Ring−Chain Interconversion in High-Performance Polymer Systems. 3. Cyclodepolymerization of Poly(*m*-phenylene isophthalamide) (Nomex) and Entropically Driven Ring-Opening Polymerization of the Macrocyclic Oligomers so Produced

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ABSTRACT: A homologous series of macrocyclic oligoamides has been prepared in high yield by reaction of isophthaloyl chloride with *m*-phenylenediamine under pseudo-high-dilution conditions. The products were characterized by infrared and ^{1}H NMR spectroscopies, matrix assisted laser desorption−ionization time-of-flight mass spectrometry, and gel permeation chromatography (GPC). A series of linear oligomers was prepared for comparison. The macrocycles ranged in size from the cyclic trimer up to at least the cyclic nonamer (90 ring atoms). The same homologous series of macrocyclic oligomers was prepared in high yield by the cyclodepolymerization of poly(*m*-phenylene isophthalamide) (Nomex). Cyclodepolymerization was best achieved by treating a 1% w/v solution of the polymer in dimethyl sulfoxide containing calcium chloride or lithium chloride with 3−4 mol % of sodium hydride or the sodium salt of benzanilide at 150 °C for 70 h. Treatment of a concentrated solution of the macrocyclic oligomers (25% w/v) with 4 mol % of sodium hydride or the sodium salt of benzanilide in a solution of lithium chloride in dimethyl sulfoxide at 170 °C for 6 h resulted in efficient entropically driven ring-opening polymerizations to give poly(*m*-phenylene isophthalamide), characterized by infrared and ^{1}H NMR spectroscopies and by GPC. The molecular weights obtained were comparable with those of the commercial polymer.

1. Introduction

There has been considerable interest in recent years in polymerizations that exploit ring−chain equilibria,[1,2] i.e., the equilibria between macrocyclic oligomers (MCO's) and the corresponding linear polymers.[3−5] At *high* concentrations the equilibria lie heavily in favor of the polymer, while at *low* concentrations they lie heavily in favor of the MCO's. Thus, subjecting *neat* MCO's, or a very concentrated solution of MCO's, to conditions under which ring−chain equilibrium is established results in polymer synthesis. It should be noted that the synthesis of polymers from MCO's requires the introduction of end groups: these are often derived from the catalyst used to establish the equilibrium. To facilitate full equilibration, it is clearly necessary to use conditions where molecular mobility is maintained throughout the reaction. For example, if neat MCO's are used, the final reaction temperature must be above the T_g and, for semicrystalline polymers, above the T_m of the polymer. Many polymers have been prepared by such ring-opening polymerizations (ROP's), including bisphenol A polycarbonate,[1,6,7] aliphatic polycarbonates,[8] polyesters,[9−12] polyurethanes,[13] and high-performance aromatic polymers—in particular poly(ether sulfone)s and poly(ether ketones).[14−25]

This type of ROP has several interesting features. First, the MCO's involved generally have little or no ring strain, in contrast to more conventional ROP's which are driven mainly by the relief of ring strain.[26] Thus, these polymerizations are essentially entropically driven; i.e., they are ED-ROP's. Ring opening is favored mainly because the conformations of the MCO's are restricted and so they have relatively low conformational entropy, whereas when such rings polymerize the open chain produced has many more conformations available to it. Second, as the polymerizations represent only a shuffling of the linkages between the repeat units, no volatiles are evolved and little or no heat is generated. This makes ED-ROP's environmentally friendly and particularly attractive for the preparation of coatings, for reaction injection molding (RIM) and for reactive fabrication of composite materials.

In many cases the MCO's required for ED-ROP's have been prepared by classical high dilution syntheses,[27] but ring−chain equilibria can also be used as a source of MCO's. Thus, treating a *dilute* solution of the polymer under conditions which establish the equilibrium brings about cyclodepolymerization (CDP) and the formation of an homologous series of MCO's. In 1950, Jacobson and Stockmayer presented a theory that, at least qualitatively, successfully predicts the proportions of the MCO's produced in polycondensations or CDP's.[28] Cyclodepolymerization is driven mainly by the fact that in *dilute solution* the MCO's have a much higher translational entropy than the polymer. Clearly the combination of CDP plus ED-ROP provides a potential means of recycling certain step-growth polymers. Many polymers have been successfully subjected to CDP including bisphenol A polycarbonate,[29,30] aliphatic polycarbonates,[8] polyesters,[2,9,10,31−34] polyurethanes,[13] and a range of high-performance aromatic polymers.[14,17,19]

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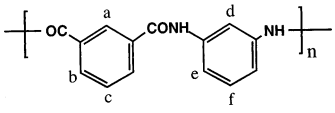
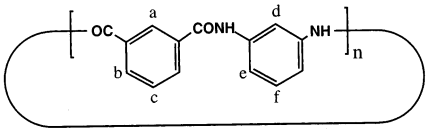
The present paper extends these studies to the CDP of an aromatic polyamide and the ED-ROP of the MCO's produced. Poly(*m*-phenylene isophthalamide) (Nomex) (**1**) was chosen as the polyamide, both because of its commercial importance and because, having only meta-substituted aromatic rings, the polymer and its derivatives tend to be more soluble than many other aromatic polyamide systems. Nomex (**1**) is therefore *relatively* easy to work with. Even so, the polymer and the various derivatives discussed in this paper are only poorly soluble in common organic solvents, and as a consequence separation and/or purification is not trivial. The work described here is concerned with the preparation of MCO's **2**, both by pseudo-high dilution syntheses and by the CDP of Nomex (**1**), characterization of the resulting MCO's **2**, and a study of their ED-ROP.



