Macrocyclic Aramids (2*n*-Aza[2$_n$]paracyclophane-2*n*-ones): New Intermediates for the Synthesis of *p*-Aramids

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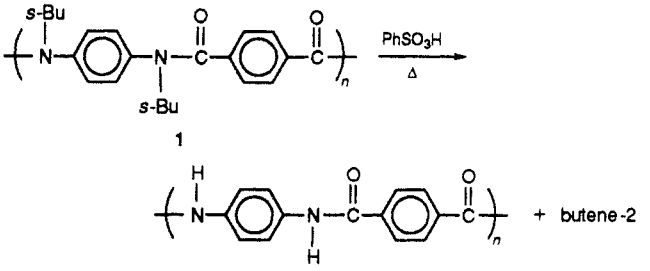
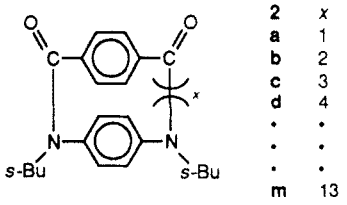
ABSTRACT: An easy route to a new class of 2*n*-aza[2$_n$]paracyclophane-2*n*-ones, *N*-substituted *para*-oriented cyclic aromatic amide (cycloaramid) oligomers, is described. The bulky diamine *N*,*N*′-di-*sec*-butyl-*p*-phenylenediamine is condensed with terephthaloyl chloride at elevated temperature in *o*-dichlorobenzene to provide a high yield of *N*,*N*′-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic oligomers (from dimer to tridecamer). (There is evidence presented for the presence of cyclic unimer (a single repeat unit), an amide analog of [2.2]paracyclophane, in the reaction product!) The cyclization is favored by the *cis* conformation of the *N*-substituted amide bonds present in the growing chain. Ring-opening polymerization of these new cycloaramids to high molecular weight linear polymers can be effected in the melt phase with highly nucleophilic catalysts such as 1,3-dialkylimidazole-2-thiones, especially when an acid cocatalyst is employed. The *N*-substituted polymers yield crystalline films and fibers with an axial repeat length which can only be explained by an unexpected *trans* conformation of the amide bonds. The facile synthesis of other macrocyclic amides by the steric control of macrocyclization by *N*-substitution of the amide bond is also described.

Introduction

In the course of extending our work on the preparation of aromatic polyamide (aramid) foams *via* the pyrolysis of *N*-alkyl-substituted aromatic polyamides,[1] we discovered a surprisingly high level of a low molecular weight fraction in one of the *para*-oriented precursors, poly(*N*,*N*′-di-*sec*-butyl-*p*-phenyleneterephthalamide) (1). HPLC and



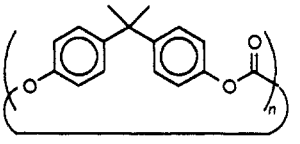
fast atom bombardment mass spectrometry (FAB MS) analyses of this material showed distinct low molar mass species assigned to be cyclic oligomers (2*n*-aza[2$_n$]-paracyclophane-2*n*-ones!) containing 2–13 repeat units (2). Potassium ion dissociation mass spectrometry (KID MS) and time-of-flight secondary ion emission mass spectrometry (TOF SIMS) showed similar results but were limited to 4 and 6 repeat units, respectively.



2	*x*
a	1
b	2
c	3
d	4
•	•
•	•
•	•
m	13

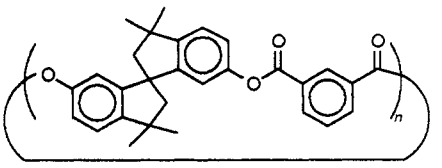
The work reported here was aimed at confirming the surprising cyclic nature of these oligomers and increasing their yields to a synthetically useful range. A further aim was to explore conditions for the ring-opening polymerization (ROP) of this novel class of macrocycles.

It has already been pointed out[2] that ROP of aromatic cyclic oligomers could offer unique advantages in the manufacture of important products such as molding and composite resins. The all-*para*-oriented structures in our work differ significantly from those recently reported[2–6] by workers at General Electric Co. All of the previously reported aromatic cyclic oligomers were prepared from intermediates having severe kinks and orientation of functional groups which would facilitate cyclic oligomer formation. The isopropylidene connecting link operates this way in the synthesis of macrocyclic aromatic carbonate precursors (*e.g.*, 3) for the preparation of aromatic poly-



3 (*n* = 2–20)

carbonates.[3] For the synthesis of other macrocyclics such as esters (4)[4] and amides (5)[5] the substitution of a spiro-fused center for the isopropylidene group led to increased yields. This was rationalized by the rigidly held orthogonal functional groups in the spiro(bis)indan system. It should be noted that both 4 and 5 contain the *meta*-oriented isophthaloyl moiety. Substitution of the *para*-oriented terephthaloyl moiety for the *meta* gave very low yields (<30% when only 10% *para* was used in synthesis of a mixed macrocycle of 4, and only about 5% when the *para* isomer was substituted for the *meta* isomer in the synthesis of the *para* analog of 5).



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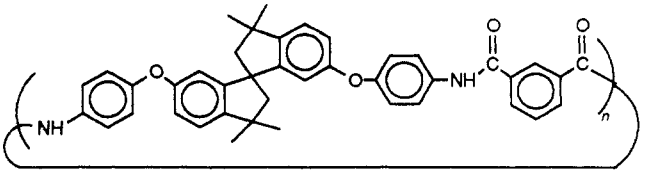

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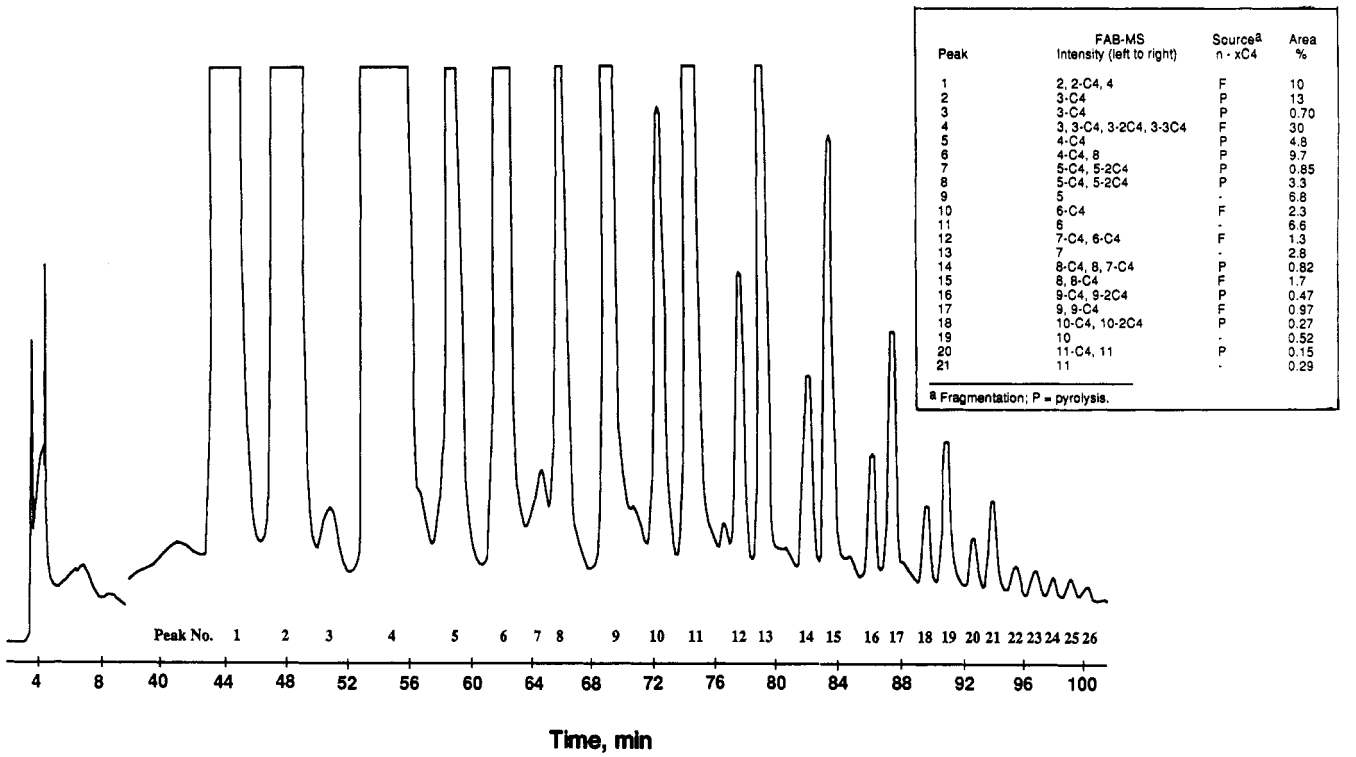


