Macrocycles. 15. The Role of Cyclization in Kinetically Controlled Polycondensations. 1. Polyester Syntheses

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ABSTRACT: Various diols were polycondensed with dicarboxylic dichlorides in the presence of pyridine or γ-picoline. Aliphatic dicarboxylic acid dichlorides were reacted with 1,4-butanediol, catechol resorcinol, methylhydroquinone or bisphenol A. Isophthaloyl chloride was polycondensed with α,ω-dihydroxyalkanes, methylresorcinol, or 4-methylcatechol. The resulting polyesters were characterized by ^{1}H NMR spectroscopy and SEC measurements. When the reaction products were analyzed by MALDI−TOF mass spectrometry, cyclic oligo- or polyesters were found to be the main products in all cases. The cycles were the only detectable products, when the reaction conditions were optimized for complete conversion and highest molecular weights. These results together with previously published results definitely prove in agreement with theoretical considerations that cyclizations are an inherent and necessary component in step-growth polymerizations conducted under ideal conditions (no side reaction and equilibrations, perfect stoichiometry, and homogeneous phase). Furthermore, cyclizations are a decisive limitation of the chain growth even under ideal conditions. Therefore, these results also indicate that the "Carothers equation" represents in two points a misleading description of step-growth polymerizations.

Introduction

If the role of cyclizations in step-growth polymerizations are discussed from a fundamental point of view, two totally different scenarios need to be distinguished and defined. The first scenario concerns polycondensations involving "backbiting degradation" and other equilibration reactions (also called transreactions or interchange reactions). This scenario may also be called polycondensations under thermodynamical control, even if in indidvidual experiments the thermodynamically stable equilibrium will not be achieved. The second scenario, which may be called polycondensations under kinetic control, excludes any kind of equilibration (interchange) reactions. The present work exclusively deals with this second type of scenario.

When a polycondensation proceeds under ideal conditions (no loss of functional groups by side reactions, no equilibration, perfect stoichiometry and homogeneous phase) this polycondensation should obey the "Carothers equation" (eq 1) and yield polymers of extremely high

$$\overline{DP} = \frac{1}{1-p} \quad \text{with } p = \frac{N_o - N_t}{N_o} \tag{1}$$

$\overline{DP}$ = average degree of polymerization

p = conversion of functional groups

$N_o - N_t$ = number of functional groups

molecular weight, with conversions approaching 100%. This is at least the standard comment and description of chain growth polymerizations found by the authors of this study in all textbooks they had in hand.[1−13] Only in few cases[4,11] is a negligible role of cyclization mentioned, as exemplarily extracted from ref 4:

"Cyclization generally plays a minor role and can be neglected, except perhaps in the very early stages of a polycondensation, or, with monomers like 6-aminohexanoic acid which can easily form the seven-membered ring ϵ-caprolactam; even in this case long linear chains are generated".

In 1912 Ruggli[14] published the first syntheses of macrocycles under conditions which later were called "Ruggli−Ziegler dilution method" (RZDM).[15] This RZDM has then become the standard procedure for the preparation of macrocycles. This method is based on the consideration that a difunctional monomer under conditions allowing for a clean and rapid reaction has the choice to undergo cyclization or dimerization. Analogously, higher oligomers have the choice between cyclization and polycondensation. High dilution is recommended for the synthesis of cycles because the chain growth step depends on the square power of the monomer (oligomer) concentration in contrast to the intramolecular cyclization step. Of particular interest for the proper understanding of step-growth polymerizations are the consequences of the RZDM, when interpreted in the inverse direction, namely from low to high concentrations. It is obvious that the average molecular weights will dramatically increase, but under the ideal conditions defined above, the tendency of cyclization will not disappear. The influence of cyclizations on the structure of the reaction products will be shifted to higher conversions, but finally, at 100% conversion, all oligomers and polymers will be cycles. Therefore, the correct interpretation of the inverse RZDM is in contradiction to the "Carothers equation" (eq 1) which does not account for cyclizations.

More than 2 decades ago two groups of British authors published detailed theoretical analyses of step-growth polymerizations.[16,17] Despite somewhat different methods of calculation, both teams reached the same conclusion summarized in Figure 1. Under ideal conditions the molar fraction of cyclic species will reach 100%

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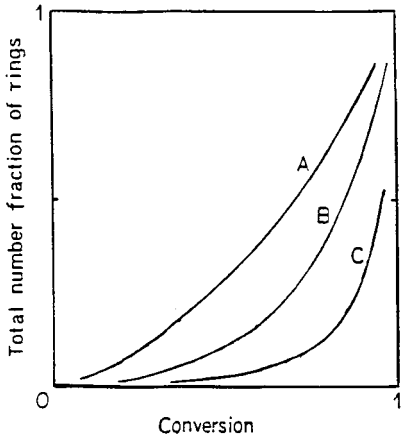
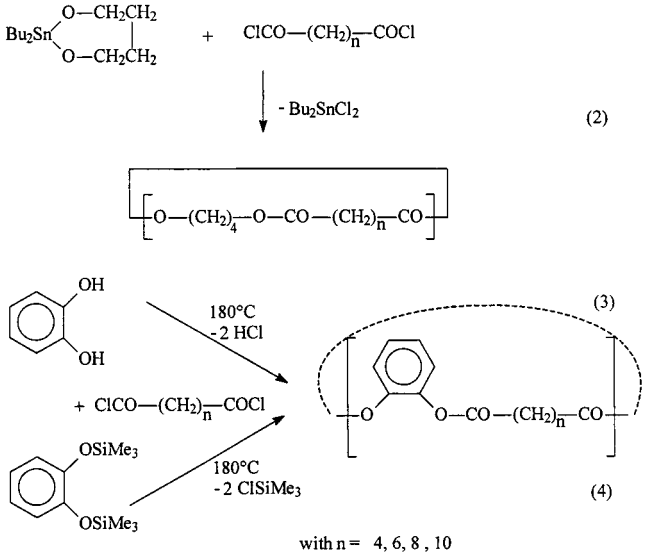


Figure 1. Molar fraction of all cyclic species in a kinetically controlled step-growth polymerization as calculated in ref 13: (A) total monomer concentration (A−A + B−B) 0.0134 mol/L, (B) 0.2194 mol/L, and (C) 0.8808 mol/L.

at 100% conversion regardless of the initial monomer concentration. The influence of the concentration illustrated in Figure 1 is nothing but a quantified version of the inverse RZDM. Interestingly neither the inverse interpretation of the RZDM nor the calculations of the British authors have ever been mentioned and discussed in textbooks of polymer science. Furthermore, to the best of our knowledge condensation experiments designed to prove or disprove the above "cyclization theory" have not been published yet.