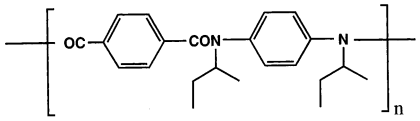
(1)



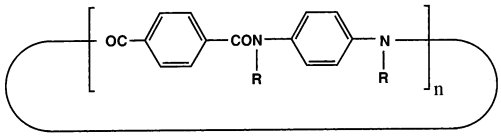
(2): n = 3 to > 9

(3): n = 3

(13): n = 4

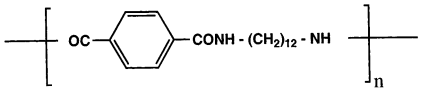


(4): n = 3 to > 13



(5): R = sec-Butyl

(6): R = H



(7)

Several ED-ROP's that afford polyamides have been reported previously. Thus, the cyclic trimer **3** and caprolactam have been copolymerized.[35,36] As noted above, for successful ED-ROP it is necessary to maintain molecular mobility throughout the polymerization. As many polyamides have very high melting points, this can be a major problem. One way of negotiating this difficulty is to use solubilizing groups which can subsequently be removed. For example, the ED-ROP of MCO's **4** produced polymer **5**,[37] and heating this product with a catalytic amount of benzenesulfonic acid resulted in the elimination of but-2-ene with formation of poly(*p*-phenylene terephthalamide) (Kevlar) (**6**).[38] The ED-ROP of MCO's to produce poly(dodecamethylene terephthalamide) (**7**) has also been reported.[39]

Table 1. Synthesis of Macrocyclic Oligomers 2 by Pseudo-High-Dilution Syntheses from Isophthaloyl Chloride and *m*-Phenylenediamine[a]

entry	solubilizing salt[b]	yield of product (%)	MALDI−TOF MS macrocyclic range[c]
1	$CaCl_2$	95	9
2	LiCl	95	6
3	none	91	8

[a] See Experimental Section for full details. [b] Solutions in DMAc containing salt contained 3% w/v. [c] From the macrocyclic trimer up to the value shown.

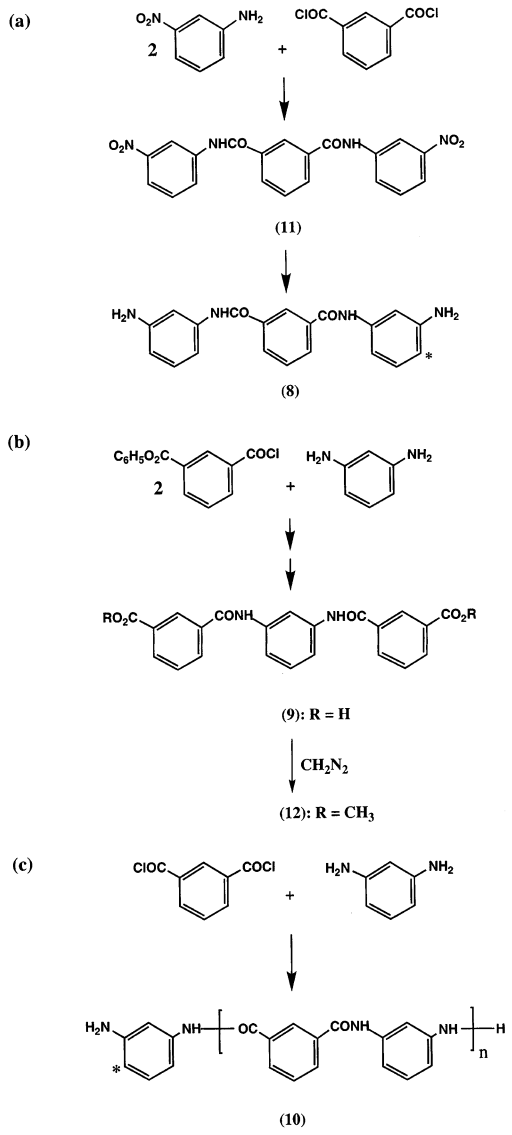
2. Results and Discussion

2.1. Pseudo-High-Dilution Synthesis and Characterization of Cyclic Oligomers 2. To facilitate the analysis of MCO's **2** produced by CDP of polymer **1**, the MCO's were first prepared by kinetically controlled pseudo-high-dilution reactions of isophthaloyl chloride with *m*-phenylenediamine. Three sets of reaction conditions were used, and the results are summarized in Table 1. Initially MCO's **2** were synthezised using the literature procedure:[35,36] see entry 1. Here, solutions of the diacid chloride in toluene and the diamine in *N*,*N*-dimethylacetamide (DMAc) were simultaneously added over 7 h to a 3% w/v solution of calcium chloride in DMAc at 165−168 °C. Reaction was then continued for a further 10 h at 168 °C. In the second synthesis (Table 1, entry 2) the conditions were the same except that lithium chloride was used in place of calcium chloride. The final synthesis (entry 3) was similar, except that no salt was added. In each case the crude products were isolated in high yields by precipitation into dilute hydrochloric acid. They were insoluble in dimethyl sulfoxide (DMSO) but were soluble in DMSO containing lithium chloride. ^{1}H NMR spectra were recorded for solutions in DMSO-d_6 containing lithium chloride. The characterization of these products is discussed later.

To facilitate characterization of the above products, model compounds **8** and **9** and the linear oligomer **10** were prepared. Compounds **8** and **9** were prepared as models for possible polymer end groups. They were synthesized as outlined in Scheme 1. The FT-IR spectrum of compound **8** showed an amide carbonyl band at 1649 cm^{-1} and the ^{1}H NMR spectrum showed a signal at δ 6.36 ppm assigned to the aromatic protons asterisked in formula **8**. As this resonance appears significantly upfield from the other aromatic protons, the corresponding signals in oligomers and/or polymers can clearly be used to estimate the number of amine end groups in such products. The spectrum of compound **9** did not show an analogous resonance that could be used to estimate the number of carboxylic acid end groups. However, treatment of compound **9** with diazomethane gave diester **12** and this shows a singlet due to the $-CO_2CH_3$ group at δ 3.94 ppm. As the repeat-unit resonances in the spectrum of compound **12** are clear of this region, this signal can be used to estimate the number of carboxylic acid end groups. The FT-IR spectrum of diacid **9** showed well resolved carbonyl bands at 1649 and at 1691 cm^{-1}, due to the amide and carboxylic acid groups, respectively.