Peak	FAB-MS Intensity (left to right)	Source[a] n - xC4	Area %
1	2, 2-C4, 4	F	10
2	3-C4	P	13
3	3-C4	P	0.70
4	3, 3-C4, 3-2C4, 3-3C4	F	30
5	4-C4	P	4.8
6	4-C4, 8	P	9.7
7	5-C4, 5-2C4	P	0.85
8	5-C4, 5-2C4	P	3.3
9	5	-	6.8
10	6-C4	F	2.3
11	6	-	6.6
12	7-C4, 6-C4	F	1.3
13	7	-	2.8
14	8-C4, 8, 7-C4	P	0.82
15	8, 8-C4	F	1.7
16	9-C4, 9-2C4	P	0.47
17	9, 9-C4	F	0.97
18	10-C4, 10-2C4	P	0.27
19	10	-	0.52
20	11-C4, 11	P	0.15
21	11	-	0.29

[a] Fragmentation; P = pyrolysis.

Figure 1. Reverse-phase HPLC trace of *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic oligomers from condensation of *N,N'*-di-*sec*-butyl-*p*-phenylenediamine and terephthaloyl chloride at 0.055 M in refluxing ODCB (see Experimental Section for conditions).

In sharp contrast to these results, we have found that both reactants can contain functional groups separated only by *p*-phenylene moieties and still lead to high yields of cyclic oligomers (**2**). Results on analogs of **2** containing (1) 4,4'-diphenyldicarbonyl, 2,6-naphthalenedicarbonyl, and oxy-4,4'-diphenyldicarbonyl moieties, respectively, in place of the terephthaloyl moiety and (2) 1-cyanoprop-2-yl in place of *sec*-butyl are also presented. Further, results are presented showing the ROP of the all-*para*-oriented cyclic oligomers (**2**).

Results and Discussion

The classical approach of the condensation of monomers at low concentrations has proven remarkably successful in the synthesis of high yields of the cycloaramid mixture **2**.[7] The addition of *N,N'*-di-*sec*-butyl-*p*-phenylenediamine and terephthaloyl chloride solutions in *o*-dichlorobenzene (ODCB) dropwise over a few hours to ODCB to a final concentration of 0.055 M, followed by extended heating at reflux, yielded up to *ca.* 86% of **2**. The yield was measured by evaporation of the ODCB followed by Soxhlet extraction of the residue with toluene. The toluene fraction (86%) showed virtually no high molecular weight polymer when analyzed by GPC. This material exhibited an η_{inh} of 0.058 dL/g (in concentrated H_2SO_4 at 30 °C) versus 0.22 dL/g for the insoluble polymeric fraction.[8] With the exception of cyclic trimer, the GPC procedure employed (see Experimental Section for details) was not effective in resolving the mixture into its components. Better resolution was obtained when reverse-phase HPLC was employed, giving relatively efficient separation of the complex mixture of cyclic species. (Inexplicably, some of the cyclic tetramer and cyclic octamer eluted very early.) The chromatogram (Figure 1) shows a multiplicity of fractions, 21 of which were collected and analyzed by FAB MS (Figure 1, insert table). Each fraction exhibited a mass corresponding to a homologue of **2** or the same minus one or more *sec*-butyl groups. The loss of *sec*-butyl groups occurred during both the preparation (Scheme I, pathways A and B) and FAB MS analysis (pathway C) of the material. When the loss of *sec*-butyl takes place during the preparation, it is easily determined by an examination of the FAB mass spectrum of small HPLC peaks associated with the larger peaks for the fully *N*-substituted cycloaramids. The more polar, partially substituted cycloaramids elute before their fully substituted analogs and are indicated in Figure 1, insert table, by 2–*x*C4 to 11–*x*C4 [cyclic dimer to cyclic undecamer minus one or more (*x*) *sec*-butyl groups as butene (C4)]. When the partially substituted cycloaramids arise due to fragmentation of the fully *N*-substituted materials, they are indicated by 2–*x*C4 to 10–*x*C4 after their fully substituted precursors. (Note: 3–C4, 4–C4, and 5–C4 have two different retention times due possibly to stereoisomerism.) As can be seen from the peak areas, the cyclic trimer is the dominant homologue. To fully characterize the structure of the cycloaramids and conduct other studies, preparative HPLC was carried out and is described below.

Preparative HPLC of Cycloaramids 2 and FAB MS of Fractions. Normal-phase HPLC of the above cycloaramid mixture yielded seven fractions of which the first three were very clean by FAB MS showing peaks only at *m/z* 701, 1051, and 1402, corresponding to cyclic dimer, trimer, and tetramer, respectively. The cyclic dimer (*ca.* 2 wt % of the total isolated yield) is crystalline and exhibits two polymorphs with DSC melting points of 277 °C (ΔH = 32 J/g) and 310 °C (ΔH = 33 J/g), respectively. On the other hand, the cyclic trimer, the major homolog isolated (*ca.* 73 wt %), and the cyclic tetramer are glasses exhibiting macroscopic melting points in the range of *ca.* 260–270 °C. FAB MS peaks for the remaining fractions indicate incomplete resolution, and details on their composition are shown in the Experimental Section.

Structure of Cycloaramids 2. The ^{1}H NMR spectrum (DMSO-d_6 at 120 °C) of the cyclic dimer (**2b**) is shown in

