ and $\mathbf{I_{end}}$ units since they lacked the symmetry of the other aromatic units. The shifts of the end groups other than Ac and Bz varied from sample to sample as the pH varied.[27]

The only cyclic monomers detected by mass spectrometry were $\mathbf{A_1}$ (Figure 1) and $\mathbf{X_1}$ (Figure 3), but mass spectra indicated that all of the cyclic dimers and trimers possible from the diacids and diamines in the feed were major components of the extracts. The NMR spectra of cyclic species larger than dimers had spectra very close to each other and to those of the linear polymer, so the species with chemical shifts differing from the linear polymer were the cyclic monomers and dimers. The spectra of extract 1 showed that dimer $\mathbf{A_2}$ had shifts very close to the linear species,[27] whereas dimer spectra were different when aromatic rings were present. Figure 8 shows the ^{1}H NMR spectrum of extract 2 as an example.

It helped greatly in making assignments that the only cyclic dimer in sample 1 was $\mathbf{A_2}$, the only cyclic dimers in samples 2 and 3 were $\mathbf{A_2}$, **AT,** and $\mathbf{T_2}$, and the only cyclic dimers in sample 5 were $\mathbf{I_2}$., **IT,** and $\mathbf{T_2}$. Sample 4 then added the last cyclic dimer, **AI**. The pronounced upfield shifts of protons opposite terephthalic units in cyclic dimers **AT**, **IT**, and $\mathbf{T_2}$ were very helpful in identifying them; isophthalic acid units are more bent than terephthalic acid units (120 instead of 180° between the two aromatic substituents) and caused much smaller NMR shifts in the dimers. Weak TOCSY peaks between the end CH_2 protons in the hexamethylene chains of dimers **IT**, **AT**, and **AI** helped to define their hexamethylene chains, and TOCSY peaks between amide NH protons and aromatic protons ortho to the amide grouping helped to show which hexamethylene chains went with which aromatic groups in the dimers.

The most difficult assignments were for the **I** units. Figure 9 shows a section of the TOCSY spectrum of extract 4 with crosspeaks between isophthalic 2 (vertical) and 5 (horizontal) protons, with the assignments of the six main types of I units. These TOCSY peaks, in an isolated area of the spectrum, are absent in the COSY spectrum since the para coupling constant

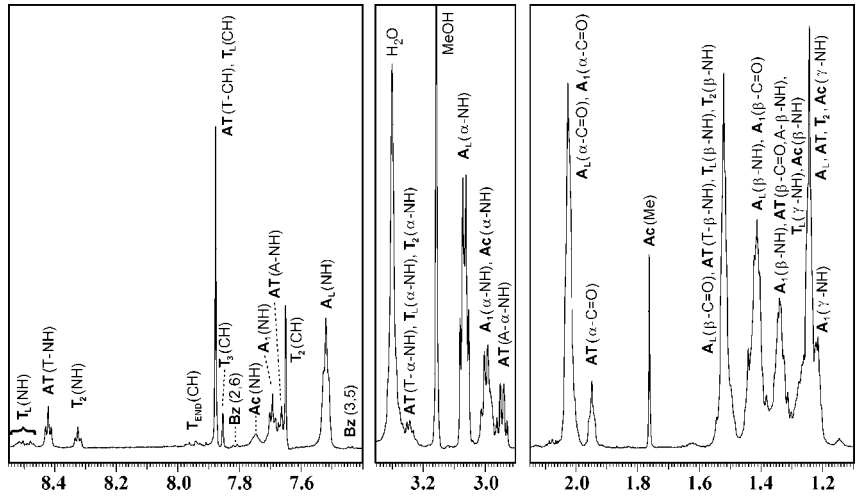

Figure 8. ^{1}H NMR spectrum of sample 2 in DMSO-d_6.