The linear oligo(*m*-phenylene isophthalamide)s **10** were prepared by reacting isophthaloyl chloride with an excess of *m*-phenylenediamine: see Scheme 1c. The FT-IR spectrum of the product displayed the amide carbonyl

Scheme 1. Synthesis of Compounds 8 and 9 and Linear Oligomers 10



band at 1656 cm^{-1}. The matrix-assisted laser desorption−ionization time-of-flight mass spectrum (MALDI−TOF MS) of the products (Figure 1a) showed a series of peaks corresponding to the linear oligomers **10** from the dimer up to the nonamer, where as expected from the method of synthesis, each oligomer was terminated by amine groups. The ^1H NMR spectrum was recorded for a solution in DMSO-d_6 containing lithium chloride. On the basis of the intensity of the signal at δ 6.58 ppm (due to the proton asterisked in formula **10**) the product had an average degree of polymerization (DP) of ca. 6. We were able to assemble in house a GPC instrument suitable for the analysis of the oligomers using a specific "oligomers" column, with DMAc containing 1% w/v of lithium chloride as eluent at 70 °C. The oligomers **10** had M_n 1000 and M_w 1500 relative to polystyrene standards (Figure 2a), corresponding to a DP of ca. 4 based on M_n.

With the information gained from these model studies, analysis of the products from high-dilution syntheses was greatly facilitated. The ^1H NMR spectra of the three sets of products contained no detectable signals due to amine end groups near δ 6.36. Nor, after treatment with diazomethane did the products show any

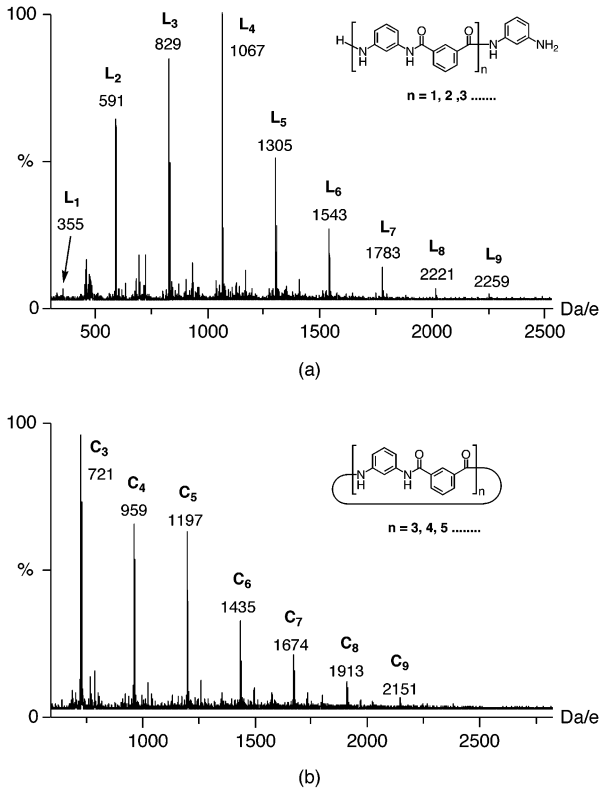


Figure 1. (a) MALDI−TOF mass spectrum of the linear oligomers **10.** (b) MALDI−TOF mass spectrum of the MCO's **2** prepared in the experiment summarized in Table 1, entry 1. Samples were prepared for MS by placing a drop of a solution of the sample in DMAc containing 8% w/v lithium chloride onto the MS sample plate and allowing the solvent to evaporate prior to the addition of dithranol as the matrix.

detectable signals near δ 3.94 due to ester end groups. Thus, the oligomers **2** are clearly cyclic. Consistent with this, the MALDI−TOF MS (obtained under the experimental conditions used successfully with the linear materials) of these oligomers showed a major series of peaks due to MCO's **2** from the trimer up to the nonamer (Figure 1b). Furthermore, FT-IR spectra showed the expected amide bands near 1656 cm^{-1} but *no* carboxylic acid bands near 1690 cm^{-1}. Thus, all the evidence indicates that the high dilution syntheses produce very largely, if not entirely, MCO's **2**. It should also be noted that previous researchers[35,36] isolated calcium chloride complexes of the cyclic trimer **3** in modest yields, and they confirmed its cyclic structure by X-ray crystallography.

Previous researchers[35,36] studying the MCO's **2** did not have the benefit of GPC to analyze their products. The chromatogram from our initial synthesis of MCO's **2** (Table 1, entry 1) is shown in Figure 2 as trace "b". This clearly indicates the presence of at least six different MCO's. The plot of log DP vs elution volume was essentially a straight line (Figure 3), indicating that the peaks were due to a homologous family of oligomers, but unfortunately the resolution of the chromatogram was not sufficient to allow the proportions of the various MCO's to be accurately determined. The GPC traces from the product of the reaction carried out in the presence of lithium chloride and also that from the reaction with no added salt were very similar: see Figure 2 traces "c" and "d" respectively. Previous researchers[35] have suggested that the formation of the cyclic trimer **3** by this *kinetically controlled* pseudo-high-

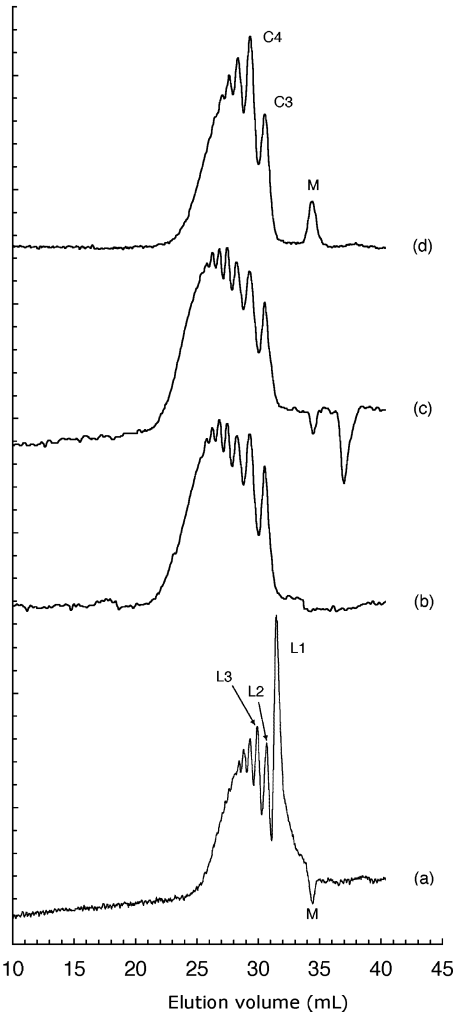


Figure 2. GPC traces of oligomers. Trace a: amine-ended linear oligomers **10**. Trace b: the product from the pseudo-high-dilution synthesis summarized in Table 1, entry 1. Trace c: the product from the pseudo-high-dilution synthesis summarized in Table 1 entry 2. Trace d: the product from the pseudo-high-dilution synthesis summarized in Table 1 entry 3. Note: "M" indicates a marker peak.