Scheme I

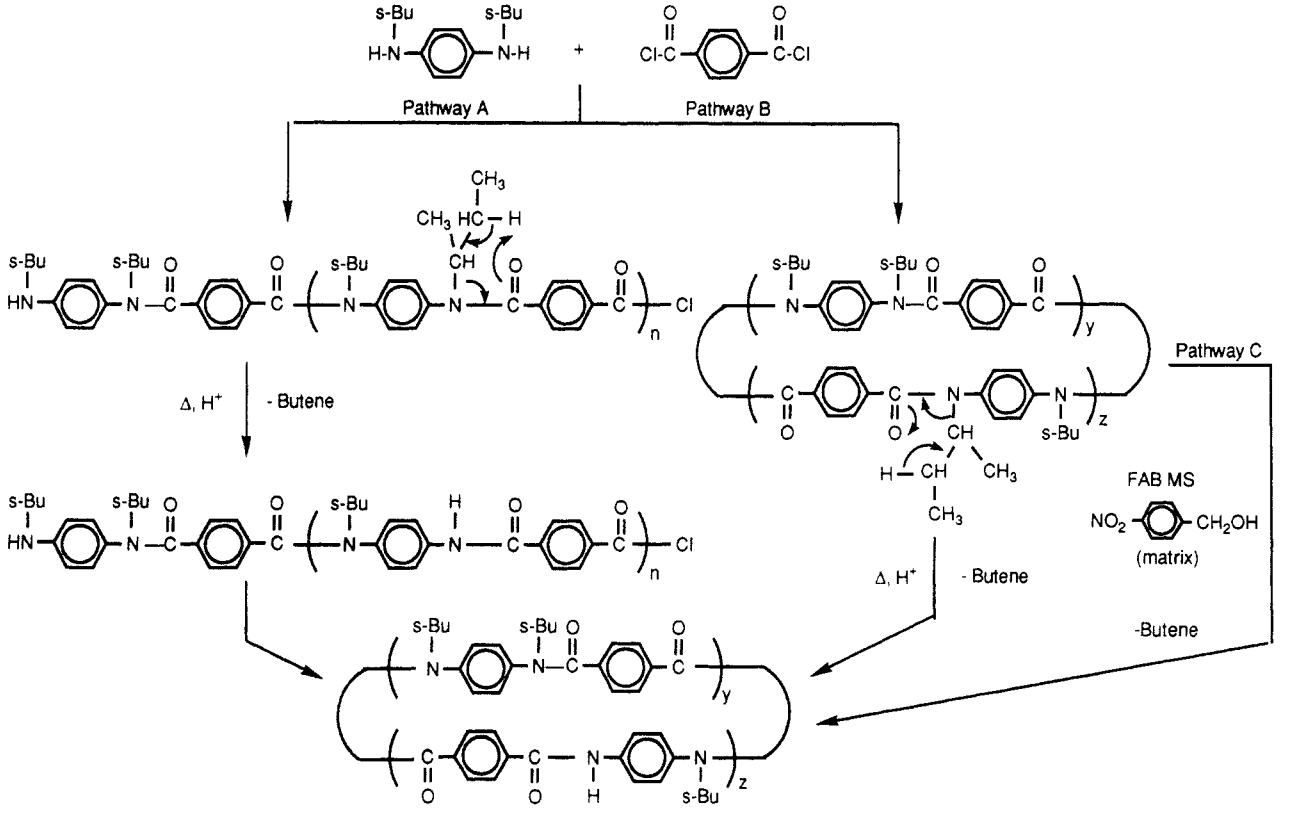
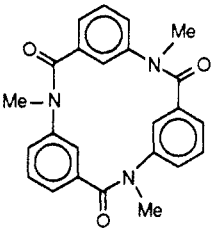


Figure 2. (At room temperature, the spectrum exhibited featureless resonances due to the lack of flexibility in the structure.) No end groups associated with linear oligomers are detectable in the spectrum. Signals for the methyl groups attached to the methine carbon are substantially more complex than the doublet (δ 1.05, J = 9.0 Hz) found in an acyclic model compound, *N,N'*-dibenzoyl-*N,N'*-di-*sec*-butyl-*p*-phenylenediamine. When Lorentzian to Gaussian enhancement was applied, the apparent complex "triplet" (1.0 ppm) in Figure 2 became a 15-line pattern with one line of double intensity (Figure 2, insert a). When the methine proton was decoupled, the resolution-enhanced methyl group signal appeared as 8 lines (Figure 2, insert b). Further, a 2-D *J*-resolved spectrum (Figure 3) showed that the methyl protons adjacent to the methine protons, just as in the model compound, are coupled only to the methine protons. If the *sec*-butyl group were the only stereogenic element involved, the collection of isomeric cyclic dimers would generate, at most, 8 different methyl groups. The number of stereoisomers increases dramatically as other stereogenic elements (*e.g.*, C–N amide bond rotors) become important to the time frame of the measurement. Thus, it would appear that the 8 lines in Figure 1, insert a, reflects all 8 possible methyl groups. The ^{1}H NMR spectrum for the cyclic trimer (**2c**) is shown in Figure 4 and is consistent with a cyclic structure. However, even after Lorentzian to Gaussian enhancement (Figure 4, insert a) and decoupling of the methine protons (Figure 4, insert b), only partial resolution of the adjacent methyl groups was realized. The ^{13}C NMR spectra of the cyclic dimer and trimer were in agreement with the ^{1}H NMR data showing no linear material.

Effect of *N*-Substitution on the Formation of Cycloaramids. In the Kevlar aramid polymerization involving the condensation of *p*-phenylenediamine (PPD) and terephthaloyl chloride (TCl), the incipient amide bonds are believed to be *transoid* and result in linear polymer (PPTA) with virtually no cyclic oligomers. On the other hand, the use of *N*-substituted *p*-phenylenediamine for PPD probably results in the formation of *cis* amide bonds. This assertion is based on literature reports which show that in *N*-substituted aromatic amides such as *N*-methyl-[9] and *N*-allylbenzanilide,[8c] the amide bonds exhibit a *cis* configuration in the crystalline state, and in solution in the former case. The *cis* amide preference in *N*-methyl amides with two aromatic groups is general.[10] Even more instructive is that the metacyclophane 1,9,17-trimethyl-1,9,17-triaza[2.2.2]metacyclophane-2,10,18-trione (**6**)[11] exhibits *cisoid* amide bonds in the crystalline



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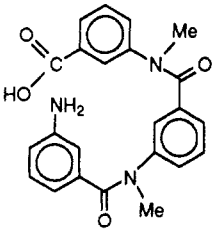

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state. The presence of *cis* amide bonds in a growing chain would seem to predispose the system toward formation of macrocycles since there would be a tendency for the chain to fold back upon itself. This would appear to be the case for the acyclic amino acid **7**, which led to **6** after a final *N*-methylation. Thus, during the condensation of an *N*-substituted PPD with TCl, formation of both linear polymer and cyclic oligomers is expected, as found in this work. The proposed steric guiding by *cis* amide bonds toward formation of macrocycles is analogous to the *gem*-dimethyl effect exerted in certain intramolecular Diels–Alder reactions where large enhancements in rates have been observed.[12]