In this connection, a paper of Horbach et al.,[18] who studied syntheses of poly(bisphenol A carbonate) under pseudoideal reaction conditions and found cyclic polycarbonates as the main products, should be mentioned. However, in this system, the interface of the water/toluene mixture might have favored the reaction (i.e., cyclization) between the polar end groups. Quite recently three different polycondensation processes were reported by Kricheldorf et al.[19,20] to yield cyclic polyesters, although they were conducted in bulk or in concentrated solution (eqs 2−4). Again the high yield



of cyclic oligo-/polyesters observed in these cases may be attributed to special structural circumstances (e.g., ortho substitution of an aromatic monomer). Therefore, the present work was designed to provide a broader experimental basis for a final conclusion whether the "Carothers equation" or the inverse RZDM give a more adequate description of polycondensations under kinetic control. Polycondensations of various diols with dicarboxylic acid dichlorides were studied in the presence of pyridine because the mild conditions of this approach prevent any formation of cycles via "backbiting degradation".

Table 1. Polycondensations of 1,4-Butanediol with ADADs

polyc no.	ADAD *n*	excess of ADAD	method	time (d)	yield (%)	η_{inh}[a] (dL/g)	M_n[b] (SEC)	M_w/M_n[b]
1	4	0	A	1	61.5	0.25	3500	2.15
2	6	0	A	1	68.0	0.90	25 000	1.70
3	8	0	A	1	68.0	0.80	20 000	1.70
4	10	0	A	1	73.5	0.91	26 000	1.75
5	4	1	B	7	80.0	0.74	15 000	2.0
6	4	3	B	7	80.5	0.63		
7	4	5	B	7	75.5	0.60		
8	6	1	B	7	72.0	0.81	21 000	1.80
9	8	1	B	7	83.0	0.90	25 000	1.80
10	10	1	B	7	82.0	0.92	28 000	1.90

[a] Measured with C = 2 g/L at 70 °C in the CH_2Cl_2. [b] SEC measurements in THF at 30 °C calibrated with the Mark−Houwink equation (eq 5).

Experimental Section

Materials. Thionyl chloride, catechol, resorcinol, bisphenol A, isophthalic acid, and terephthalic acid were gifts of Bayer AG (Leverkusen, Germany). Thionyl chloride was distilled and all other monomers were recrystallized prior to use. 1,4-Butanediol, 1,6-hexanediol, 1,10-decanediol, 1,12-dodecanediol, methylhydroquinone, 4-methylcatechol, and phenylhydroquinone were purchased from Aldrich Co. (Milwaukee, WI). The diphenols were recrystallized under nitrogen. 1,4-Butanediol was azeotropically dried with toluene and distilled in vacuo. The solid diols were dried over P_4O_{10} in vacuo. The aliphatic α,ω-dicarboxylic acids (purchased from Aldrich Co.) and the aromatic dicarboxylic acids were transformed into their dichlorides by means of refluxing thionyl chloride. They were twice distilled before use. Dichloromethane and 1,2-dichloroethane were distilled over P_4O_{10}; pyridine was stored over KOH pellets and distilled over freshly powdered CaH_2.

Polycondensations. Method A. 1,4-Butanediol (60 mmol) and sebacoyl chloride (60 mmol) were dissolved in dry CH_2Cl_2 (120 mL) and dry pyridine (121 mmol) was added dropwise with stirring. After 24 h the reaction mixture was concentrated in vacuo to approximately 50% and precipitated into methanol. The precipitated polyester was isolated by filtration, washed with methanol, and dried at 40 °C in vacuo.

Method B. Resorcinol (30 mmol) and sebacoyl chloride (30 mmol) were dissolve in dry CH_2Cl_2 (60 mL) and cooled with ice to 3−5 °C. Ice-cold, dry pyridine (120 mmol) was added dropwise under permanent cooling with ice. After complete addition, the ice was removed, and the reaction mixture was allowed to stand at 20−22 °C for 7 days. Finally it was poured into methanol, and the precipitated polyester was isolated by filtration.

Method C. Methylhydroquinone (30 mmol) and isophthaloyl chloride (30 mmol) were dissolved in dry 1,2-dichloroethane (60 mL), and dry pyridine (120 mmol) was added dropwise under cooling with ice. After complete addition, the ice was removed and the reaction mixture was stirred for 20 h at 20−22 °C. Afterward, the reaction mixture was refluxed for 8 h and after cooling poured into cold methanol.

Measurements. The inherent viscosities were measured with an automated Ubbelohde viscometer, thermostated at 20 °C.

The SEC measurements (Table 1) were performed with a Kontron HPLC apparatus equipped with a Waters differential

refractometer Md 410 and four Ultrastyragel columns having pore sizes of 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5}Å.

Dry tetrahydrofuran served as eluent.

The fast atom bombardement (FAB) mass spectra were obtained on a VG-70S mass spectrometer using *m*-nitrobenzyl alcohol as matrix.

The MALDI−TOF mass spectra were performed with a "Micromass Tof Spec E" spectrometer equipped with a nitrogen laser (4 ns pulse time, $\lambda = 337$ nm). All spectra were recorded in the reflectron mode with an acceleration potential of 20 kV and a reflection potential of 26 kV. 1,8,9-Trihydroxyanthracene (dithranol) served as the standard matrix and CH_2Cl_2 as solvent. The substrates were doped with potassium ions. Selected samples of the polyesters **1**−**5** and **7** were also measured with 2,5-dihydroxybenzoic acid, α-cyanocinnamic acid, and 2,4,6-trihydroxyacetophenone hydrate as matrices. The best signal-to-noise ratio was obtained with dithranol, and this matrix involves the lowest risk of hydrolysis during the sample preparation. Finally, it should be mentioned that all the polyesters prepared from ADADS are biodegradable and degrade upon storage, when they were before in contact with moist air (e.g., upon filtration). Thereby the fraction of cyclic polyesters decreases dramatically. The mass spectrum of Figure 6 was recorded with a Bruker "Biflex 2" mass spectrometer.