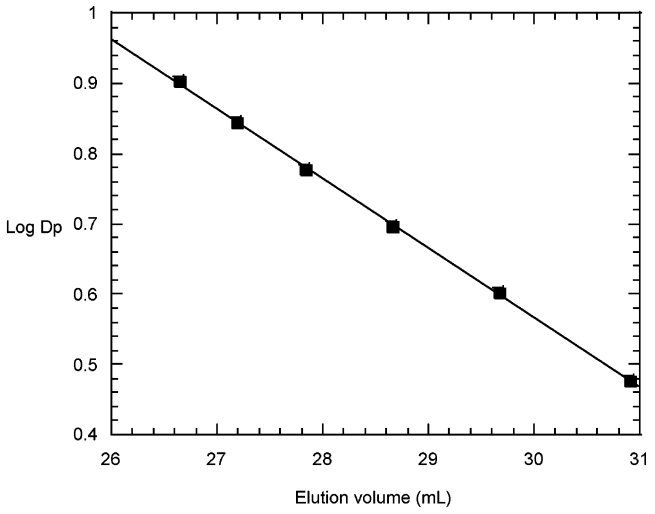


Figure 3. Plot of log DP vs elution volume for the peaks present in the GPC traces of the pseudo-high-dilution syntheses shown in Figure 2.

dilution synthesis is strongly favored by the presence of calcium chloride, but our GPC results suggest that, at least in our experiments, this was not the case.

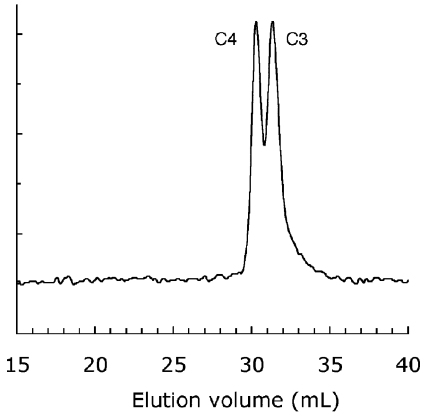
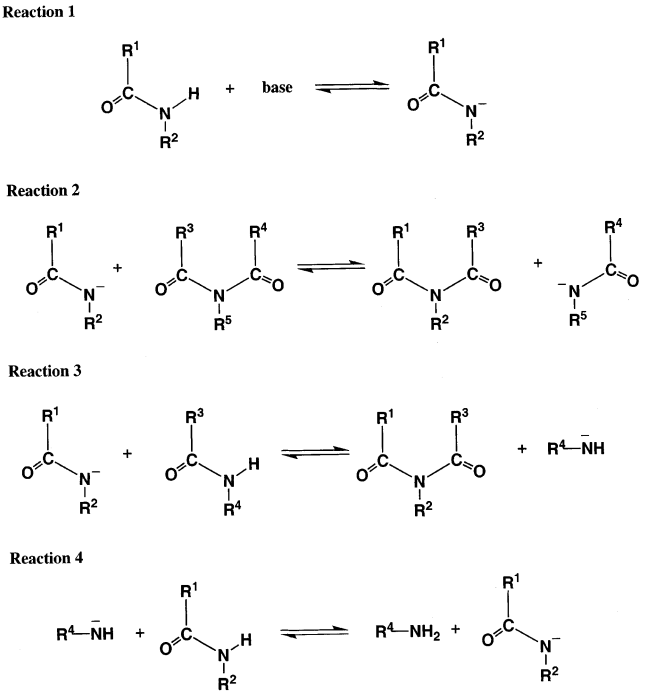


Figure 4. GPC trace for the mixture of cyclic trimer **3** and cyclic tetramer **13**.

Scheme 2. Proposed Reactions Occurring during the Cyclodepolymerization of Polymer 1

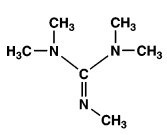


To assign the GPC peaks to specific MCO's, attempts were made isolate and characterize some specific MCO's. Extraction of the crude cyclization product from the initial high dilution synthesis, using hot tetrahydrofuran (THF) in a Soxhlet apparatus, gave a 9% yield of what was found by GPC to be a 50:50 mixture of two cyclic oligomers: see Figure 4. Analysis by MALDI−TOF MS indicated that these were the cyclic trimer **3** and cyclic tetramer **13**. The last eluted peak on the GPC trace would be the smaller of the two MCO's, i.e., the cyclic trimer **3**. With this sample in hand, all the oligomer GPC peaks could be confidently assigned. This assignment showed that the crude reaction products contained macrocycles ranging from the cyclic trimer **3** up to at least the cyclic nonamer (90 ring atoms). The failure to detect the cyclic dimer is not surprising, as simple modeling suggests that it would be very significantly strained.

2.2. Cyclodepolymerization of Polymer 1 To Give Cyclic Oligomers 2. Attention was next turned to the CDP of poly(*m*-phenylene isophthalamide) (**1**). This has not been previously investigated. It was expected that

CDP would proceed most satisfactorily using a basic catalyst strong enough to remove a proton from an amide group: see reaction 1, Scheme 2. It was expected that this would take part in transacylations of the type shown in reaction 2. The type of imide required would be generated initially by reaction 3. The initiation process is completed by reaction 4. We believe that the CDP proceeds via reaction 2 because an imide is much more reactive to nucleophiles than a simple amide. It should be noted that the proposed reactions are analogous to those involved in the anionic ring-opening polymerization of ϵ-caprolactam.[40]