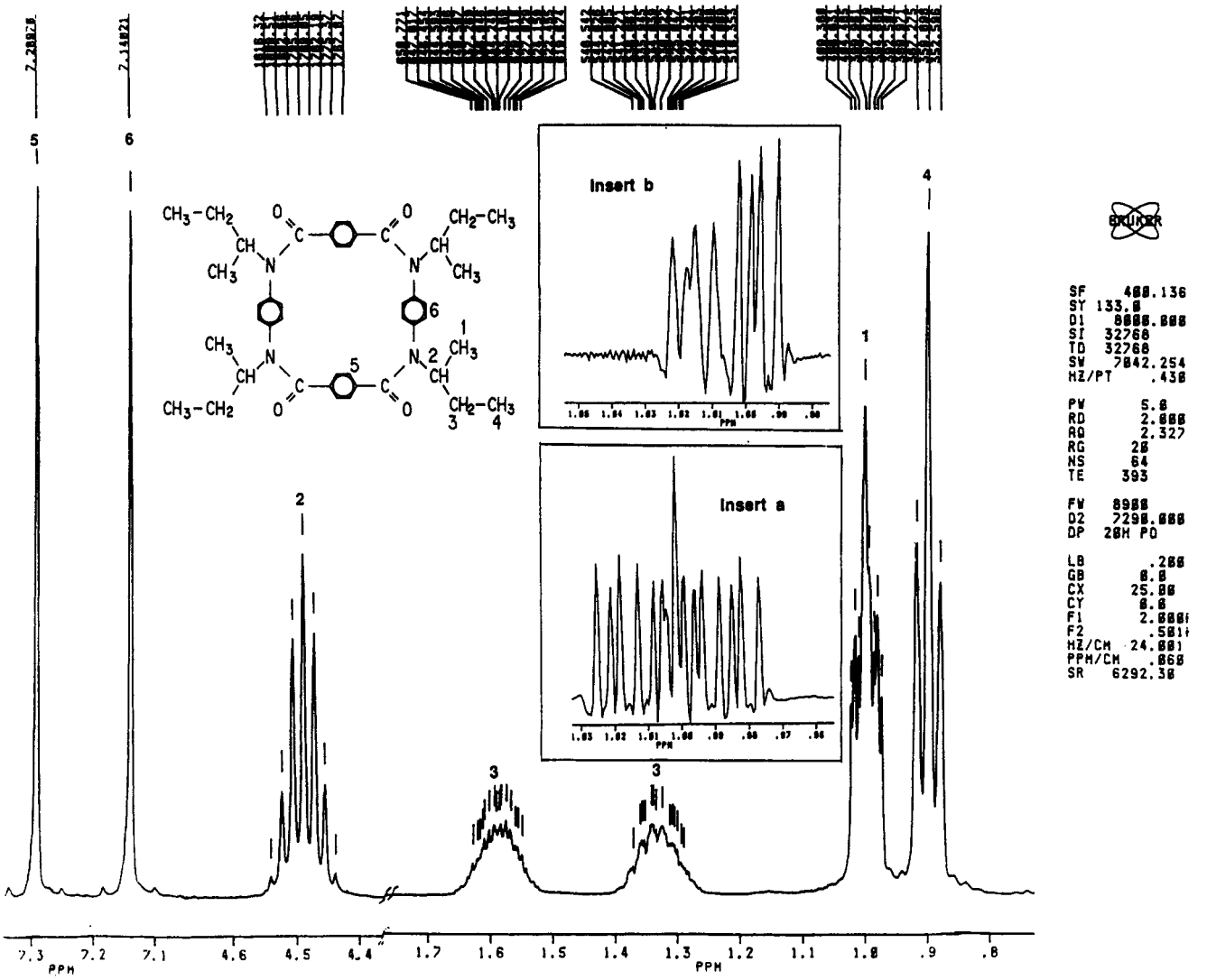


Figure 2. Proton NMR spectrum at 400 MHz of *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic dimer: (insert a) Lorentzian to Gaussian resolution enhanced ^1H NMR spectrum of methyl group adjacent to methine carbon in *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic dimer; (insert b) Lorentzian to Gaussian resolution enhanced ^1H NMR spectrum of methyl group with the adjacent methine proton decoupled.

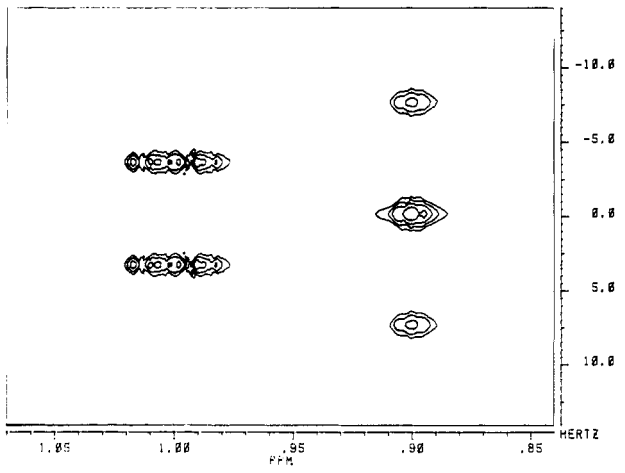


Figure 3. Proton NMR 2-D *J*-resolved spectrum of *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic dimer.

An Amide Analog (2a) of [2.2]Paracyclophane? The FAB mass spectrum of the unresolved cyclic oligomer mixture **2** (2*n*-aza[2$_n$]paracyclophane-2*n*-ones) invariably shows the presence of a peak with a mass close to that of a single repeat, $C_{22}H_{26}N_2O_2$, with a calculated exact mass of 350.1994. This homolog would correspond to a highly strained amide analog of [2.2]paracyclophane. The ion at *m/z* 351 was accurately mass measured in duplicate experiments; we obtained masses 351.1769 and 351.1782 against an internal reference, and masses 351.2365 and 351.2357 against an external reference. The difference between the measured and theorectical values, ±0.030 amu's, is too large to be unambiguous. (In contrast, the calculated and measured masses for the cyclic dimer were 701.4066 and 701.4037, respectively, which are in excellent agreement.) However, a B/E-Link Scan MS experiment, where the mass 351 ion was selected out and allowed to fragment spontaneously, shows a qualitatively different fragmentation pattern than the 701 ion (Table I). It might be expected for the fragmentation pattern of a highly strained cyclic unimer to be different from that of a less strained cyclic dimer. These results, at least, show that the peak at *m/z* 351 is not a doubly charged cyclic dimer and are consistent with a [2.2]paracyclophane analog structure. In addition to the FAB MS data, a direct probe EI MS experiment on the mixture of homologs showed a peak at *m/z* 350 and a peak at *m/z* 322 (parent ion minus CO). All of the data, taken together with the relatively good accurate mass results, suggest that we have probably prepared an amide analog (**2a**) of [2.2]paracyclophane, but to date we have not obtained any other corroborating evidence for its presence in the mixture of cycloaramids **2**.

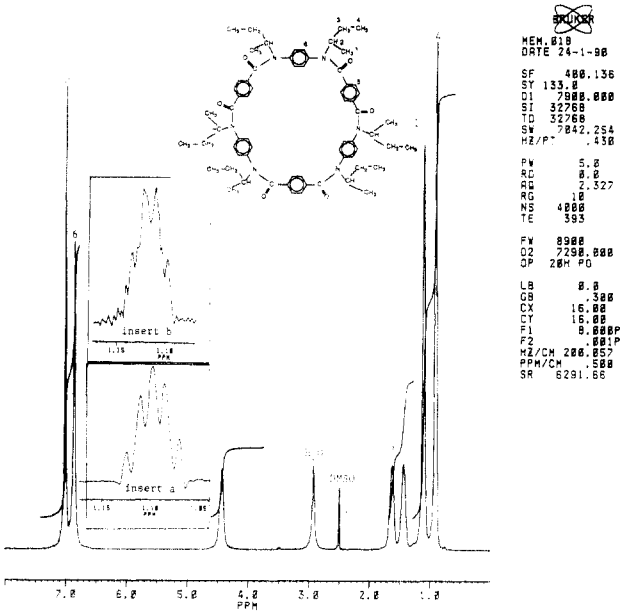
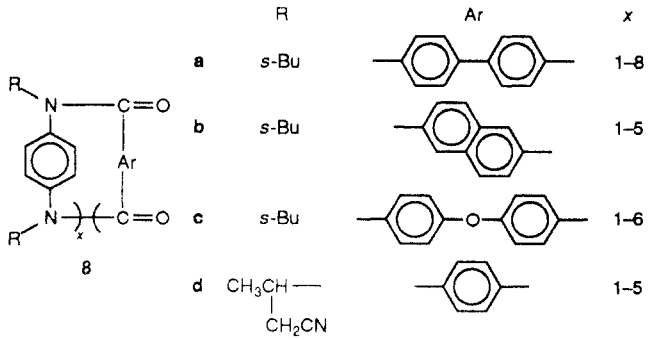


Figure 4. Proton NMR spectrum at 400 MHz of *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic trimer: (insert a) Lorentzian to Gaussian resolution enhanced ^1H NMR spectrum of methyl group adjacent to methine carbon in *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic trimer; (insert b) Lorentzian to Gaussian resolution enhanced ^1H NMR spectrum of methyl group with the adjacent methine proton decoupled.