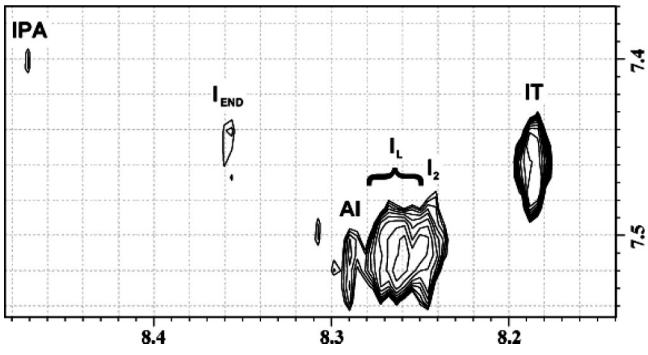

Figure 9. TOCSY crosspeaks between the H-2 (vertical scale) and H-5 (horizontal scale) protons of the I units in sample 4, in DMSO-d_6.

between the 2 and 5 protons is zero. The peaks are elongated in the vertical direction because the 5 protons have ortho coupling constants of about 8 Hz to the 4 and 6 protons, whereas the 2 protons have meta coupling constants of only about 2 Hz to the 4 and 6 protons. The **I$_{end}$** assignment was clear because only in the **I$_{end}$** groups are the couplings to protons 4 and 6 different (peaks not shown). The **IPA** assignment was verified by running a spectrum on an authentic **IPA** sample.

The ^{13}C NMR spectra of all of the extracts from polymers with aromatic diacids in the feed showed peaks at δ127.05, 129.7, 133.35, and 133.5 from benzamide end groups as in extract 10, where these peaks are stronger and benzamides are known to be present from capping with benzoic acid in the polymerization. These benzoyl groups presumably came from thermal decarboxylation of terephthalic or isophthalic groups, either in the diacids themselves or after amide formation on one end. As decarboxylation produces inert end groups, it reduces the polymer molecular weight.

Extra peaks for Ac carbonyl carbons in the extract ^{13}C NMR spectra in HFIP at δ175.6 (about 30% of the expected peaks at δ 175.5) were probably due to relatively large amounts of *cis*-amide in this solvent.

After making assignments of most of the peaks of the cyclic and linear species in the extract samples, it was possible to quantitate the amounts of many of the components of these samples from integration of the ^{1}H NMR spectra as summarized in Table 3. Not included in Table 3 are starting materials **IPA** and **TPA**, shown by NMR absorptions (e.g., Figure 9) to be present in trace amounts in some of the extracts. The analysis was accurate for compounds like **IT** which had nonoverlapping peaks but approximate for those which had none. The main peaks used were as follows: **A$_1$**, 2.99 − **Ac**; **AI**, 8.29; **AT**, 1.95; **I$_2$**, 3.35; **IT**, 8.20; **T$_2$**, 7.66; **T$_3$**, 7.86; **A$_L$**, 3.06; **I$_L$**, 8.28; **T$_3$**, 7.85; **Ac**, 1.76; **Bz**, 7.82; **A$_{end}$**, 2.18; **I$_{end}$**, 8.36; **T$_{end}$**, 7.95; **HMDA$_{end}$**, 2.73.

It is clear from Table 3 that the relative amounts of incorporation of the acids into dimers under these conditions is adipic > isophthalic > terephthalic. For example, in extract 2, with a feed of 60% **TPA** and 40% adipic acid, if the incorporation rates were the same, the **AT/ T$_2$** ratio would be 57/43, whereas it is observed as 81/19 (**A$_2$** could not be distinguished from **A$_L$** by NMR, so it could not be included here). Similarly, the calculated **I$_2$/IT/T$_2$** ratios for extract 4 and 5 are 5/35/60 and 9/42/49, respectively, whereas their observed ratios from Table 3 are 21/50/29 and 14/57/29, respectively. These results are presumably due to the great flexibility of adipic acid and the bent nature of **IPA** compared to **TPA**.

Conclusions

Our NMR and mass spectroscopy study of polyamides from mixtures of adipic, isophthalic, and terephthalic acids with hexamethylenetetramine and *m*-xylylenediamine, like those of Kricheldorf with other polymers,[1−5] showed that significant amounts of small cyclic oligomers (especially cyclic dimers and trimers) were formed. The methanol extraction procedure we used concentrated the small linear and cyclic oligomers sufficiently that we could find ^{1}H NMR peaks characteristic of the cyclic monomers and dimers and learn their relative amounts by integration of the ^{1}H NMR spectrum. The mass spectra showed that the extraction procedure was selective for the smallest cyclics. The acid found most in small cyclics was adipic and that found the least was terephthalic. All polymers containing terephthalic and/or isophthalic acid units contained linear oligomers with benzoyl end groups from thermal decarboxylation, presumably lowering the polymer molecular weight and affecting its other properties.