Results and Discussion

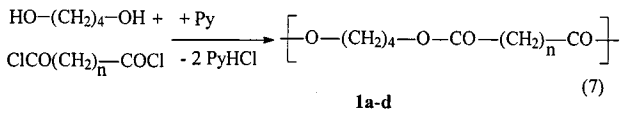
Polycondensations of Aliphatic Dicarboxylic Acid Dichlorides (ADADs) and 1,4-Butanediol. The presentation of the experiments performed in this work is subdivided according to the structure and reactivity of the acid chlorides into two groups: the first one dealing with ADADs and the second one dealing with isophthaloyl chloride (IPC). All polyesters were characterized by ^{1}H NMR spectroscopy, and a perfect agreement of spectra and expected structures was found. Since the polyesters prepared in this work are not new and the synthetic method has been known for a long time, a detailed discussion of the ^{1}H NMR spectra is not needed. Furthermore, most polyesters soluble in tetrahydrofuran (THF) were characterized by SEC measurements. Monomodal elution curves were obtained in all cases. The calibration of the number-average molecular weights (M_ns) was performed via poly(ϵ-caprolactone) and not by means of polystyrene standards. For this purpose the "*K*" and "*a*" values of the Mark−Houwink equation (eq 5) elaborated by Schindler et al.[21] for THF solutions of poly(ϵ-caprolactone) were used. This procedure was applied because three research groups[22−24] have demonstrated by different methods that calibration with polystyrene overestimates the molecular weights of poly(ϵ-caprolactone) by at least 50% (rather by 100% in the low molar mass region). Since the aliphatic polyesters prepared in this work resemble very much the structure and flexibility of poly(ϵ-caprolactone) a calibration via eq 5 may yield more accurate molecular weights. Even when an aliphatic and an aromatic monomer were combined calibration via eq 5 seemed to be the more reliable alternative. Calibration with the Mark−Houwink equation of polystyrene (eq 6)[22] or PS standards gave again

$$[\eta] = 1.395 \times 10^{-4} M_w^{0.786} \quad \text{(THF at 30 °C)} \quad (5)$$

$$[\eta] = 1.25 \times 10^{-4} M_w^{0.717} \quad \text{(THF at 30 °C)} \quad (6)$$

molecular weights which were by 50% to 80% higher than those obtained with (eq 5) in agreement with a lower exponent of the Mark−Houwink equation. However, several semiaromatic polyesters (e.g., structures **3**, **4**, **5** and **7**) may have higher Mark−Houwink exponents than poly(ϵ-CL) in eq 5 ($a = 0.80-0.85$) due to greater chain stiffness, and thus, the calibration with eq 5 is certainly the better alternative and may even slightly overestimate the real M_ns.

The ADADs were polycondensed with five different classes of diols. The first discussed reaction partner was 1,4-butane diol (eq 7) which was selected from the class

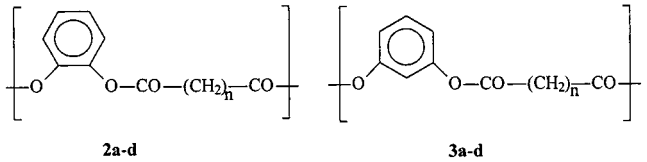


(7)

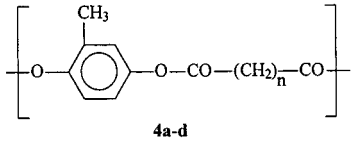
1a-d

a: n = 4 **c:** n = 8
b: n = 6 **d:** n = 10

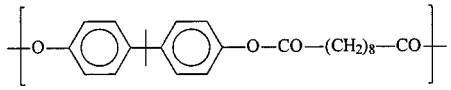
of α,ω-diols for a comparison with the previously published[19] polycondensation of 2,2-dibutyl-2-stanna-1,3-dioxepane (eq 2). In addition to the aliphatic polyesters **1a**−**d** three classes of semiaromatic polyesters were prepared namely **2a**−**d** from catechol, **3a**−**d** from resorcinol and **4a**−**d** from methylhydroquinone (MeHy).



2a-d **3a-d**



4a-d



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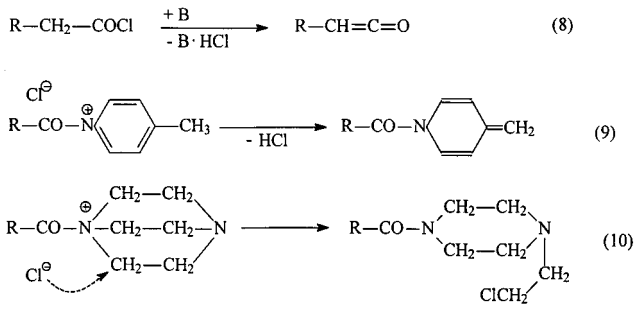
These diphenols were selected to study the influence of the substitution pattern on the course of the polycondensations. MeHy was used instead of hydroquinone to obtain polyesters soluble in THF or $CHCl_3$ with the smallest possible substituent (to avoid steric hindrance of the coupling steps). Furthermore, one polyester of bisphenol A (**5**) was included to vary the length of the para-functionalized diphenols.

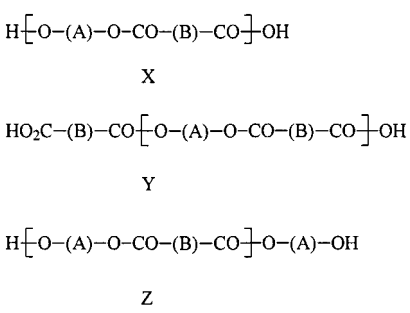
For the polyconensation of the ADADs two different procedures were used labeled "method A" and "method B". Both procedures are based on the dropwise addition of pyridine to solutions of diol (or diphenol) and ADAD in CH_2Cl_2. In the case of method A a stoichiometric amount of pyridine was added, the reaction mixture was not cooled and was worked up after 24 h. This procedure gave satisfactory results with 1,4-butanediol (Table 1), but when diphenols were used the viscosities remained rather low and the reaction products contained rather high fractions of linear oligo- and polyesters having free OH end groups (see discussion below). It was assumed that these results were a consequence of incomplete conversion, and thus, the procedure was varied. For method B, pyridine was used in 100% excess, the reaction mixture was initially cooled and worked up after standing at 20−22 °C for 7 days. Furthermore, the glass walls of the reaction vessel were silanized by means of Me_2SiCl_2.

In numerous preliminary experiments (not discussed here in detail), pyridine was replaced by γ-picoline, which is a stronger base and stronger nucleophile than pyridine. Interestingly, poorer results were obtained with regard to both yields and molecular weights. The most likely side reaction to occur whenever ADADs are combined with bases is their deprotonation (eq 8) followed by side reactions of the unstable ketene group. The risk of this side reaction increases with the basicity of base and it is particularly high for succinyl chloride, and thus, this chloride was excluded from this work. The quarternized γ-picoline which is responsible for the catalytic effect may also loose HCl with formation of a chinoidic structure (eq 9). Sterically unhindered tert.aliphatic amines such as DABCO may have a stronger catalytic effect than pyridine, but the quaternized form may undergo side reactions with the chloride ions (eq 10).[25] Therefore, pyridine was preferentially used as catalyst and HCl acceptor throughout this study.



The results obtained from polycondensations of 1,4-butane diol (eq 6) were interesting for two reasons. First, the molecular weights were higher than those obtained via the stannacycle (eq 2) despite the lower concentration of the monomers in the reaction mixture. Second, the MALDI−TOF spectra revealed that at least up to M_n of 5000 Da the cyclic oligo-/polyesters were the main reaction products (obviously ≥95% of the reaction products in this molecular weight range). This finding is a further confirmation of our previous conclusion that the cyclic oligo-/polyesters obtained from the ring-opening polycondensation of 2-stanna-1,3-dioxacycloalkanes (e.g., eq 2)[19] at moderate temperatures neither result from a complexation or template effect of the tin nor result from "backbiting degradation".