Table I. FAB MS B/E-Link Scan: Spontaneous Metastable-Ion Decomposition

measd *m/z*	calcd *m/z*	assignment
	mass 351 selected	
351.0	351.2	M + 1 of $C_{22}H_{26}N_2O_2$
323.2	323.1	(M + 1) − CO
294.2	294.1	(M + 1) − C_4H_9
280.5	280.1	(M + 1) − C_4H_9N
252.1	252.1	(M + 1) − (C_4H_9 + C_3H_6)
222.1	222.1	(M + 1) − (C_4H_9N + C_4H_9 + H)
209.0	209.1	(M + 1) − $2C_4H_9N$
180.3	180.1	(M + 1) − ($2C_4H_9N$ + CHO)
	mass 701 selected	
701.9	701.4	M + 1 of $C_{44}H_{52}N_4O_4$
672.8	672.4	(M + 1) − CHO
645.8	645.3	(M + 1) − C_4H_8
615.7	616.3	(M + 1) − (C_4H_8 + CHO)
589.6	589.3	(M + 1) − $2C_4H_8$
568.6	568.0	(M + 1) − $C_8H_5O_2$
533.4	533.2	(M + 1) − $3C_4H_8$
483.6	484.0	(M + 1) − ($C_8H_5O_2$ + C_4H_8 + CO)
455.5	456.0	(M + 1) − ($C_8H_5O_2$ + C_4H_8 + 2CO)

Other Cycloaramids. The formation of other cycloaramids is under present investigation and will be the subject of future communications. For example, we have found that other *para*-oriented cycloaramids (**8a–d**) can



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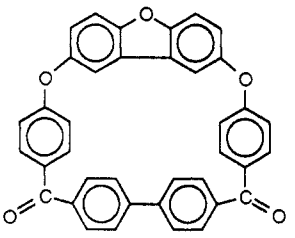
be prepared under conditions similar to those used for the preparation of a cyclic oligomer mixture of the type **2**. Just as with **2**, the [2.2]paracyclophane analog of each homologous series needs to be confirmed or ruled out. The presence of a FAB MS peak in the mixture **8a** corresponding to the [2.2]paracyclophane analog (x = 1) is particularly surprising since in this case severe strain would be expected. The mixed phenylene/biphenyl [2.2]-paracyclophane is not known, making it imperative that corroborative evidence to support the analogous homolog of **8a** (x = 1) be found. Nevertheless, there is precedence for a highly strained and contorted 4,4'-bibenzoyl moiety in the macrocycle **9** wherein the normally collinear carbonyl to aryl bonds were reported to subtend instead at an angle 65°.[13]



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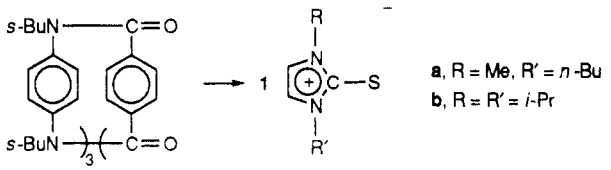
Ring-Opening Polymerizations of Cycloaramids 2. We have succeeded in the ring-opening polymerization (ROP) of *N,N'*-di-*sec*-butyl-*p*-terephthalamide oligomers. Using the cyclic trimer **10** as a model for studying the ROP to linear polymer, we have found that the highly nucleophilic 1,3-dialkylimidazole-2-thiones **11**[14a,b] are ef-



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fective catalysts. For example, when the cyclic trimer was heated at 265 °C with 1-methyl-3-*n*-butylimidazole-2-thione (**11a**)[14b] as the initiator, ROP occurred to give a polymer with an η_{inh} of 0.6 dL/g (concentrated H_2SO_4 at 30 °C) versus 0.04 dL/g for the cyclic trimer. However, the polymer contained residual **10** and other oligomers. Addition of an acidic cocatalyst, *e.g.*, phenylphosphinic acid (**12**), resulted in complete conversion but also catalyzed appreciable *N*-dealkylation of the polymer as evidenced by N–H absorption in the FTIR (3320 cm^{-1}) and ^1H NMR spectra (peaks of nearly equal intensity at 10.14 and 10.34 ppm in DMSO-d_6). In one case, loss of 33% of the *sec*-butyl groups was calculated from the ratio of N–H to *sec*-butyl absorption in the ^1H NMR spectrum. This resulted in a desirable increase in the T_g (179 to 218 °C) for the polymer. In contrast to the very promising results with **11a**, the less nucleophilic acyclic analogue thiourea gave lower conversions (TLC analysis), even with an acid cocatalyst. Relatively poor nucleophiles such as MeO^- and NH_2^- gave little ROP. On the acid side, phenylphosphinic acid, phenylphosphonic acid, and phenylsulfonic acid are effective ROP catalysts, but all gave substantial dealkylation. Phenylsulfonic acid was used in previous studies for the acid-catalyzed pyrolytic dealkylation of **1** to PPTA foams.[1,2] As found in previous ROP studies of other mixtures of cyclic oligomers, such as carbonates,[2] we have found that the mixture of cyclic oligomers **2** polymerizes under the same conditions as **10**.

Table II. Molecular Weight and Molecular Weight Distribution[a] via GPC of Polymer from ROP versus N-Butylated Kevlar Aramid Polymer

	cat.	η_{inh}, dL/g	M_w	M_n	MWD
ROP	11a	0.57	61000	7410	8.2
ROP	11a + 12	0.59	38000	9220	4.2
ROP	11a + 12	0.82	c	c	c
butylated Kevlar aramid[b]		0.73	73900	18300	4.1

[a] Two linear Shodex GPC columns were employed. The polymer was run at 0.1 wt % in hexafluoro-2-propanol containing 0.1 M sodium trifluoroacetate with a poly(ethylene terephthalate) standard. [b] Data for this polymer, which contained 83% N-butyl groups by ^{1}H NMR were supplied by R. R. Burch.[8a] [c] Insoluble in hexafluoro-2-propanol.

Molecular weight and molecular weight distribution (MWD) data for the above polymers, prepared *via* ROP of **10** using **11a** and **12** as catalysts, are compared with N-butylated Kevlar aramid polymer[8a] in Table II. When **11a** was used alone as the initiator, a very broad bimodal MWD was obtained while addition of a proton source gave polymer with a monodisperse MWD in the range of N-butylated Kevlar aramid polymer. The bimodal polymer contained a significant amount of unconverted cyclic trimer and higher molecular weight oligomers when analyzed by TLC. When the low molecular fraction was subtracted (approximately 30% calculated from log (molecular weight) versus cumulative curve), the higher molecular weight fraction had a calculated M_w of 78 600 and an M_n of 48 700, giving a polydispersity of 1.6. The cocatalysis by **11a** and **12** has been found to be particularly effective, giving polymer with an η_{inh} as high as 0.82 dL/g, but unfortunately not soluble in hexafluoro-2-propanol for GPC analysis. Undoubtedly, this polymer has a molecular weight in the Kevlar polymer range, assuming no degradation of the latter during butylation.[8a] It gave tough drawable films directly from the ROP carried out at 275–290 °C.

