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Mass Spectral Determination of Cyclic Oligomer Distributions in Polymerization and Degradation Reactions

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ABSTRACT: Mass spectral data have been directly used for the first time to determine the distributions of cyclic oligomers formed during polymerization and degradation reactions. In the text are presented several cases illustrating polymerization and thermal degradation reactions occurrring in polyesters, polyamides, and polysulfides. The experimental distributions of cyclic oligomers allow discrimination between thermodynamically and kinetically controlled cyclization processes. In the former case the cyclic oligomer concentration decreases with $n^{-2.5}$, and in the latter with $n^{-1.5}$. The exponent in the cycle distribution law indicates therefore if the cyclization process is occurring through a back-biting or an end-biting reaction.

Introduction

The production of synthetic polymers in polycondensation and ring-opening reactions is often accompanied by the formation of sizable amounts of cyclic oligomers,[1–4] and it has been also observed that cyclic oligomers are formed in the thermal decomposition processes of several polymers.[1,5–7] Usually, cyclic oligomers of different size are produced in the above processes, and it is of great interest to determine their relative abundances (distributions), since the latter are related to the mechanism of formation of the cyclic species.[1–4]

Mass spectrometry (MS) is a powerful and rapid analytical method and, being able to look at the mass of individual molecules in a mixture, is particularly suitable for the detection of these materials. In fact, it has been often used to identify the cyclic oligomers formed during polymerization and pyrolysis reactions.[1,7–10] However, mass spectra have not yet been exploited to estimate the cyclic oligomer distributions, due to the lack of correlation between EI (electron impact) peak intensities and concentration of the oligomers in the mixture.[1,11]

The introduction of soft-ionization techniques, such as FAB[12–14] (fast atom bombardment), has largely eliminated this problem, and sizable evidence has been now accumulated showing that, in many cases, peak intensities of molecular ions appearing in FAB spectra reflect the relative amounts of oligomers present in the mixture.[15]

Therefore, MS can now be used both to identify the low molecular weight species formed during polymerization and degradation reactions and to determine rapidly the distributions of cyclic oligomers, thus obtaining quick hints on the mechanisms controlling the cyclization processes involved.

Distribution Laws for Cyclic Oligomers

In step-growth polymerizations the molecular weights obtained depend solely on the extent of reaction p and, since they follow a Flory distribution at any p, oligomers should be absent for values of p close to unity, and the same is true for ring-opening polymerizations.

If some oligomers are pesent at the end of these polymerizations, they might originate (a) from an intramolecular cyclization reaction which is competing with the polymerization process or (b) from a concurrent depolymerization reaction acting on the linear polymer formed.

Depolymerization of a high molecular weight polymer to cyclic oligomers may be induced by opportune catalysts[3] or may occur during its thermal degradation.[1]

Studies on the mechanism of formation of the cycles have focused attention on the distribution laws of the cyclic compounds produced.[2–4]

Macrocyclization equilibria are able to describe the behavior of linear polymer chains when they are allowed to reach thermodynamic equilibrium and to generate cyclic oligomers.[16] Historically, a satisfactory theory of macrocyclization equilibria was formulated by Jacobson and Stockmayer[16] (JS), long before the availability of experimental data. The JS theory includes the following assumptions: chains in solution obey Gaussian statistics, all rings formed are stainless, reactivity of all reactive sites along the polymer chain is the same, a thermodynamic distribution is obtained, and end-group effects are negligible.

Therefore, the cyclization probability is related to the mean separation of the reaction sites, and the equilibrium concentration of each cyclic oligomer is predicted to decrease proportionally to $n^{-2.5}$, where n is the ring size expressed as the number of repeating units present.[16] Systems that depend on ring–chain equilibria have been found and the theory has been verified in detail.[2–4]

A situation where the thermodynamic distribution may be violated occurs when preferred or restricted conformations arise in the cyclic oligomers, since the JS theory requires the formation of strainless rings.[16] These effects result often in sensible deviations of some oligomers from the expected distributions.[2–4]