In the beginning of this work, the ADADs were polycondensed with 1,4-butanediol by method A (nos. 1−4, Table 1). With exception of the polyadipate **1a**, relatively high molecular weights were obtained. The MALDI−TOF mass spectra revealed for the high molecular weight polyesters, nos. 2−4, a predominant formation of cycles and linear oligoesters of structure X, Y,



or Z were barely detectable (quite analogous to Figure 2). However, the spectrum of polyadipate no. 1 displayed

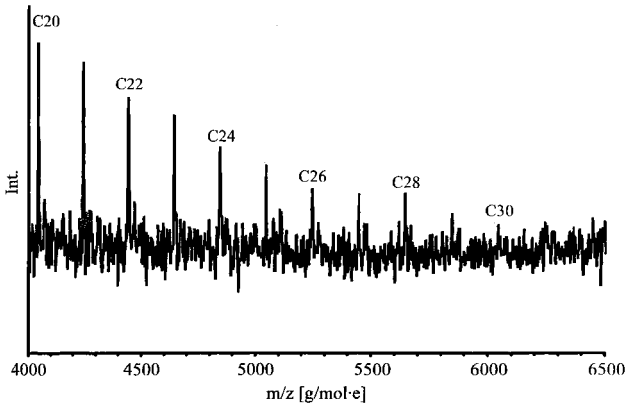


Figure 2. MALDI−TOF mass spectrum (segment) of poly(1,4-butanediol adipate), **1a**, prepared by method B (no. 5, Table 1).

a significant fraction of linear oligoesters of structure X and Z. Therefore, the syntheses of **1a**−**d** were repeated using method B. Furthermore, a slight excess of ADADs was used, because it was learned from polycondensation no. 1, Table 1 and from polycondensations of diphenols (see below) that the isolated polyesters contained a considerable fraction of linear oligoester having structure Z whenever an equimolar amount of ADADs was added. The polycondensations nos. 5−7, Table 1, yielded significantly higher molecular weights than no. 1 and indicated that an excess of 1% adipoyl chloride is the optimum. Therefore, all polycondensations of the higher ADADs were conducted with an excess of 1%, but the resulting molecular weights were quite similar to those obtained from method A. Linear oligoesters of structure Z were not detectable in the MALDI−TOF mass spectra of the polyesters prepared by method B (nos. 5−10) and only traces of oligoesters X were found. Figure 2 illustrates exemplarily the predominance of the cyclic polyesters even above masses of 4000 Da and shows that in the case of **1a**, no 5. (Table 1), the cyclic polyesters were detectable up to a degree of polymerization (DP) of 30. In this connection, it should be mentioned that the molecular weights of **1a**−**d** were by 50% higher than those obtained from the cyclic tin monomer according to eq 2.[19] The aforementioned results also indicate that the cyclic polyesters isolated from the polycondensation of the tin monomer (eq 2) were not a result of a special template effect of the dibutyltin group.

Polycondensations of ADADs and Various Diphenols. When the four ADADs used in this work were polycondensed with catechol according to method A, poor results were obtained. no polyester precipitated from methanol when adipoyl chloride was used, and from the higher ADADs, polyesters with low viscosities ($\eta_{inh} \leq 0.15$ dL/g) were obtained. The MALDI−TOF mass spectra showed the presence of cycles, but the linear oligoesters of structures X, Y, and (mainly) Z were prevailing. These results (and analogous results of resorcinol and methylhydroquinone) prompted us to use method B with variation of the stoichiometry (Table 2). The advantage of method B is documented by a low yield of a methanol insoluble polyadipate **2a** and by higher viscosities of **2b** and **2c**, even when only equimolar amounts of monomers were used. When an excess of adipoyl chloride was added (nos. 2−6, Table 2) the molecular weight has doubled with a molar excess of 5 or 7%. In the MALDI−TOF mass spectra of these

Table 2. Polycondensations of Catechol with ADADs via Method B

polyc no.	ADAD *n*	excess of ADAD	yield (%)	η_{inh}[a] (dL/g)	M_n[b] (SEC)	M_w/M_n[b]
1	4	0%	25.5	0.10	2200	2.45
2	4	1%	27.0	0.13	2800	2.65
3	4	3%	35.5	0.15	3200	2.70
4	4	5%	36.0	0.20	3900	2.70
5	4	7%	35.0	0.21	4200	2.90
6	4	10%	36.5	0.17	3600	2.80
7	6	0%	65.5	0.23	4500	3.00
8	6	1%	38.5	0.22	4500	3.00
9	6	3%	0			
10	8	0%	66.5	0.30	5500	3.10
11	8	1%	57.0	0.23	4500	3.00
12	8	3%	57.0	0.19	4000	2.90

[a] Measured with $C = 2$ g/L at 70 °C in the CH_2Cl_2. [b] SEC measurements calibrated with the Mark−Houwink equation (eq 5).

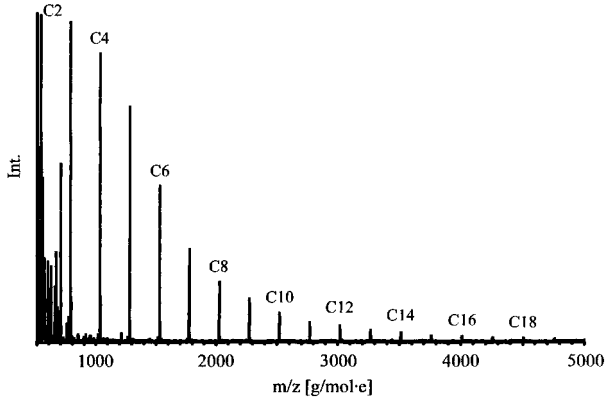
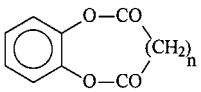


Figure 3. MALDI−TOF mass spectrum of poly(catechol suberate) **2b**, prepared by method B (no. 7, Table 2).

optimized samples only traces of linear oligo- or polyesters were detectable. The longer ADADs did not give higher molecular weights when added in excess, and linear oligoesters were barely detectable in the MALDI−TOF mass spectra even when the monomers were used in equimolar amounts (Figure 3 the largest cycle assigned in this Figure has DP 18, but the cycles are detectable up to DP 23 in the expanded spectrum). The soluble fractions of the poly(catechol ester)s **2a**−**d** were characterized by fast atom bombardment or MALDI−TOF mass spectrometry and proved to consist exclusively of macrocycles including the monomeric cycles **6**.



6 a-d (n = 4,6,8,10)

In the case of the adipate **2a** a particularly high fraction of the monomeric cycle **6** ($n = 4$) was found. These results agree well with those of a previous study, where two different synthetic methods were applied (eqs 3 and 4). In other words the high cyclization tendency proved to be independent of the synthetic method, provided that nearly ideal reaction conditions were established.