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References and Notes

(1) Kricheldorf, H. R. *Macromol. Symp.* **2003**, *199*, 15.
(2) Kricheldorf, H. R.; Al Masri, M.; Schwarz, G. *Macromolecules* **2003**, *36*, 8648.
(3) Kricheldorf, H. R.; Rabenstein, M.; Maskos, M.; Schmidt, M. *Macromolecules* **2001**, *34*, 713.
(4) Kricheldorf, H. R.; Schwarz, G. *Macromol. Rapid Commun.* **2003**, *24*, 359.

(5) Kricheldorf, H. R.; Al Masri, M.; Schwarz, G. *J. Macromol. Sci. A, Pure Appl. Chem.* **2006**, *43*, 1.
(6) Goeltner, W. In *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*; Scheirs, J., Long, T. E., Eds.; Wiley: New York, 2003; pp 459−465.
(7) Sibila. J. P.; Murthy, N. S.; Gabriel, M. K.; McDonnell, M. E.; Bray, R. G.; Curran, S. A. In *Nylon Plastics Handbook*; Kohan, M. I., Ed.; Hanser/Gardner Publications: Cincinnati, OH, 1995; pp 75−77.
(8) Aharoni, S. M. *n-Nylons: Their Synthesis, Structure, and Properties*; Wiley: New York, 1997; pp 210−213 and 000508−511.
(9) Nelson, W. E. *Nylon Plastics Technology*; Newnes-Butterworths: Boston, MA, 1976; pp 46−48.
(10) Stetter, H.; Marx, J. *Angew. Chem.* **1957**, *69*, 439.
(11) Stetter, H.; Marx, J. *Liebigs Ann. Chem.* **1957**, *607*, 59.
(12) Stetter, H; Marx-Moll, L. *Chem. Ber.* **1958**, *91*, 677.
(13) Zahn, H; Kunde, J. *Angew. Chem.* **1957**, *69*, 713.
(14) Zahn, H; Dietermann, H. *Chem. Ber.* **1957**, *90*, 2176.
(15) Zahn, H; Miro, P.; Schmidt, F. *Chem. Ber.* **1957**, *90*, 1411.
(16) Zahn, H.; Kunde, J. *Angew. Chem.* **1958**, *70*, 189.
(17) Zahn, H.; Kunde, J. *Liebigs Ann.Chem.* **1958**, *618*, 158.
(18) Zahn, H.; Schmidt, F. *Chem. Ber.* **1959**, *92*, 1381.
(19) Zahn, H.; Kunde, J.; Heidemann, G. *Makromol. Chem.* **1961**, *43*, 220.
(20) Zahn, H. *Bull. Inst. Textile Fr.* **1963**, *106*, 557.
(21) Zahn, H.; Kusch, P. *Chem. Ber.* **1965**, *98*, 2588.
(22) Kusch, P.; Zahn, H. *Angew. Chem.* **1965**, *77*, 720.
(23) Stetter, H.; Marx-Moll, L; Rutzen, H. *Chem. Ber.* **1958**, *91*, 1775.
(24) Weidner, S.; Just, U.; Wittke, W.; Rittig, F.; Gruber, F; Friedrich, J *Int. J. Mass Spec* **2004**, *238*, 235.
(25) Somogyi, A; Elandaloussi, E. H.; Hall, D. E.; Padias, A. B.; Bates, R. B; Hall, H. K, Jr *Macromolecules* **2007**, *40*, 5311.
(26) Jacobsen, N. E. *NMR Spectroscopy Explained*; Wiley-Interscience: Hoboken, NJ, 2007.
(27) Davis, R.; Steadman, S.; Jarrett, W.; Mathias, L. *Macromolecules* **2000**, *33*, 7088.
(28) Akiyama, T.; Tsukamoto, C, Chiaki, N, Nanpei, M.; Ozeki, T Jpn. Kokai Tokkyo Koho JP 48084854, **1973**.

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