To achieve CDP it is critical that the polymer has at least some solubility in the reaction solvent. Poly(*m*-phenylene isophthalamide) (**1**) is insoluble in *N*,*N*-dimethylformamide (DMF), DMAc or *N*-methylpyrrolidone (NMP), but it dissolves in these solvents in the presence of calcium chloride or lithium chloride. In an initial series of experiments it was found that when polymer **1** in these solvents, with added lithium chloride, was treated at their boiling points with bases such as diazabicyclo-octane (DABCO), pentamethylguanidine (PMG) (**14**), cesium carbonate or sodium hydride, some



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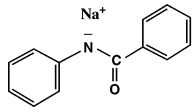

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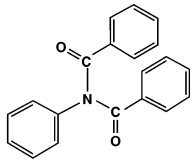

(16)

CDP did indeed occur but the reaction mixtures became insoluble gels, possibly because the amide solvents themselves became involved in the reaction. When, however, DMSO containing lithium chloride or calcium chloride was used as the solvent, gelation did not occurr and clean CDP products were obtained. A series of reactions was carried out at 150 °C under dry nitrogen, and their progress was monitored by GPC and MALDI−TOF MS. The results are summarized in Table 2. With DABCO, PMG, or cesium carbonate as catalysts at 4 mol % relative to the polymer repeat unit, only modest yields of MCO's **2** were formed over 5 days: see entries 1−3. However, sodium hydride proved a much superior catalyst and, after 5 days at 150 °C, CDP yields of over 90% (by GPC analyses) were obtained: see entries 4 and 5.

Sodium hydride is not particularly convenient to dispense in small amounts due to its high sensitivity to moisture, but it was expected that the sodium salt of benzanilide (**15**) would be equally effective as a catalyst: compare reaction 1 in Scheme 2. This indeed proved to be the case, as shown by entries 6 and 7 in Table 2. If generation of an imide species was rate-determining, adding a catalytic amount of an imide to the reaction would facilitate the CDP. When, however, CDP was carried out using catalytic amounts of sodium salt of benzanilide (**15**) and *N*,*N*-dibenzoylaniline (**16**) (5 mol % of each) the result was essentially the same as when the sodium salt alone was used: compare entries 6 and 7.

The GPC traces for the products obtained using catalyst **15** in the presence of either calcium chloride (Table 2 entry 4) or lithium chloride (entry 5) are shown in Figure 5. The compositions of the products did not change with more extended reaction times. It is evident that the compositions of the two products are markedly different, with the cyclic trimer **3** being more prominent in the product formed in the presence of calcium chloride. This suggests that under these *equilibrating* conditions the presence of calcium chloride favors the formation of **3.**

2.3. Ring-Opening Polymerizations of the Mixture of Cyclic Oligomers 2. In most other systems ED-ROP's have usually been carried out in the melt.[1,2] However the present MCO's **2** melt at ca. 400−440 °C and, while attempts to achieve ED-ROP's by heating the neat MCO's with 2 mol % of sodium hydride at 430 °C gave what were certainly very tough polymeric materials, they were discolored and insoluble in all solvents investigated, including 98% sulfuric acid. This clearly indicates that cross-linking had occurred.

Attention was therefore turned to ED-ROP using solutions of the MCO's **2** (25% w/v) in DMSO containing 8% w/v of lithium chloride. Both sodium hydride (5 mol %) or the sodium salt of benzanilide (**15**) (5 mol %) were used as catalysts and the reactions were carried out at 170 °C over 6 h. The products were isolated by precipitation into dilute hydrochloric acid. After drying, the solids were analyzed by FT-IR and ^{1}H NMR spectroscopies, GPC and solution viscometry. The results are summarized in Table 3. In all cases FT-IR and ^{1}H NMR spectra confirmed that the product was indeed polymer **1**. Inherent viscosities were invariably greater than the value of 0.17 dL g^{-1} obtained by previous workers for the ED-ROP copolymerization of the cyclic trimer **3** (91%) with caprolactam (9%).[36] In the present work, the highest molecular weights were obtained using sodium hydride as a catalyst and these, as determined by GPC, were M_n = 29200 and M_w = 46000. These values are comparable to those found, M_n = 22500 and M_w = 53000, for a sample of the commercial polymer **1**.

Table 2. Cyclodepolymerizations of Polymer 1

entry	solubilizing salt[a]	catalyst (mol %)	yield of product (%)	inherent viscosity (dL g^{-1})[b]	% macrocycles[c]	MALDI−TOF MS macrocycle range[d]
1	LiCl	DABCO (4%)	91	0.25	ca. 10[e]	5
2	LiCl	PMG (4%)	89	0.20	ca. 25[e]	6
3	LiCl	Cs_2CO_3 (4%)	93	0.22	ca. 40[e]	6
4	$CaCl_2$	NaH (4%)	91	0.17	ca. 100	7
5	LiCl	NaH (3%)	94	0.16	ca. 100	10
6	$CaCl_2$	salt (**15**) (4%)	97	0. 12	ca. 100	9
7	LiCl	salt (**15**) (4%)	93	0.15	ca. 100	6
8	LiCl	salt (**15**) + imide (**16**) (both 5 mol %)	93	0.16	ca. 100	6

[a] 50 mol % of salt based on polymer repeat unit. [b] Measured in 98% sulfuric acid. The starting material had an inherent viscosity of 1.8 dL/g under similar conditions. [c] By GPC analysis. The remainder was polymer. [d] From the cyclic trimer up to the value shown. [e] Approximate value as polymer and MCO's were not well resolved.