Morphology of Polymers from ROP versus Condensation Polymerization. The polymers prepared *via* ROP became oriented and semicrystalline when drawn at elevated temperature. A film deposited on the wall of the reactor during polymerization, due to the shear forces exerted by stirring, was stripped away and drawn 2.5× its original length over the surface of a cylinder (diameter 18 mm) set at 354 °C. The drawn film was tough (*e.g.*, creasable) and exhibited an X-ray orientation of 33° (Figure 5a). Crystallinity is also observed in the as-cast and drawn film of **1** from the condensation polymerization route (Figure 5b,c, respectively). As shown, the latter is also highly oriented but contains some amorphous phase. The as-cast film was prepared directly from the polymerization mixture by dry casting the 39% w/v solution of polymer (η_{inh} = 0.82 dL/g in concentrated H_2SO_4) in ODCB using a doctor blade. The drawn film was obtained by stretching the as-cast film 7.4× at 210 °C.[15] The layer lines in the X-ray diffraction pattern of drawn film derived from ROP can be rationalized by an axial repeat length of 12.8 Å, which is close to that for PPTA (12.9 Å).[16] On the other hand, the pattern for the drawn film from the condensation polymerization can only be rationalized by an axial repeat length of 25.4 Å, which is double that for PPTA. Both sets of results indicate that the polymer chains in the drawn films are in the *trans* configuration since the *cis* conformation would exhibit a much shorter repeat unit. Although the X-ray pattern of the undrawn film shows significant crystallinity, it also shows evidence for a mixture of isomeric configurations. In stark contrast to our results, the similarly partially and fully N-alkyl (*n*-propyl and *n*-butyl) substituted poly(*p*-phenyleneterephthalamides) prepared by previous workers were amorphous by DSC and/or X-ray diffraction.[8a,b] (Significant crystallinity was noted in previous work in the case of long-chain N-alkyl substituents such as *n*-dodecyl and *n*-octadecyl owing to their crystallization.[8b]) It was believed that crystallization was inhibited by the introduction of N-alkyl substituents giving *cis* conformations which cause the polymer chains to exhibit conformations which inhibit crystallization. No completely satisfactory rationale is apparent at this time for lack of crystallinity in the analogous N-alkyl-substituted poly(*p*-phenyleneterephthalamides) obtained in previous studies *via* N-alkylation of the anionic form of PPTA versus the evidence of fairly high levels of crystallinity in our work. One factor inhibiting crystallization in previous work may have been the rapid rate of precipitation of the polymer solutions into water.

Conclusions

Remarkably, a new class of *para*-oriented cycloaramid oligomers (2*n*-aza[2$_n$]paracyclophane-2*n*-ones) can be easily prepared *via* the condensation of bulky N-substituted *p*-phenylenediamine with *para*-oriented diacid chlorides using classical medium to high dilution techniques. We believe cyclization is favored by the *cis* conformation of the amide bonds formed in the growing chain bringing reactive ends within close proximity for intramolecular condensation. No evidence exists for the presence of cyclic oligomers in the Kevlar aramid polymer, prepared commercially from the condensation of the unsubstituted *p*-phenylenediamine and terephthaloyl chloride. Just as remarkable as the above ring formation reaction is that ring-opening polymerization of the cycloaramid oligomers, to give high molecular weight polymers, can be effected by highly nucleophilic 1,3-dialkylimidazole-2-thiones. The latter are particularly effective when an acid source, such as phenylphosphinic acid, is present. Surprisingly, the poly(*N*,*N*′-di-*sec*-butyl-*p*-phenyleneterephthalamide) prepared in this work by ROP and by condensation polymerization exhibits crystallinity versus an amorphous morphology for the N-alkyl-substituted aramids reported by previous workers.

Experimental Section

Instruments and Procedures. Nuclear magnetic resonance spectra were recorded on a Bruker WM-400 NMR spectrometer or a GE QE-300 NMR spectrometer. The FAB MS spectra were recorded on a double-focusing VG-ZAB E mass spectrometer. The FTIR spectra were recorded on a Perkin-Elmer 1760 infrared spectrophotometer. The GPC analysis on cyclic oligomer mixtures was carried using six 500-Å pore size Ultragel columns in series (each 300 mm × 7.8 mm i.d.; effective MW range from 100 to 10 000; minimum efficiency 12 000 plates/300 mm column). The carrier was THF, the UV detector was at 230 nm/0.50 AUFS, the flow rate was 1.0 mL/min, and 100 mg of sample/250 μL of carrier was injected. Reverse-phase HPLC was carried out using a Vydac-C18 (semiprep size column, 250 mm × 9.4 mm i.d., 5-μm packing). Carrier A was 25% THF/75% water and carrier B was THF. A UV detector was employed at 254 nm/0.50 AUFS attenuation. The flow rate was 3.0 mL/min at 35 °C. A 500-μL sample was used: 10 mg dissolved in 50% carrier A/50% carrier B. Note: The sample was first dissolved in carrier B, and carrier A was then added. Differential scanning calorimetry (DSC) measurements were made using a Du Pont 2200 series instrument. Wide-angle diffraction patterns were obtained using a Philips generator.

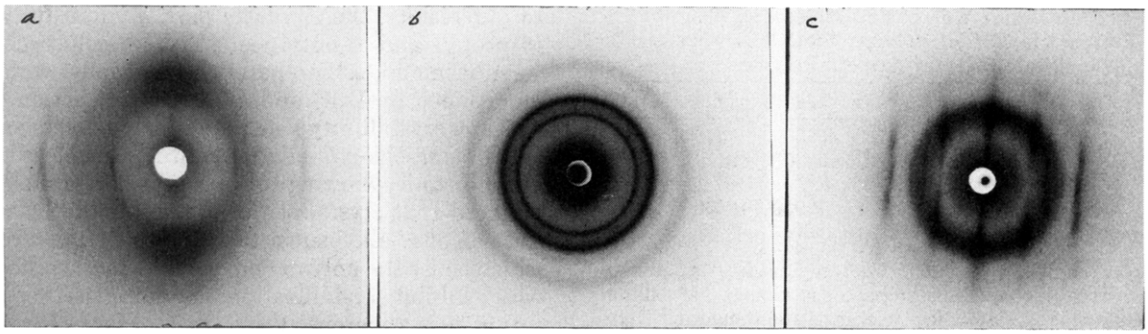

Figure 5. Wide-angle X-ray scattering pattern of (a) drawn film of poly(*N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide) from ROP, (b) as-cast film of poly(*N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide) from condensation polymerization, and (c) drawn film of poly(*N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide) from condensation polymerization.

Intermediates and Solvents. *N,N'*-Di-*sec*-butyl-*p*-phenylenediamine. Antioxidant 22 from Du Pont Chemicals containing 86% *N,N'*-di-*sec*-butyl-*p*-phenylenediamine (**13**), 3% *N,N,N'*-tri-*sec*-butyl-*p*-phenylenediamine, and 0.8% *N,N,N',N'*-tetra-*sec*-butyl-*p*-phenylenediamine was quadruply vacuum distilled through a 30-cm Vigreux column, giving **13** with a GC purity of 99.7%, bp 108 °C/0.05 mm. **Terephthaloyl chloride** was Kevlar aramid grade material from the Du Pont Co. and was used without further purification. **1-Methyl-3-*n*-butylimidazole-2-thione** was prepared according to ref 13b. **Phenylphosphinic acid** was from Aldrich Chemical Co. and was used without further treatment. ***o*-Dichlorobenzene** was from EM Science and was dried over Type 4Å molecular sieves prior to use.