In cyclization reactions that occur during polymerization reactions, the distribution of cyclic oligomers may deviate from the thermodynamic equilibrium because of kinetic factors.[2–4] In fact, the end groups may be capable of reacting at a higher rate compared to the reaction rate of the functional groups attached to the inner portion of the chain molecule. When this happens, an end-biting process takes place (violating the equal-reactivity principle), and a kinetically controlled distribution results. The concentration of the cyclic oligomers formed by end-biting is predicted to decrease proportionally to $n^{-1.5}$, where n is the ring size expressed in number of repeat units present.[2–4]

Consequently, we may conclude that determining the experimental distributions of cyclic oligomers should allow discrimination between thermodynamically and kinetically controlled cyclization processes. In the former case the cyclic oligomer concentration should decrease with $n^{-2.5}$, and in the latter with $n^{-1.5}$. Then the exponent in the cycle distribution law would indicate if the cyclization

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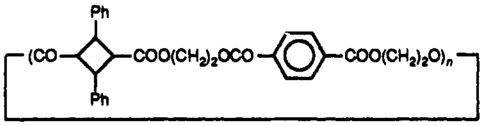
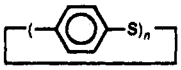
Table I
Distribution of Cyclic Oligomers Generated in Polymerization Reactions[a]

no.	structure of cyclic oligomer	n	m/z	FAB-MS abundance obsd	FAB-MS abundance calcd
1[b]	$-(COCH_2OCH_2COOCH_2CH_2O)_n-$	2	321[b]	17.7[c]	17.7[d]
		3	481	7.1	6.4
		4	641	5.8	3.1
		5	801	1.9	1.8
		6	961	1.1	1.1
		7	1121	0.5	0.8
		8	1281	0.2	0.5
2[b]	$-(COCH_2CH_2CH_2CH_2COOCH_2CH_2O)_n-$	2	345[b]	17.7[c]	17.7[d]
		3	517	6.0	6.4
		4	689	3.7	3.1
		5	851	2.1	1.8
		6	1033	1.4	1.1
		7	1205	0.8	0.8
		8	1377	0.5	0.5
		9	1549	0.3	0.4
		10	1721	0.3	0.3
3[b]	$-(COCH_2CH_2CH_2COOCH_2CH_2O)_n-$	3	475[b]	6.4[c]	6.4[d]
		4	633	4.3	3.1
		5	791	2.8	1.8
		6	649	1.5	1.1
		7	1107	0.9	0.8
		8	1265	0.5	0.5
		9	1423	0.35	0.4
		10	1589	0.2	0.3
		11	1739	0.1	0.25
4[e]		2	515[e]	35.3[c]	35.3[f]
		4	1029	17.6	12.5
		6	1543	7.6	6.8
5[g]	$-(CO(CH_2)_5O)_n-$	3	343[g]	6.4[c]	6.4[d]
		4	457	3.2	3.1
		5	571	2.2	1.8
		6	685	2.6	1.1
6[g]	$-(CO(CH_2)_5NH)_n-$	1	114[g]	100[c]	100[d]
		2	227	20.0	17.7
		3	340	11.0	6.4
7[g]	$-(CO(CH_2)_4CONH(CH_2)_6NH)_n-$	1	277[g]	100[c]	100[f]
		2	453	42.0	35.3
		3	679	11.0	12.5
8[h]	$-(SCH_2CH_2CH_2)_n-$	4	297[h]	3.1[c]	3.1[d]
		6	445	1.2	1.1
		8	593	0.5	0.5
		10	741	0.5	0.3
		12	889	0.25	0.2
		14	1037	0.19	0.13
9[h]	$-(SCH_2CH_2CH_2CH_2CH_2CH_2)_n-$	2	233[h]	35.3[c]	35.3[f]
		4	465	23.0	12.5
		6	697	7.7	6.8
		8	929	3.4	4.4
		10	1161	2.5	3.2
		12	1393	1.5	2.4
10[h]		3	324[h]	6.4[c]	6.4[d]
		4	432	3.1	3.1
		5	540	2.6	1.8
		6	648	0.7	1.1
		7	756	1.4	0.8
		8	864	1.3	0.5
		9	972	0.8	0.4
		10	1080	0.5	0.3
		11	1188	0.4	0.25