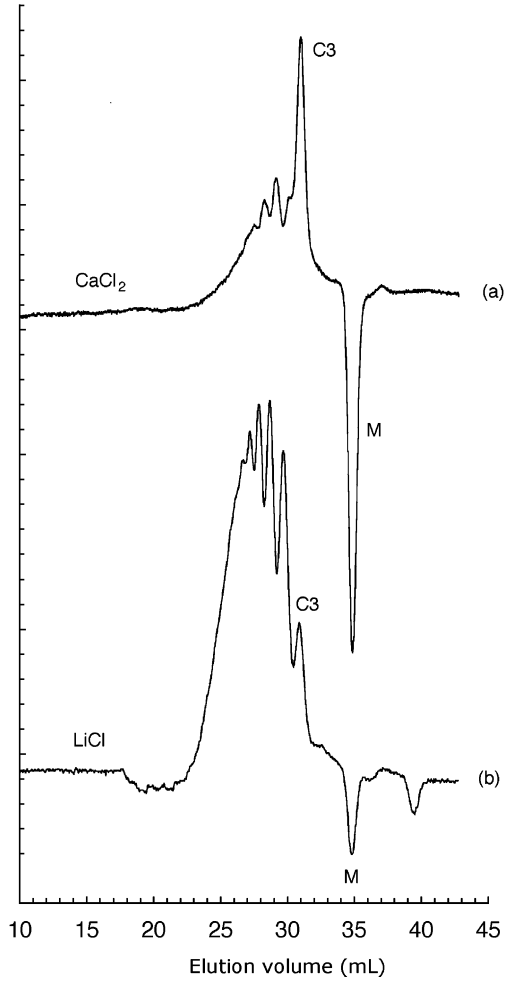

Figure 5. GPC traces obtained for the CDP experiment summarized in Table 2. Trace a: reaction summarized in entry 4 carried out in the presence of calcium chloride. Trace b: reaction summarized in entry 6 carried out in the presence of lithium chloride.

Table 3. Entropically Driven Ring-Opening Polymerizations (ED-ROP's) of Macrocyclic Oligomers 2[a]

entry	catalyst[b]	reacn time (h)	inherent viscosity of product (dL g^{-1})[c]	mol wt[d] M_n	mol wt[d] M_w	polydisp index
1	sodium hydride	6	0.65	23200	46000	1.98
2	sodium salt **15**	3	0.30	4000	7500	1.88
3	sodium salt **15**	6	0.42	13300	30300	2.28
4	sodium salt **15** plus imide **16**	6	0.40	13300	26000	1.95

[a] Reaction carried out at 170 °C in DMSO containing 8% w/v LiCl: see Experimental Section for details. [b] All 5 mol % relative to the repeat unit. [c] Measured in 98% sulfuric acid. [d] Determined by GPC relative to polystyrene standards.

3. Conclusions

The MCO's **2** were obtained in high yield from a pseudo-high-dilution synthesis involving the reaction of isophthaloyl chloride with *m*-phenylenediamine. Yields were much higher than those reported previously.[35,36] The products were characterized by ^{1}H NMR and FT-IR spectroscopies, MALDI−TOF MS, and GPC. These macrocyclic aromatic amides ranged in size from the cyclic trimer up to at least the cyclic nonamer (90 ring atoms). Conditions have been identified for the efficient CDP of poly(*m*-phenylene isophthalamide), **1**, to give the same series of MCO's **2**—the first time this polymer has been successfully cyclodepolymerized. As in the high dilution syntheses, the macrocycles ranged in size from the cyclic trimer **3** up to at least the cyclic nonamer. When lithium chloride was the solubilizing salt for the CDP, six homologous cyclic oligomers were all present in similar proportions, but with calcium chloride as the solubilizing salt the cyclic trimer **3** predominated. This is consistent with the fact that calcium chloride,[35] but not lithium chloride, selectively binds to the cyclic trimer **3** and so shifts the ring−chain equilibrium position in its favor. Treatment of the MCO's **2** (25% concentration w/v) with 5 mol % of sodium hydride or the sodium salt of benzanilide (**15**) in dimethyl sulfoxide containing lithium chloride, at 170 °C for 6 h results in efficient ED-ROP to regenerate high molar mass poly(*m*-phenylene isophthalamide) (**1**), characterized by GPC and ^{1}H NMR spectroscopy.

4. Experimental Section

4.1. Methods and Instrumentation. All chemicals were standard reagent grade and, unless stated otherwise, were used without purification. Dimethylacetamide, dimethylformamide, and *N*-methylpyrrolidone were distilled from calcium hydride and stored under nitrogen. Granules of polymer **1** were purchased from the Aldrich Chemical Co. Macrocyclic oligomers and polymer products were dried in a vacuum oven at 50 °C and 0.1 Torr. Infrared spectra (FT) were recorded for KBr disks using a Perkin-Elmer 1710 instrument. Unless indicated otherwise ^{1}H nuclear magnetic resonance spectra were recorded for solutions in deuteriochloroform at 300 MHz on a Varian Unity instrument. Mass spectra (MALDI−TOF) were obtained using a Micromass TofSpec-2E instrument. Best results were obtained by placing the sample solution (in DMAc containing 8% w/v lithium chloride) on the sample plate and allowing the solvent to evaporate prior to the addition of dithranol as matrix. For GPC analyses the eluting solvent was DMAc containing 1% w/v of lithium chloride. *Oligomers* were analyzed using an in-house-assembled GPC instrument comprising a Waters 501 pump operating at a flow rate of 0.3 cm^3 min^{-1}, four PL-gel 30 cm columns packed with 3 μm−500 Å mixed-E stationary phase operating at 70 °C, and a Knauer HT differential refractometer as detector. *Polymers* were analyzed using a different instrument. This was equipped with a Waters M45 pump operating at a flow rate of 0.3 cm^3 min^{-1}, a PL-gel 3 μ Mixed E four-column set operating at 65 °C, and a Knauer HT differential refractometer as detector. In both cases the system was calibrated using a series of polystyrene standards, each with a narrow polydispersity, and the data were collected and analyzed using software developed by the Manchester Polymer Group from Lab-VIEW software (National Instruments).

4.2. Synthesis of Compound 8. 4.2.1. Dinitro Compound 11. A solution of isophthaloyl chloride (0.1 mol) in toluene (50 mL) was added dropwise to a magnetically stirred solution of 3-nitroaniline (0.25 mol) and triethylamine (0.20 mol) in DMA (100 mL) at 0 °C under nitrogen. The reaction was then allowed to proceed at 20 °C for 6 h. The solvent was removed under reduced pressure and the solid residue was filtered off and washed with water several times. The product was recrystallized from ethanol to give bright yellow crystals (37.4 g, 92% yield), which had mp 182−183 °C; *m/z* (E/I) [100%, (M)$^+$] 407;^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.98 (s, 2 H), 8.85 (s, 2 H), 8.68 (s, 1H), 8.27 (d, 4 H), 8.03 (d, 2 H), 7.80 (t, 1 H) and 7.72 ppm (t, 2 H). Anal. Calcd for $C_{20}H_{14}N_4O_6$: C, 59.11; H, 3.45; N, 13.79. Found: C, 59.07; H, 3.45; N, 13.70.