Preparation of *N,N'*-Di-*sec*-butyl-*p*-phenyleneterephthalamide Cyclic Oligomers (A). To a 3-L three-necked Morton flask equipped with a mechanically driven stirrer, dry nitrogen purge tube, and two dropping funnels was added ODCB (900 mL). The ODCB was heated to 80 °C whereupon *N,N'*-di-*sec*-butyl-*p*-phenylenediamine (22.0 g) in 450 mL of ODCB and terephthaloyl chloride (20.3 g) in 450 mL of ODCB were added dropwise over a 3-h period. A nitrogen purge tube with a coarse fritted glass tip was inserted beneath the surface of the reaction mixture, the oil bath temperature was increased to 190 °C, and the mixture was stirred for 5 days. The translucent, almost clear, mixture was allowed to cool to room temperature, and the ODCB was removed on a rotary evaporator. The solid obtained was transferred to a Soxhlet extractor and extracted for 4 days with toluene. The grayish residue left in the thimble was dried under a stream of nitrogen, ground up, and further air-dried: yield 8.6 g (sample A). The clear toluene fraction was evaporated under reduced pressure, giving a foamy light yellow solid which smelled of ODCB. The solid was ground up in a mortar with pestle and was further dried at about 90 °C under reduced pressure: yield 22.8 g (sample B); mp 210 °C. The inherent viscosity was 0.05 dL/g (0.5% in concentrated H_2SO_4 at 30 °C) versus 0.22 dL/g for sample A. FAB MS analysis indicated that sample A contained unextracted cyclic dimer, trimer, and tetramer in addition to *linear* oligomers, while sample B showed only peaks for cyclic dimer, trimer, tetramer, pentamer, hexamer, and heptamer. Preparative HPLC showed that sample B contained cyclic dimer (9%) [mp 277 °C (32 J/g); 310 °C (33 J/g) by DSC], cyclic trimer (32%) (mp 260–270 °C in a melting point apparatus; DSC analysis showed no endotherm), the remainder consisting of higher cyclic oligomers. Anal. Calcd for cyclic trimer ($C_{66}H_{78}N_6O_6$): C, 75.44; H, 7.48; N, 8.00. Found: C, 75.42; H, 7.62; N, 8.02.

Preparation of *N,N'*-Di-*sec*-butyl-*p*-phenyleneterephthalamide Cyclic Oligomers (B). To a 3-L three-necked Morton flask equipped with a mechanically driven stirrer, dry nitrogen line, and two dropping funnels was added ODCB (900 mL). The ODCB was heated to 80 °C whereupon *N,N'*-di-*sec*-butyl-*p*-phenyleneamine (22.0 g) in 450 mL of ODCB and terephthaloyl chloride (20.3 g) in 450 mL of ODCB were added dropwise over a 3-h period. The cloudy mixture was heated to reflux and stirred for 1 week. The mixture became translucent but not clear during heating. The mixture was allowed to cool and the ODCB was removed on a rotary evaporator under pump vacuum using a 100 °C oil bath. The yield was 36.7 g, 105% of theoretical, the excess weight due to residual ODCB according to thermogravimetric analysis. The product exhibited an inherent viscosity of 0.058 dL/g (0.5% in concentrated H_2SO_4 at 30 °C). The material was found to be 86% soluble in toluene, of which the GPC showed no high molecular weight polymer. The reverse-phase HPLC analysis (Figure 1) showed this material contained a multiplicity of peaks, which by FAB MS correspond to cyclic oligomers of *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide. In addition, peaks are found which correspond to cyclic oligomers where one or more of the *sec*-butyl groups was eliminated during the reaction.

Chart I

fraction	RT, min	wt, g	cyclic oligomer composition: FAB MS	cyclic oligomer composition: mp, °C
1	12.5	0.053	dimer	277, 310[a]
2	20.0	1.721	trimer	260–270[b]
3	33.0	0.107	tetramer	260–270[b]
4	37.5	0.258	pentamer, tetramer, trimer minus *sec*-butyl	
5	47.0	0.099	hexamer, hexamer minus *sec*-butyl	
6	56.0	0.059	heptamer, hexamer	
7	61.0	0.080	hexamer to undecamer, each with a satellite corresponding to parent cyclic minus *sec*-butyl	
total		2.377 (95% recovery)		

[a] DSC endotherms of 32 and 33 J/g, respectively. [b] Macroscopic melting point in Electrothermal Engineering, Ltd., melting point apparatus.

Fractionation and Characterization of Cyclic *N,N'*-Di-*sec*-butyl-*p*-phenyleneterephthalamide Oligomers. Normal-phase preparative HPLC was carried out on the directly above toluene-soluble fraction using a Waters Delta Prep 3000 chromatograph employing tandem Zorbax silica columns (250 × 21.2 mm i.d.). A UV detector was employed at 254 nm/0.50 AUFS attenuation. Carrier A was 100% chloroform, and carrier B was 98% chloroform + 2% methanol. The gradient was changed from 100% A to 60% A at 20 min and from 60% A to 0% A at 70 min. The flow rate was 20 mL/min. The 2.4997-g sample was injected in 150 mg/1.5 mL of chloroform increments. Seven fractions were collected (Chart I). Figure 2 shows the ^1H NMR spectrum for fraction 1 and is consistent with cyclic dimer. The ^{13}C NMR spectrum is also consistent with a cyclic dimer structure, exhibiting resonances (DMSO-d_6, 120 °C) at 10.33 (methyls adjacent to methylene), 17.31 and 17.36 (methyls adjacent to methines), 26.78 and 26.89 (methylenes), 54.70 and 54.82 (methines), 127.79 (carbon 2, terephthaloyl moiety), 129.57 (carbon 2, *p*-phenylenediamide moiety), 137.72 (carbon 1, terephthaloyl moiety), 138.91 (carbon 1, *p*-phenylenediamide moiety), and 167.56 ppm (amide carbonyl carbon).

Ring-Opening Polymerization of *N,N'*-Di-*sec*-butyl-*p*-phenyleneterephthalamide Cyclic Trimer. To a 10-mL round-bottom flask equipped with a three-necked adapter with a nitrogen line, condenser with a drying tube, and mechnically

driven glass paddle stirrer were added *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic trimer (0.350 g) (the major homolog from preparative HPLC) and 1-methyl-3-*n*-butylimidazole-2-thione (0.005 g). After sweeping with nitrogen for a few minutes, the flask was placed in a 260 °C oil bath without stirring. Within a few minutes, a clear slightly viscous melt was obtained. The rate of stirring was set at a few rpm, sufficient to mix the ingredients. After 30 min the stirrer was stopped, and the temperature was raised to 265 °C and held for 2 h, at which point an increase in viscosity was perceptible. Stirring on an intermittent basis was continued for 4 h. The moderately viscous melt was allowed to cool, giving a caramel colored clear solid. The recovered yield was 0.303 g. The inherent viscosity was 0.57 dL/g (0.5% in concentrated H_2SO_4 at 30 °C). The polymer exhibited a melting point (PMT) of 284 °C on a gradient hot bar.[17] Fibers could be pulled from a melt at 300 °C. The FTIR spectrum exhibited absorption at 1645 cm^{-1} for the carbonyl group, absorption at 2820, 2920, and 2970 cm^{-1} for the *sec*-butyl group, and virtually no N–H absorption, all consistent with poly(*N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide) and unconverted cyclic trimer. The latter was evident (using the long wavelength of a Mineralight Lamp Multiband 254/366 nm) from a spot with an R_f of 0.58 on a Kieselgel 60 F 254 thin-layer chromatography plate using chloroform to spot and ethyl acetate to develop. The polymeric fraction remained at the origin. Other faint spots corresponding to low molecular weight polymer or oligomers were observed. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) were 61 100 and 7410, respectively, giving a polydispersity of 8.2. When the low molecular weight fraction was subtracted (approximately 30% calculated from log (molecular weight) versus cumulative curve), the higher molecular weight fraction was calculated to have an M_w of 78 600 and an M_n of 48 700, giving a polydispersity of 1.6. A control polymerization without catalyst showed virtually no polymer *via* TLC.