In the case of resorcinol the variation of the reaction conditions had an even greater influence on structure and properties of the products. Therefore, the results obtained with method A were also listed in Table 3. The polyesters generated by this method contained cycles, but also large fractions of linear species (mainly having structure Z) as illustrated by Figure 4A. The polycondensation nos. 5, 11, 12, and 13 demonstrate a significant increase of the molecular weights when method B was used. This improvement was paralleled by a considerably higher ratio of cyclic to linear oligo- and polyesters. Furthermore, the stoichiometry was varied in the case of adipoyl chloride (nos. 5−10) and an enormous increase of the molecular weight was found. Quite analogous to the polycondensations of catechol the maximum molecular weights were achieved with a 5−7% excess of the acid chloride. The MALDI−TOF mass spectrum of Figure 4B demonstrates the dramatic increase of cyclic reaction products when the reaction conditions are optimized in direction of high conversion.

In the case of methylhydroquinone, the same trends were observed as for resorcinol. The unsatisfactory results initially obtained with method A will not be

Table 3. Polycondensations of Resorcinol with ADADs

polyc no.	ADAD *n*	excess of ADAD	method	time (d)	yield	η_{inh}[a] (dL/g)	M_n[b] (SEC)	M_w/M_n[b]
1	4	0%	A	1	58.5	0.14		
2	6	0%	A	1	73.0	0.25		
3	8	0%	A	1	88.0	0.38		
4	10	0%	A	1	72.0	0.35		
5	4	0%	B	7	83.5	0.19	3000	2.00
6	4	1%	B	7	60.0	0.21	4000	2.65
7	4	3%	B	7	72.0	0.33	5000	2.55
8	4	5%	B	7	86.0	0.78	9500	2.70
9	4	7%	B	7	87.5	0.82	11 500	2.65
10	4	10%	B	7	92.5	0.43	6000	2.80
11	6	0%	B	7	93.0	0.51	6500	2.50
12	8	0%	B	7	95.5	0.59	8000	2.70
13	10	0%	B	7	88.5	0.60	8500	2.30

[a] Measured at 20 °C with $C = 2$ g/L in CH_2Cl_2. [b] SEC measurements in THF at 30 °C calibrated with the Mark−Houwink equation (eq 5).

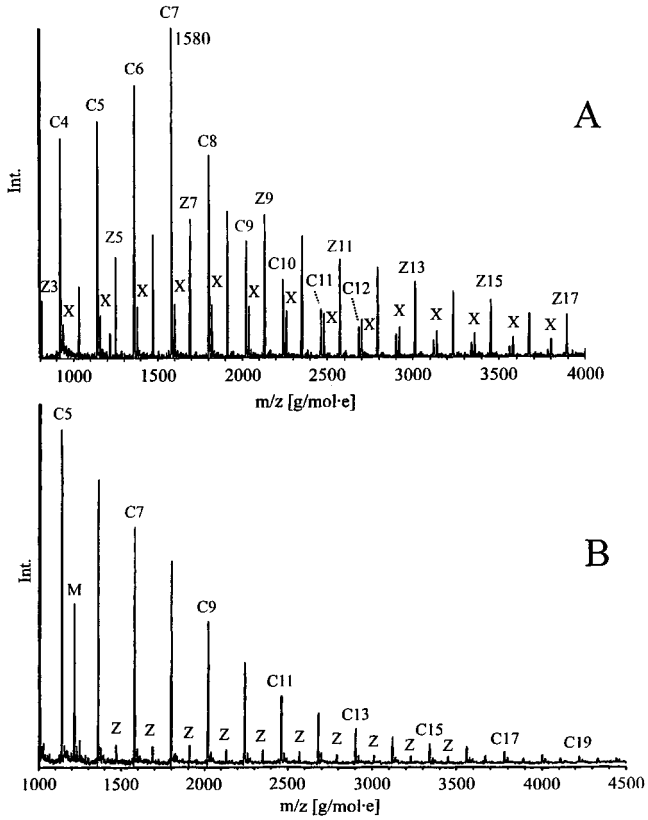


Figure 4. MALDI−TOF mass spectrum of poly(resorcinol adipate) (**3a**): (A) prepared by method A (no. 1, Table 3); (B) prepared by method B (no. 8, Table 3).

Table 4. Polycondensations of Methylhydroquinone with Adipoyl Chloride by Method B

polyc no.	excess of adip. chloride	yield (%)	η_{inh}[a] (dL/g)
1	0%	92.0	0.35
2	1%	94.0	0.51
3	3%	90.0	0.69
4	5%	89.5	1.20
5	7%	93.5	1.26
6	10%	85.5	1.04

[a] Measured at 20 °C with $C = 2$ g/L in CH_2Cl_2.

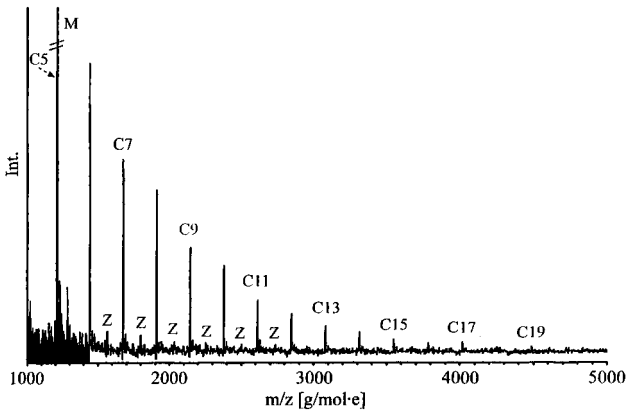


Figure 5. MALDI−TOF mass spectrum of poly(methylhydroquinone adipate) (**4a**) prepared by method B (no. 4, Table 4).

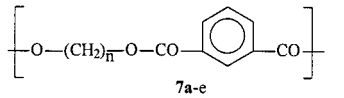
Table 5. Polycondensations of Bisphenol A with Sebacoyl Chloride

polyc no.	method	excess of sebac chloride	yield (%)	η_{inh}[a] (dL/g)	M_n[b] (SEC)	M_w/M_n[b]
1	A	0%	79.5	0.17		
2	B[c]	0%	94.0	0.24	5000	2.2
3	B	0%	93.5	0.56	13 000	2.1
4	B	1%	97.0	0.73	21 000	1.9
5	B	3%	97.0	0.65	17 000	2.4
6	B	5%	82.5	0.54	12 000	2.4

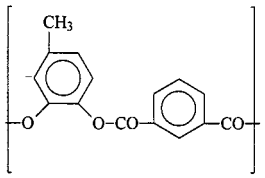
[a] Measured with $C = 2$ g/L at 20 °C in CH_2Cl. [b] SEC measurement in THF at 30 °C calibrated with the M. H. Equation 5. [c] γ-Picoline was used.