4.2.2. Synthesis of Diamino Compound 8. The dinitro compound (**11**) (5.00 g, 12.30 mmol), palladium catalyst 10 wt % (0.90 g), dry THF (70 mL), and ethanol (30 mL) were placed in an hydrogenation apparatus and shaken for 2 days under 40 psi of hydrogen. The reaction mixture was then passed through Celite filter-aid and the solvent was removed in vacuo. Recrystallization of the residue from ethanol gave product **9** as pale yellow crystals (3.96 g, 93% yield), mp (by DSC) 216

°C. It had FT-IR 1656 cm^{-1}; *m/z* (E/I) [100%, $(M)^+$] 347; ^1H NMR (DMSO-d_6 containing 0.5 % w/v of LiCl, 300 MHz) δ 10.15 (s, 2 H), 8.45 (s, 1 H), 8.08 (d, 2 H), 7.64 (t, 1 H), 7.15 (s, 2 H), 7.01 (t, 2 H), 6.90 (d, 2 H), 6.36 (d, 2 H) and 5.15 ppm (b, 4 H). Anal. Calcd for $C_{20}H_{18}N_4O_2$: C, 69.36; H, 5.20; N, 16.18. Found: C, 69.10; H, 5.05; N, 16.15.

4.3. Synthesis and Methylation of Compound 9. 4.3.1. Phenyl 3-Chloroformylbenzoate. This compound was prepared as described by Rabilloud et al. in 35% yield.[41] It had mp 70 °C (lit.[41] 70−71 °C).

4.3.2. Synthesis of Compound 9. Phenyl 3-chloroformylbenzoate (5.00 g, 19.20 mmol) in toluene (30 mL) was added slowly at 20 °C to a solution of *m*-phenylenediamine (1.03 g, 9.60 mmol) in DMAc (60 mL) under nitrogen. The mixture was heated gradually to 90 °C over 4 h. After removing the solvent was removed under reduced pressure, the solid residue was resuspended in a mixture of ethanol (150 mL) and 2% aqueous sodium hydroxide (20 mL). The mixture was heated under reflux for 2 h then cooled to 20 °C. The mixture was then added, with vigorous stirring, to 20% hydrochloric acid (200 mL). The white precipitate that formed was collected by filtration, washed with water and then with methanol, and finally dried. This gave compound **9** as a white powder (6.20 g, 80% yield). It had mp 349 °C (by DSC); ν_{max} 1691 cm^{-1}; *m/z* (ES) [100%, $(M)^+$] 405; ^1H NMR (DMSO-d_6 with 0.5% w/v of LiCl, 300 MHz) δ 10.65 (s, 2 H), 8.61 (s, 1 H), 8.48 (s, 2 H), 8.20 (d, 2 H), 8.10 (d, 2 H), 7.73 (m, 3 H) and 7.51 ppm (t, 2 H). Anal. Calcd for $C_{22}H_{16}N_2O_6$: C, 65.35; H, 3.96; N, 6.93. Found: C, 65.19; H, 4.11; N, 6.78.

4.3.3. Methylation of Compound 9. An ethereal solution of diazomethane containing between 0.030 and 0.035 g mL^{-1} was prepared as described in the literature.[42] To a tube containing a sample of the diacid **9** (50 mg) in of DMSO (2 mL) was added the ethereal diazomethane solution (10 mL). The mixture was shaken every few minutes, and after 15 min, glacial acetic acid (1 mL) was added to destroy the excess of diazomethane. Methanol (3 mL) was then added and the white precipitate was filtered off, washed with water and with methanol, and then finally dried. The solid **12** had ^1H NMR (DMSO-d_6, 300 MHz)^1H NMR (DMSO-d_6, plus 0.5 % w/v of LiCl, 300 MHz) δ 10.60 (s, 2 H), 8.59 (s, 1 H), 8.40 (s, 2 H), 8.24 (d, 2 H), 8.20 (d, 2 H), 7.78 (t, 2 H), 7.60 (d, 2 H), 7.40 (t, 2 H) and 3.38 ppm (s, 3 H from $-CO_2CH_3$).

4.4. Synthesis of Linear Oligomers 10. To a flask (50 mL) equipped with a magnetic stirrer, nitrogen inlet, thermometer, and condenser were added *m*-phenylenediamine (2.16 g, 20 mmol), isophthaloyl chloride (2.03 g, 10 mmol), anhydrous lithium chloride (0.42 g, 10 mmol), DMAc (30 mL), and toluene (6 mL). The mixture was stirred magnetically and heated under reflux for 10 h. The reaction mixture was then cooled and precipitated into methanol. The beige product was filtered off and washed several times with hot methanol. The dried product **10** (1.47 g, 80% yield) had ν_{max} 1656 cm^{-1}; the MALDI−TOF mass spectrum is shown in Figure 1a; GPC showed $M_n = 1000$ and $M_w = 1500$; ^1H NMR (DMSO-d_6 + 0.5% w/v LiCl), 300 MHz) δ 11.10−10.58 (s, 2 H), 9.00−8.80 (s,1 H), 8.64−8.50 (s,1 H), 8.28−8.02 (d, 2 H), 7.80−7.59 (m, 3 H) and 7.42−7.19 ppm (t, 1 H), with end group signals appearing at δ 6.58 ppm.

4.5. Synthesis of Cyclic Oligomers 2 under Pseudo-High-Dilution Conditions.[35] The reactions carried out are summarized in Table 1. The following procedure is typical.