Ring-Opening Polymerization of *N,N'*-Di-*sec*-butyl-*p*-phenyleneterephthalamide Cyclic Trimer with Cocatalysis by 1-Methyl-3-*n*-butylimidazole-2-thione and Phenylphosphinic Acid. To a 10-mL round-bottom flask equipped with a three-necked adapter with a nitrogen line, condenser with a drying tube, and mechanically driven glass paddle stirrer were added *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic trimer (0.175 g), 1-methyl-3-*n*-butylimidazole-2-thione (0.002 g)), and phenylphosphinic acid (0.0015 g). After sweeping with nitrogen for a few minutes, the flask was placed in a 275 °C oil bath without stirring. Within 5 min a clear, slightly viscous melt was obtained which was stirred slowly for 5.5 h, during which time the viscosity increased to the point where the mixture became unstirrable. The temperature was raised to 290 °C and held for 45 min without stirring. Upon disassembling the apparatus, a tough partly foamy product was found with a smooth surface on the bottom side next to the glass. The other surfaces were smooth but bore shear lines and folds from the action of the stirrer. Also found was a tough film which adhered to the surface of the bulk of the polymer and the wall of the flask. This film was peeled away and was found to be both flexible and creasable and, hence, tough. The total recovered yield was 0.120 g. The polymer was free of unconverted cyclic trimer, by TLC, and had an η_{inh} of 0.82 dL/g (0.5% in concentrated H_2SO_4 at 30 °C). (This polymer of apparent higher molecular weight than the above was not soluble in hexafluoro-2-propanol for molecular weight determination.) The above film had a PMT of 310 °C. Short lengths (up to 3 cm) of the film were removed with scissors and drawn 2.5× its original length over the surface of a cylinder (diameter 18 mm) set at 354 °C. The film maintained its toughness and exhibited orientation and crystallinity (Figure 5a).

A polymer prepared under conditions similar to those above but using a different heating cycle time (hours/temperature °C): 5/264–275; 0.5/282–289) yielded a polymer which was foamy and had an η_{inh} of 0.43 dL/g. The polymer exhibited an M_w of 38 200 and an M_n of 9220. Again a flexible tough film adhered to the wall of the flask.

Still another polymer prepared under conditions similar to those above, but with 20% additional phenylphosphinic acid catalyst, had an η_{inh} of 0.58 dL/g, a DSC T_m of 362 °C (heat of fusion was 43 J/g), and a T_g of 245 °C.

Ring-Opening Polymerization of *N,N'*-Di-*sec*-butyl-*p*-phenyleneterephthalamide Cyclic Oligomer Mixture with 1-Methyl-3-*n*-butylimidazole-2-thione. The *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic oligomer mixture from the above toluene-soluble fraction (see procedure B) was polymerized as follows. To a 10-mL round-bottom flask equipped with a three-necked adapter with a nitrogen line, a condenser with a drying tube, and a mechanically driven glass paddle stirrer were added 0.700 g of the *N,N'*-di-*sec*-butyl-*p*-phenyleneterephthalamide cyclic oligomer mixture and 0.011 g of 1-methyl-3-*n*-butylimidazole-2-thione. After sweeping with nitrogen for a few minutes, the flask was placed in a 260 °C oil bath without stirring. Within 5 min, a clear, slightly viscous melt was obtained. The oil bath was set up to 265 °C and the melt stirred slowly. After 1.5–2 h a noticeable increase in viscosity was observed. Heating was continued. After 4 h of additional reaction, the viscosity had increased substantially to the point where a solid clear streamer clung between the stirrer and the bulk melt when the former was pulled from the latter as it was allowed to cool to form a clear light amber glass: yield 0.634 g. The material was broken up in a mortar with a pestle. The polymer exhibited an η_{inh} of 0.35 dL/g (0.5% in concentrated H_2SO_4 at 30 °C) versus 0.05 dL/g for the starting cyclic oligomer mixture. TLC (spotted with toluene and eluted with ethyl acetate) of the product versus the starting cyclic oligomer mixture indicated some of the unconverted latter. Spots corresponding to cyclic dimer (R_f of 0.69), cyclic trimer (R_f of 0.58), tetramer (R_f of 0.48) were detected along with a faint smear for unresolved higher molecular weight oligomers. The polymer was found at the origin. The polymer exhibited an M_w of 27 700 and an M_n of 5330 with a polydispersity of 5.31. The GPC curve exhibits trimodality. When the two lower molecular weight peaks were subtracted, the higher molecular weight fraction was found to have an M_w of 44 100 and an M_n of 28 500 with a polydispersity of 1.54.

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References and Notes

(1) (a) Memeger, W. U.S. Patent 4,178,419, 1979. (b) Memeger, W. U.S. Patent 4,226,949, 1980.
(2) (a) Boden, E. P.; Brunelle, D. J.; Shannon, T. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 571. (b) *Chem. Eng. News 70 (18)*, May 4, 1992.
(3) Brunelle, D. J.; Boden, E. P.; Shannon, T. G. *J. Am. Chem. Soc.* **1990**, *112*, 2399.
(4) Guggenheim, T. L.; McCormick, S. J.; Kelly, J. J.; Brunelle, D. J.; Colley, A. M.; Boden, E. P.; Shannon, T. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 579.
(5) Guggenheim, T. L.; McCormick, S. J.; Guiles, J. W.; Colley, A. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 138.
(6) (a) Brunelle, D. J.; Evans, T. L.; Shannon, T. G. U.S. Patent 4,644,053, 1987. (b) Brunelle, D. J.; Evans, T. L.; Shannon, T. G. U.S. Patent 4,736,016, 1988. (c) Brunelle, D. J.; Shannon, T. G. U.S. Patent 4,829,144, 1989. (d) Guggenheim, T. L.; Guiles, J. W.; McCormick, S. J. U.S. Patent 4,808,754, 1989. (e) Guggenheim, T. L.; McCormick, S. J.; Colley, A. M.; Guiles, J. W. U.S. Patent 4,868,279, 1989.
(7) For a discussion of formation of macrocycles under dilute conditions, see: Rossa, L.; Vogtle, F. Synthesis of Medio- and Macrocyclic Compounds by High Dilution Principle Techniques. In *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: New York, 1983; No. 113, Chapter 12.
(8) The insoluble fraction represents relatively high molecular weight linear polymer. It should be noted that *N*-substitution of *p*-aramids results in a loss of chain rigidity and hence much lower η_{inh}'s for a given molecular weight than poly(*p*-phenyleneterephthalamide). See: (a) Burch, R. R.; Manring, L. E.;

Macromolecules **1991**, *24*, 1731. (b) Takayanagi, M.; Katayose, T. *J. Polym. Sci., Poly. Chem. Ed.* **1981**, *19*, 1133. (c) Kim, Y. H.; Calabrese, J. C. *Macromolecules* **1991**, *24*, 2951.
(9) Itai, A.; Toriumi, Y.; Tomioka, N.; Kagechika, H.; Azumaya, I.; Shudo, K. *Tetrahedron Lett.* **1989**, *30*, 6177.
(10) Itai, A.; Toriumi, Y.; Saito, S.; Kagechika, H.; Shudo, K. *J. Am. Chem. Soc.* **1992**, *114*, 10649.
(11) Elhadi, F. E.; Ollos, W. D.; Stoddart, J. E.; Williams, D. J.; Woode, K. A.; *Tetrahedron Lett.* **1980**, *21*, 4215.
(12) Jung, M. E.; Gervay, J. *Tetrahedron Lett.* **1988**, *29*, 2429.
(13) Colquhoun, H. M.; Dudman, C. C.; Thomas, M.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 336.
(14) (a) Arduengo, A. J., III. U.S. Patent 5,104,993, 1992; (b) Benac, B. L.; Burgess, E. M.; Arduengo, A. J. *Org. Synth.* **1986**, *64*, 92.
(15) Sorenson, W.; Campbell, T. W. *Preparative Methods of Polymer Chemistry*, 2nd ed.; Interscience: New York, 1968; pp 28–29.
(16) Northolt, M. G.; Aartsen, J. J. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 333.
(17) Sorenson, W.; Campbell, T. W. *Preparative Methods of Polymer Chemistry*, 2nd ed.; Interscience: New York, 1968; p 50.