[a] Data from step-growth and ring-opening polymerization are reported here. [b] FAB-MS data from ref 17. [c] The relative intensity of the first MS peak has been taken equal to that calculated theoretically for the corresponding cyclic oligomer. [d] Theoretical values calculated according to the $n^{-2.5}$ distribution law (see text). [e] FAB-MS data from ref 18. [f] Theoretical values calculated according to the $n^{-1.5}$ distribution law (see text). [g] FAB-MS data from ref 19. [h] FAB-MS data from ref 20.

process is occurring through a back-biting or an end-biting reaction.[1-4]

Cyclic Oligomers Formed in Polymerization Reactions

The first three examples reported in Table I (sections 1–3) are concerned with the distribution of cyclic oligomers formed in the polymerization of cyclic stannoxanes such as 2,2-di-*n*-butyl-1,3,2-dioxastannolane with diacyl chlorides.[17] The relative abundances of cyclic oligomers, obtained by GPC,[17] have provided unambiguous evidence that the product mixtures are well-behaved equilibrium distributions, showing that the experimental data are in essential agreement with the $n^{-2.5}$ law predicted by the JS

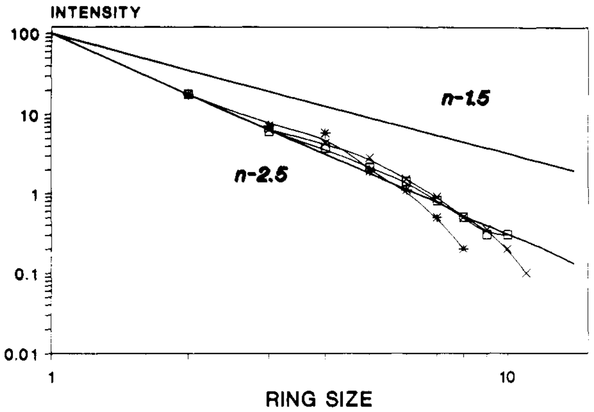


Figure 1. Experimental cycle concentrations for polymerization data reported in Table I: (*) polymer 1; (□) polymer 2; (×) polymer 3, compared with theoretical distribution laws.

theory.[17] FAB mass spectra were used[17] to identify the oligomeric species but not to estimate their distributions.

On the basis of the molecular ion intensities in the reported FAB spectral,[17] we now have obtained the abundances relative to the cyclic esters formed in the polymerization reaction. When these experimental data are compared (Figure 1, Table I) with the distributions calculated according to the JS theory, a very reasonable agreement is found in all three cases.

This result supports the reliability of the MS method (which also has the advantage of being simpler and faster with respect to the current chromatographic methods), which can therefore be applied to other polymerization reactions yielding cyclic oligomers for which FAB-MS data are available.[18-20]

In Table I, section 4, are reported the relative MS abundances for the cycles formed in the polycondensation of bis(2-hydroxyethylene) terephthalate with truxilloyl chloride.[18] They appear to follow a distribution law of the type $n^{-1.5}$, which would indicate a kinetic control (through an end-biting reaction) in the ring formation.

In Table I, section 5, are reported the relative MS abundances for the cycles contained in a solid sample of polycaprolactone.[19] Their concentration decreases in proportion to $n^{-2.5}$, following therefore the thermodynamic equilibrium JS theory, a result which is in agreement with GPC estimates.[21]

The same result is obtained by analyzing the MS data for polycaprolactam,[19] reported in Table I, section 6. In this case there are sensible deviations from equilibrium values, and this fact has already been observed by chromatographic methods.[4] FAB-MS data concerning the relative abundances for the cyclic oligomers contained in a solid sample of nylon-6,6 are reported in Table I, section 7. Their concentration decreases in proportion to $n^{-1.5}$, indicating the presence of kinetic factors in this cyclization process.

The last three examples in Table I (sections 8–10) are concerned with the distributions of some cyclic sulfides formed in polycondensation reactions of dithiols with dibromides.[20] The FAB spectra have[20] a sufficient number of peaks, and therefore the distribution laws can be derived with some confidence. Poly(trimethylene sulfide) and poly(*m*-phenylene sulfide) appear to yield mixtures of cyclic oligomers corresponding to JS equilibrium conditions. Instead, MS data for poly(hexamethylene sulfide) show a better fit for the $n^{-1.5}$ distribution law, indicating the possible control of an end-biting reaction.