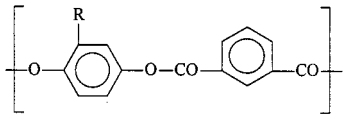
discussed in detail. The data summarized in Table 4 concentrate on method B and on polycondensations of adipoyl chloride with variation of the stoichiometry. Again a conspicious increase of the inherent viscosities was found with a maximum at 7% excess of adipoyl chloride. No linear products were detectable in the MALDI−TOF mass spectrum of sample no. 5, Table 4, whereas small amounts of oligoesters Z were still detectable in the spectrum of sample no. 4 (Figure 5). Finally bisphenol A was polycondensed with sebacoyl chloride under various reaction conditions (see Table 5). Again method B gave the best results and the highest molecular weight was obtained with an excess of 1% sebacoyl chloride. The MALDI−TOF mass spectrum of this optimized sample (no. 4, Table 5) did not display peaks of linear species in contrast to the mass spectra of all other samples listed in Table 5. In summary, it may be concluded from the data compiled in Tables 2−5 that the extent of cyclization does not depend on the structure of the diphenol, it exclusively depends on the optimization of conversion and molecular weight.

Polycondensations of IPC with Various Diols. All polycondensations conducted with an aromatic dicarboxylic acid dichloride were based on IPC and not on terephthaloyl chloride to obtain polyesters soluble in THF or chloroform. Three classes of polyesters were prepared namely **7a-e** from α,ω-alkane diols, **8** from methylcatechol, and **9a**,**b** from substituted hydroqui-



a: n = 4
b: n = 6
c: n = 8
d: n = 10
e: n = 12





9a: R = CH_3
9b: R = C_6H_5

nones. Substituted hydroquinones were selected despite a moderate steric hindrance of one OH group to obtain soluble polyesters. The reaction conditions, yields, and viscosities (or molecular weights) associated with these polyesters are summarized in Tables 6−8.

IPC is less reactive than terephthaloyl chloride and far less reactive than ADADs. Therefore, it was expected in the beginning of this work that the stronger nucleophile γ-picoline might give higher conversions than pyridine (inasmuch as side reactions resulting from a deprotonation of the acid chloride cannot occur). The polycondensations of α,ω-alkane diols (nos. 1−6, Table 6) gave indeed satisfactory results. The MALDI−TOF mass spectra showed a clear predominance of the cyclic esters over the linear ones. The comparison of γ-picolines having different purities revealed that the polyesters prepared with the purer amine (nos. 4−6, Table 6) contained less linear oligoesters. When it was learned from the aforementioned experiments with ADADs that method B in combination with an excess of acid chloride might give better results four additional polycondensations of 1,12-dodecane diol were performed on this basis (nos. 7−10). Higher molecular weights were indeed obtained with a maximum when 1% excess of IPC was used. The MALDI−TOF mass spectrum of this optimized sample were almost free of linear oligoesters, and the cyclic esters were detectable up to DP 30 corresponding to a mass around 10 000 Da (Figure 6).

Polycondensations of IPC with methylcatechol yielded low molar mass products regardless of the reaction conditions (Table 7). SEC measurements calibrated with polystyrene suggested M_n in the range of 500−800 Da. In agreement with these low molar masses FAB measurements exclusively showed the formation of cyclic oligoesters as demonstrated by Figure 7. For the polycondensations of methyl and phenylhydroquinone, the reaction conditions were varied over a broader range. Taking into account the steric hindrance of one OH group and the low reactivity of IPC, a "method C" was used based on 1,2-dichloroethane as solvent, which allowed the heating of the reaction mixture up to approximately 80 °C. Regardless of which procedure was used, the viscosities fell into a rather narrow range, and the MALDI−TOF mass spectra resembled each other. Possibly because the stoichiometry was not varied, the conversion of the OH groups was not complete. None the less, the cyclic oligoesters were prevailing in all mass

Table 6. Polycondensations of α,ω-Alkane Diols with Isophthaloyl Chloride (IPC) via Method B

polyc no.	diol *n*	excess (%) of diol	tertiary amine (purity)[a]	yield (%)	η_{inh}[b] (dL/g)	M_n[c] (SEC)	M_w/M_n[c]
1	6	0	γ-picoline (techn., distilled[a])	62.0	0.16		
2	8	0	γ-picoline (techn., distilled[a])	73.0	0.20		
3	10	0	γ-picoline (techn., distilled[a])	72.5	0.32		
4	6	0	γ-picoline (99% Aldrich)	72.0	0.20	7500	2.2
5	8	0	γ-picoline (99% Aldrich)	73.5	0.29	10 500	2.0
6	10	0	γ-picoline (99% Aldrich)	71.0	0.32	12 500	2.3
7	12	0	pyridine (purum, distilled[a])	92.0	0.48	20 000	1.7
8	12	1	pyridine (purum, distilled[a])	94.5	0.70	29 000	1.7
9	12	3	pyridine (purum, distilled[a])	97.0	0.55	21 500	1.7
10	12	5	pyridine (purum, distilled[a])	97.5	0.35	14 000	1.8

[a] Distillation over freshly powdered calcium hydride. [b] Measured at 20 °C with $C = 2$ g/L in CH_2Cl_2. [c] SEC measurements in THF at 30 °C calibrated with the Mark−Houwink equation (eq 5).

Table 7. Polycondensations of 4-Methylcatechol with Isophthaloyl Chloride

polyc no.	method, amine	solvent	temp (°C)	time	yield[a] (%)	η_{inh}[b,c] (dL/g)
1	B, pyridine	CH_2Cl_2	20	7 d	61.5	0.05
2	C, pyridine	$ClCH_2-CH_2Cl$	20, 80	24 h, 8 h	71.5	0.04
3	B, γ-picoline	CH_2Cl_2	20	7 d	79.0	0.04
4	C, γ-picoline	$ClCH_2-CH_2Cl$	20, 80	24 h, 6 h	58.0	0.03

[a] After precipitation into methanol. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2.

Table 8. Polycondensations of Methylhydroquinone (MeHy) or Phenylhydroquinone (PhHy)with Isophthaloyl Chloride

polyc no.	diphenol	method, amine	solvent	temp (°C)	time	yield[a] (%)	η_{inh}[b,c] (dL/g)
1	MeHy	B, pyridine	CH_2Cl_2	20	7 d	100[a]/89[b]	0.25
2	MeHy	C, pyridine	$ClCH_2CH_2Cl$	20, 80	1 d, 8 h	101[a]/91[b]	0.
3		B, γ-picoline	CH_2Cl_2	20		101[a]/91[b]	0.39
4		C, γ-picoline	ClH_2CH_2Cl	20, 80	24 h, 8 h	99[a]/89[b]	0.27
5		B, pyridine	CH_2Cl_2	20	7 d	103[a]/91[b]	0.38
6		C, pyridine	$ClCH_2CH_2Cl$	20, 80	24 h, 8 h	102[a]/93[b]	0.25

[a] After precipitation into methanol. [b] After reprecipitation into methanol. [c] Measured at 20 °C with $C = 2$ g/L in CH_2Cl_2.