4.5.1. Synthesis Summarized in Table 1, Entry 1. A solution of isophthaloyl chloride (11.00 g, 54.18 mmol) in toluene (70 mL) was drawn into a 100 mL syringe. A solution of *m*-phenylenediamine (5.85 g, 54.18 mmol) in DMAc (70 mL) was drawn into a second syringe. A dual syringe pump was then used to add these solutions simultaneously at a rate of 10 mL/h each to a three-necked, 500 mL flask containing a solution of calcium chloride (6.01 g, 54.18 mmol) in DMAc (200 mL) at reflux temperature (165−168 °C) under nitrogen. A clear brown solution was formed and, after addition was complete, the reaction mixture was stirred at 150 °C for a further 10 h, reduced in volume to ca. 80 mL using a rotary evaporator, and then added slowly to a vigorously stirred mixture of distilled water (300 mL) and concentrated hydrochloric acid (10 mL). The desired MCO's precipitated out as a white solid which was collected by vacuum filtration and washed with water until the washings were neutral. The product was resuspended in methanol (100 mL) and stirred at 60 °C for 30 min, then filtered off and dried. This gave a white solid (12.25 g, 95% yield). It had ν_{max} 1656 cm^{-1}; *m/z* (MALDI, dithranol, LiCl, DMAc) 721, 959, 1197, 1435, 1674, 1913, and 2151 corresponding to a series of macrocyclo oligomers from the trimer $[(M \times 3) + Li]^+$ up to the nonamer $[(M \times 9) + Li]^+$. GPC analysis revealed a series of low MW oligomers (see Figure 1b).

4.6. Treatment of MCO's 2 with Diazomethane. This was carried out using the procedure described in section 4.3.3.

4.7. Isolation of a Mixture of Cyclic Trimer 3 and Cyclic Tetramer 13. A portion of the crude cyclic product (3.0 g) from the reaction summarized in Table 1 (entry 1) was placed in a Soxhlet apparatus and extracted with THF for 24 h. Evaporation of the solvent left a residue (0.27 g, 9% of the original mass), which decomposed at >400 °C and was shown by GPC to be a mixture of two cyclic oligomers: see Figure 4. Analysis by MALDI−TOF MS confirmed these were the cyclic trimer **3** (*m/z* 722 $[(M \times 3) + Li]^+$) and the cyclic tetramer **13** (*m/z* 959 $[(M \times 4) + Li]^+$).

4.8. Preparation of Catalysts. 4.8.1. Benzanilide Sodium Salt (15). Benzanilide (5.00 g, 0.025 mol) was dissolved in dry THF (40 mL) under nitrogen. Sodium hydride (0.63 g, 0.026 mol) was quickly added, and the mixture was stirred under reflux for 5 h. The reaction solvent was then removed under reduced pressure. The residue (5.40 g) was dried in a vacuum oven at 60 °C and then stored in a desiccator under nitrogen.

4.8.2. Preparation of *N,N*-Dibenzoylaniline (16). To a cold solution (ca. − 50 °C) of benzanilide (6.00 g, 0.030 mol) in dry THF (50 mL) under nitrogen was cautiously added a solution of *n*-butyllithium (1.34 g, 0.021 mol) in hexane. The resultant mixture was stirred at room temperature for 1 h. Benzoyl chloride (17 g, 0.12 mol) was then added dropwise under vigorous stirring and the mixture heated under reflux for 4 h. The cooled solution was poured into acidified water (150 mL) and the precipitate filtered off and washed with water and then methanol. Recrystallization from ethanol/chloroform gave white crystals (8.8 g, 85% yield). These showed mp 180 °C (lit.,[43] 179−180 °C); ν_{max} 1694 cm^{-1}.

4.9. Cyclodepolymerization. The various reactions carried out are summarized in Table 2. The procedure below (4.10.1) is typical. From a similar preliminary experiment samples were removed every 10 h, precipitated into water, collected, dried and analyzed by GPC. This showed that the optimum reaction time for CDP was 70 h.

4.9.1. Reaction Summarized in Table 2, Entry 6. To a warm solution containing poly(*m*-phenylene isophthalamide) (Nomex) (**1**), (M_n 22500, M_w 53000, η_{inh} = 1.8 dL g^{-1} in 98% H_2SO_4) (2.00 g, 8.40 mmol) and lithium chloride (0.350 g, 8.40 mmol) in dry DMSO (200 mL) was added the sodium salt of benzanilide (**15**) (74 mg, 4 mol %). The reaction mixture was heated at 150 °C under nitrogen for 70 h and then cooled and carefully added to dilute hydrochloric acid (500 mL, 1 M). The precipitate was collected, washed with water and methanol, and then dried to afford a white solid (1.85 g, 93% yield). It had mp 400−440 °C; η_{inh} = 0.15 dL g^{-1}; *m/z* (MALDI−TOF mass spectrum, dithranol, LiCl, DMAc) 721, 960, 1198, 1436, 1675, 1913, and 2151, corresponding to a series of cyclic oligomers from the trimer $[(M \times 3) + Li]^+$ up to the nonamer $(M \times 9 + Li)^+$. The results of the GPC analysis are summarized in Table 2.

4.10. ED-ROP of Cyclic Oligomers (2) in Solution. The various ED-ROP's carried out are summarized in Table 3. The following procedure is typical.

4.10.1. Experiment Summarized in Entry 1. Cyclic oligomers (**2**) (1.00 g, 4.2 mmol), lithium chloride (0.32 g, 4.2 mmol), and DMSO (4 mL) were placed in a tube (10 mL) equipped with a Claisen adapter, mechanical stirrer and gas inlet. After purging the vessel with nitrogen, the solution was heated gradually to 100 °C in an oil bath until it become clear

and homogeneous. Sodium hydride (4.0 mg, 0.166 mmol) was then added quickly, and the reaction mixture was heated at 170 °C over a period of 6 h, during which time the solution increased significantly in viscosity. The mixture was then cooled and the polymer was precipitated in dilute hydrochloric acid (30 mL, 3 N). The precipitate was filtered off, washed with methanol and dried. The crude product was washed with hot acetone to remove low molecular weight materials. The polymer (0.88 g, 88% yield) had ν_{max} 3200 and 1709 cm^{-1}; by GPC $M_n = 23200$ and $M_w = 46000$; ^1H NMR (DMSO-d_6 + 50% w/v LiCl), 300 MHz) δ 11.10−10.58 (s, 2H, NH), 9.00−8.80 (s, 1H, H_a), 8.64−8.50 (s,1H, H_d), 8.28−8.02 (d, 2H, H_b), 7.80−7.59 (m, 3H, H_c and H_e) and 7.42−7.19 ppm (t, 1H, H_f); see formula **1** for assignments.

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