Origin of Linear Oligomers in Polymerization Reactions

The formation of linear oligomers in polymerization reactions is well-known in nylons,[20] polyesters,[20] and polycarbonates,[22] although there is scant evidence in the literature about the mechanism of their origin.[1]

In fact, apart from the trivial case of low degrees of monomer conversion, which necessarily results in low molecular weight linear oligomers, their formation might be difficult to explain in polymerization reactions at high conversion, where the molecular weight distribution curves are shifted toward high weights. A further complication ought to be taken into account, i.e., the simultaneous presence of linear and cyclic oligomers in many of the systems quoted above.

A reasonable hypothesis that can be put forward to explain the formation of linear oligomers is that cyclic oligomers are first produced in the polymerization process and then hydrolyzed to linear compounds during the polymerization or in the workup process (extraction, precipitation, washing, drying, etc.). If that is the case, the relative abundances of linear and cyclic oligomers contained in a crude polymer sample should be comparable.

In Table II are compared the relative amounts of cyclic and linear oligomers formed in a copolyester obtained by solution polycondensation[18] and in a polycaprolactone obtained by ring-opening polymerization.[19] The relative abundances have been deduced from the FAB spectra[18,19] of the crude polymer samples, assuming a direct proportionality between peak intensity and oligomer concentration in the mixture.

A fairly good correspondence is observed between the two sets of data, thus confirming the above hypothesis and yielding direct evidence for the origin of the linear oligomers from the cleavage of the cycles.

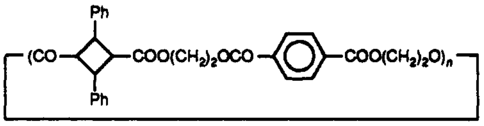
Cyclic Oligomers Formed in Thermal Degradation Reactions

Direct pyrolysis–mass spectrometry (DP–MS) has been used to investigate the thermal degradation processes in polymers, and it has been found that a distribution of cyclic oligomers is often formed in the pyrrolysis of polyesters, polyamides, polycarbonates, polysulfides, and polysiloxanes.[1,7-11] FAB-MS cannot be used in direct pyrolysis experiments, and therefore one may resort to chemical ionization (CI) as a soft-ionization technique capable of yielding a correlation between MS peak intensities and cyclic oligomer concentrations.[23,24]

The direct pyrolysis of aliphatic polyesters into the MS[23] produces CI spectra sufficiently rich in cyclic oligomers to attempt the characterization of their distributions.

In Table III, section 1, are reported the relative MS abundances of the cycles formed in the DP–MS of polyvalerolactone, which appear to follow the $n^{-2.5}$ distribution law. Instead, polycaprolactone (Table III, section 2) appears to produce oligomers that decrease in proportion to $n^{-1.5}$. The case of polypivalolactone has been discussed in detail elsewhere,[24] and data in Table III, section 3, show that its pyrolysis yields a thermodynamic distribution of oligomers. The data available for poly(glycolic acid) and poly(lactic acid) (Table III, sections 4 and 5, respectively) are in favor of an end-biting process, as indicated by the $n^{-1.5}$ decrease of the cyclic oligomer concentration. Finally, the mixture of cycles produced in the pyrolysis of poly(ethylene succinate) (Table III, section 6) appear in thermodynamic equilibrium, favoring therefore a backbiting process.

Table II
Comparison of the Relative Abundances of Cyclic and Linear Oligomers Formed in Polymerization Reactions

no.	polymer	n	cyclic oligomers m/z[a]	cyclic oligomers inten obsd[b]	linear oligomers m/z	linear oligomers inten obsd[b]
1[a]	$(CO(CH_2)_5O)_n$	2	229	59	247	77
		3	343	100	361	100
		4	457	50	475	60
		5	571	34	589	52
		6	685	41	783	39
2[c]		2	515[c]	100[b]	531	100[b]
		4	1029	50	1045	40
		6	1543	22	1543	16

[a] FAB-MS data from ref 18. [b] Normalized peak intensities. [c] FAB-MS data from ref 19.