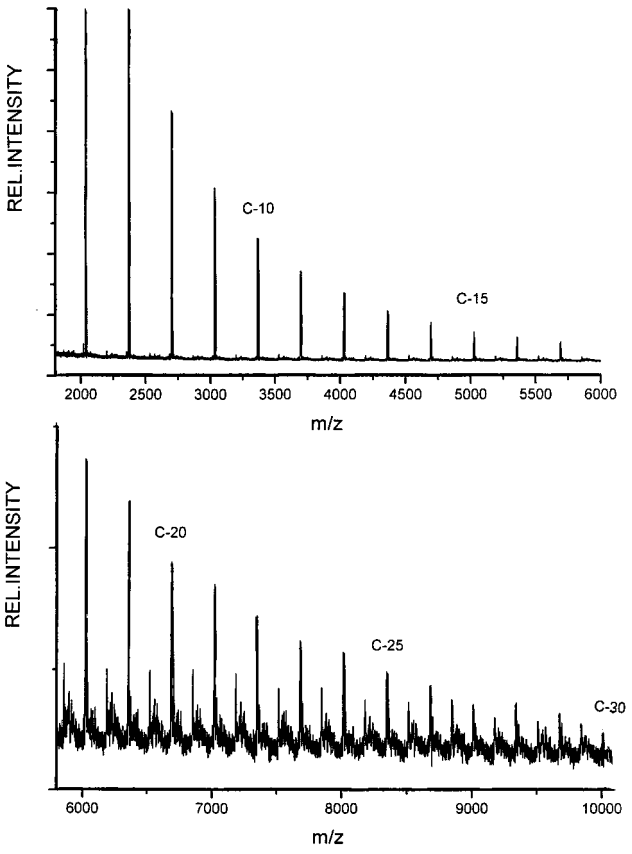


Figure 6. MALDI−TOF mass spectrum of poly(1,12-dodecane diol isophthalate) (**7e**, no. 8, Table 6).

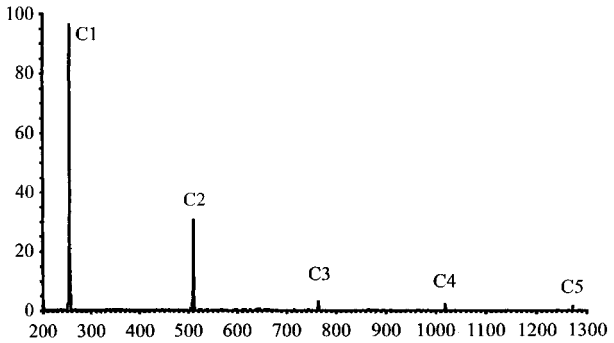


Figure 7. FAB mass spectrum of polyester **8** (no. 1, Table 7).

spectra (Figure 8) a surprising result when the stiffness of these polyesters is taken into account. In summary, the polycondensations based on IPC confirm the main trends derived from the experiments performed with ADADs.

Discussion

The most important aspects of the experimental results described above may be summarized in two points. First, within the technical limits of the MALDI−TOF method we had in hands cyclic oligo- and polyesters were found to be the main reaction products of all optimized polycondensations. The monomer structure did not play a significant role, and when our previous results[19,20] are taken into account, it is also evident that the extent of cyclization does not depend on the synthetic method provided it approaches the ideal conditions. Second, it was found for all classes of polyesters that optimization of the reaction conditions toward higher conversions and molecular weights automatically favored the formation of cycles at the expense of linear species. Both points agree perfectly with the predictions

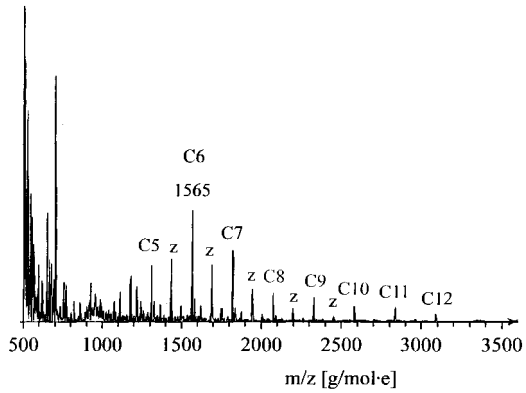


Figure 8. MALDI−TOF mass spectrum of polyester **9a** (no. 3, Table 8).

of the inverse RZDM and qualitatively with the calculations presented by Gordon and Temple[16] or Stepto and co-workers.[17] Therefore, these results and the pertinent theories represent one important deviation from the predictions of the "Carothers equation (eq 1)".

At this point it may be objected that the cyclic oligo- and polyesters detected by the MALDI−TOF method only represent a small nonrepresentative fraction of most of the polyesters studied in this work. Therefore, it may be useful to point out that the molecular weight distribution of polycondensates in terms of the frequency distribution obeys eq 11. This equation means that the

$$n_x = p^{x-1}(1-p)$$

n_x = number (molar fraction) of chains with DP = x (11)

p = conversion of functional groups (see eq 1)

dimer represents the maximum of the number distribution curve, or in other words, the most abundant condensation product. For a sample having an average DP ($\overline{DP}$) of 50 the oligomers and polymers up to a DP of 37 make up approximately 50% of the total number molecules. For a sample of $\overline{DP} = 100$ the oligomers and polymers up to a DP of 55 represent 50% of all reaction products. For the optimized polyesters **1a**−**d** and **5** the $\overline{DP}$ fall into the range 80−110. Taking into account that the products soluble in methanol consisted almost exclusively of cycles (as evidenced by FAB and MALDI−TOF mass spectroscopy) it may be stated that at least 20−25% of all molecules in one sample certainly consisted of cycles. In the case of polyesters **3a**−**d** the fractions soluble in methanol all consisted of cycles. The $\overline{DP}$s of the insoluble polyesters were in the range of 30−50. Taking into account that the MALDI−TOF mass spectra detected cycles up to a DP of 22 (visible up to a DP of 18 in Figure 5) at least 35−50% of these polyesters consisted of cycles. For polyester **7e**, cycles were detected up 10 000 Da (Figure 6) meaning that at least 40−50% of this polyester were cycles. In the case of polyesters **2a**−**d** the large soluble fractions again consisted of cycles. The $\overline{DP}$s are around 20−30 and thus, it is obvious that here around 90% of these polyesters have a cyclic structure. The same conclusion may be drawn for polyester **8**. Therefore, it is clear that the analytical methods used in this work allowed the characterization of a significant fraction of all polycondensates even in the least favorable case (**1a**−**d**).