Table III
Distribution of Cyclic Oligomers Generated in the Pyrolysis of Some Aliphatic Polyesters[a]

no.	cyclic oligomer	n	m/z[a]	CI-MS abundance obsd[b]	CI-MS abundance calcd
1	$(CO(CH_2)_4O)_n$	1	99	100	100[c]
		2	199	13.6	17.7
		3	299	10.0	6.4
		4	399	5.9	3.1
		5	499	2.3	1.8
2	$(CO(CH_2)_5O)_n$	2	246	35.3	35.3[d]
		3	360	26.7	19.2
		4	474	20.5	12.5
		5	588	8.2	8.9
3	$(COC(CH_3)_2CH_2O)_n$	1	118	100	100[c]
		2	218	0.3	17.7
		3	318	10.0	6.4
		4	418	1.5	3.1
4	$(COCH_2O)_n$	3	175	19.2	19.2[d]
		4	233	15.4	12.5
		5	291	8.5	8.9
5	$(COCH(CH_3)O)_n$	3	217	19.2	19.2[d]
		4	289	12.8	12.5
		5	361	10.0	8.9
6	$(CO(CH_2)_2COO(CH_2)_2O)_n$	1	145	100	100[c]
		2	289	13.3	17.7
		3	433	10.0	6.4

[a] CI-MS data from ref 23. [b] The relative intensity of the first MS peak reported here has been taken equal to that calculated theoretically[c,d] for the corresponding cyclic oligomer. [c] Theoretical values calculated according to the $n^{-2.5}$ distribution law (see text). [d] Theoretical values calculated according to the $n^{-1.5}$ distribution law (see text).

In Figure 2 are collected all six polyester pyrolysis examples reported in Table III. The MS data appear to fit the two distribution laws with a sufficient level of differentiation, and this might indicate that it is possible to discriminate between the mechanism of cyclization.

The examples reported in Table III are concerned with aliphatic polyesters, whereas DP-MS data are also available for numerous other condensation polymers whose thermal decomposition occurs by intramolecular exchange processes (polyesters, polyamides, polycarbonates, polysulfides, polysiloxanes)[1,7-11] These polymers yield distributions of cyclic oligomers, as evidenced by their CI mass spectra, but the relative abundances are not amenable to one of the distribution laws that we have discussed above. This failure probably indicates that CI is not always suitable as a quantitative technique to detect the actual distribution of the cyclic oligomers produced in the pyrolysis of polymers and that other soft-ionization methods have to be used. Another reason might be that the existing MS data were produced only with the purpose of identifying the structure of the oligomers formed in the pyrolysis and that the MS peak intensities were not recorded under optimal conditions, as would be necessary to test the experimental distributions against the theoretical models.

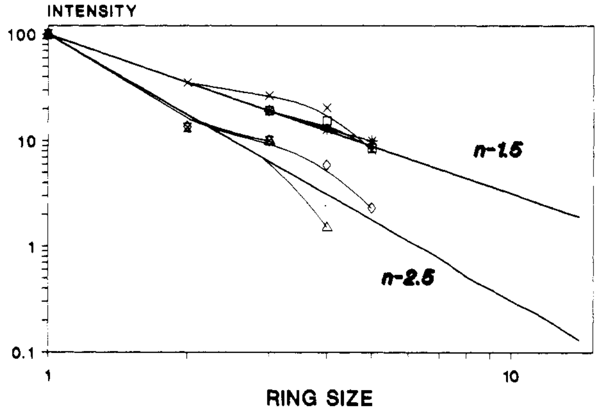


Figure 2. Experimental cycle concentrations for pyrolysis data reported in Table III: (◇) polymer 1; (×) polymer 2; (△) polymer 3; (□) polymer 4; (*) polymer 5; (⧖) polymer 6, compared with theoretical distribution laws.

However, it is opportune to note here that distributions of cyclic oligomers are what one should expect if thermal decomposition reactions would proceed through macrocyclization processes involving exchange reactions. In other words, if an intramolecular exchange reaction is activated by increasing the temperature of a polymeric chain, ring-chain processes begin to take place (the reaction being displaced in favor of the rings at high temperature), with the consequent formation of cycles.[1]

The merit of DP-MS studies has been to show that distributions of cyclic oligomers are frequently formed in the pyrolysis of condensation polymers, allowing one to conclude that these are diagnostic for the occurrence of exchange reactions as the primary pyrolysis mechanisms.[24] To ascertain if the exchange occurs by an end-biting or a back-biting process is a further step in understanding the pyrolysis mechanisms and, in this respect, distribution laws followed by the cycles formed in the pyrolysis become important.

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