From these results another important conclusion may be drawn which was not discussed by the British authors.[16,17] If cyclization is an inherent, unavoidable component of any kinetically controlled step-growth polymerization in a homogeneous phase, cyclization is the only, but decisive, factor for the limitation of the chain growth. This is the second important deviation from the theories of Carothers and Flory. All textbooks[1−15] suggest that according to the "Carothers equation" nearly unlimited molecular weights can be obtained provided extremely pure monomers are used in perfect stoichiometry. In contrast, our results and the inverse RZDM predict that for each system (i.e., polymer structure plus reaction conditions) a maximum $\overline{DP}$ must exist which results from the competition between cyclization and propagation. In other words the $\overline{DP}_{max}$ is a function of the V_{pr}/V_{cy} ratio. Unfortunately a reliable calculation of the V_{pr}/V_{cy} ratio is not easily performed. The rate constant (k_{pr}) of the propagation may be considered to be constant in a homogeneous system and may, in principle, be determined via a model reaction of monofunctional compounds. However, the rate constants of cyclizations (k_{cy}) decrease with increasing length of the oligomers and polymers. For flexible polymers, the Jacobsen−Stockmayer theory[26] suggests a relationship such as $k_{cy} \approx DP^{-3/2}$. The flexibility of the polymer backbone plays, of course, an important role. In this connection, it should be mentioned that conformation-dependent cyclization probabilites were calculated by several research groups for a variety of polymers. The calculations were performed in combination with studies of ring−chain equilibria.[27,28] This scenario is, of course, quite different from the scenario of kinetically controlled step-growth polymerizations studied in the present work. However, the mathematical procedures developed for conformation dependent cyclization probabilities may be useful to calculate maximum $\overline{DP}$s.

For a qualitative estimation how the polymer structure will influence the rate of cyclization, eq 12 is

$$V_{cy} \approx \frac{N_{fc}}{N_{uc}} \qquad (12)$$

N_{fc} = number of chain conformations favoring cyclization

N_{uc} = number of conformations unfavorable for cyclization

helpful. Relatively few conformations of the oligomers or polymers will favor the cyclization, and the vast majority of conformations is unfavorable, but may undergo propagation steps. Flexible polymer chains (such as **1a**−**d**) which can adopt a high number of conformations will have a low N_{fc}/N_{uc} ratio and thus may reach relatively high $\overline{DP}$s. The finding that the polyesters **1a**−**d**, **5e**, and **7e** have the highest viscosity values agrees well with this consideration. When flexible monomers are replaced by rigid ones, the total number of conformations decreases, the N_{fc}/N_{uc} ratio increases, and lower $\overline{DP}$s should result. The low viscosities of the polyester samples **8** represent this extreme.

For polymers exclusively built up by rigid aromatic monomers, the total number of low energy conformations is particularly low, but here the substitution pattern is decisive for the course of the polycondensa-

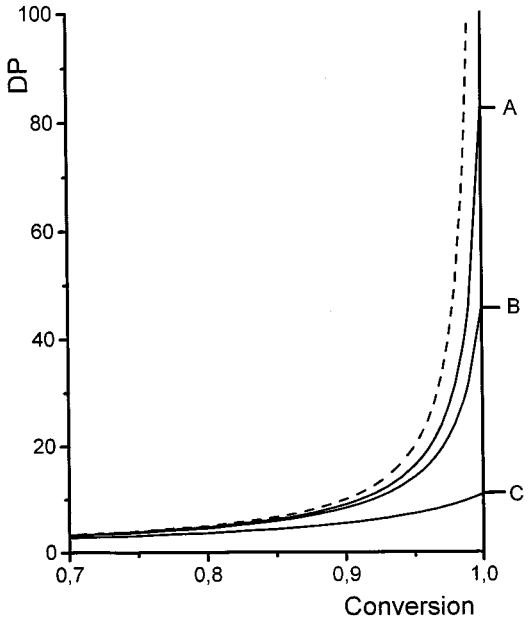


Figure 9. "Carothers Equation" (eq 1) (dotted line) in comparison with real polycondensations involving cyclization (solid lines A, B, and C).

tion. When an ortho-functionalized monomer (e.g., catechol) is involved, the rate of cyclization is particularly high. The results presented for the polyesters **2a**−**d** or **8** agree perfectly with this picture. In other words, even under ideal conditions the $\overline{DP}$ of a polycondensation will not follow the "Carothers equation" (dotted line in Figure 9) but will follow a course schematically presented by the solid lines in Figure (9). In a qualitative sense, curve A may be attributed to the syntheses of flexible polyesters such as **1a**−**d**, **5**, or **7e**. Considering the ortho-functionalization of catechol, curve B in Figure 9 may represent the polyesters **2a**−**d** and curve C the polyester **8**. Regardless of the structure, the growth curve of the $\overline{DP}$ hits the ordinate at a finite value representing the maximum possible $\overline{DP}$ according to eq 11.

Conclusion

The data elaborated in the present work and in two previous studies[19,20] allow interesting conclusions in two directions. First, the long known but rarely used polycondensation of diols and dicarboxylic acid dichlorides in the presence of pyridine may yield high molecular weight polyester when carefully optimized. An excess of pyridine, long reaction times and a slight excess of the acid chloride play the key role for the success of the optimization. Second, cyclic oligo- and polyesters are the main reaction products regardless of the monomer structures. Optimization in direction of high conversion, and high molecular weights automatically favors the formation of cycles over that of linear products. These results perfectly agree with the inverse RZDM and the kinetic calculations of two groups of British authors, but they stand in sharp contrast to the previous theories of Carothers and Flory exclusively based on chain growth via linear oligomers and polymers. It is now clear that the cyclization steps are inherent and unavoidable in any kinetically controlled step-growth polymerization in a homogeneous system. Ring closure is not a side reaction; it is a main reaction like the chain growth itself, and under ideal conditions quantitative conversion results in cycles only regardless of the molecular weight.

Another important conclusion which deviates from the classical theory of Carothers is the prediction of maximum average $\overline{DP}$, which is characteristic for each combination of chain structure and reaction conditions. This $\overline{DP}_{max}$ cannot be surpassed even under ideal conditions. The flexibility of the polymer backbone and the concentration of the monomers are the main factors influencing this $\overline{DP}_{max}$. In this connection, it should be emphasized that the high cyclization tendency reported here and recently[19,20] for several different syntheses of polyesters has also been observed for kinetically controlled syntheses of polyamides and polyethers as will be reported in future publications.

Finally, it should be mentioned that this work also demonstrates that the classical "pyridine method" is well suited for the synthesis of high molecular weight biodegradable polyesters, when the reaction conditions are carefully optimized. All polyesters of this work derived from ADADS are biodegradable and degraded upon storage after contact with moist air, whereby the content of cyclic polyesters dramatically decreased.

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