Comment on "Macrocycles 21. Role of Ring−Ring Equilibria in Thermodynamically controlled Polycondensations"

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This paper[1] reviewed some of the theoretical and experimental studies on macrocycle formation in condensation polymerizations and puts forward an alternative mathematical description based on cyclization rates. The main conclusions are

1. Macrocycle formation predominates at very high conversions for almost all condensation polymerizations, whether kinetically (KCP) or thermodynamically (TCP) controlled. This was claimed to be supported by several pieces of experimental evidence.
2. The mathematical theory of macrocyclic formation of Jacobson and Stockmayer,[2] later modified by Flory and co-workers[3] which applies to thermodynamically controlled polymerizations must therefore be wrong.

This attack on the Jacobson−Stockmayer (J−S) theory, which has never been fundamentally questioned before, needs very serious evidence to back it up. Unfortunately, most of the experimental and theoretical evidence that is presented in the paper is of uncertain validity, as seen below.

The J−S theory starts off with a simple treatment of the end-to-end distance of a freely jointed chain. The probability that a chain comes back on itself can then be calculated, and using simple statistical arguments, the ring−chain equilibria (under thermodynamic conditions) can be calculated as a function of concentration, chain stiffness, and conversion. The chain stiffness and initial monomer concentration (c) are rolled up into a factor B'/c in the original J−S paper. It is true that the freely jointed model that Jacobson and Stockmayer used in their paper was simplistic, but this was later extended by Flory into a more realistic model, which also included end-to-end conformation effects.[3] However, as some factors such as excluded volume are impossible to take into effect in any mathematical treatment, these theories are only approximate in real systems. It should also be noted that the theory does not *always* predict low levels of cyclics at high concentration as stated by Kricheldorf. This is a function of chain stiffness and for very flexible polymers the J−S theory would predict almost complete cycle formation even in the melt at high conversion. This was noted by Jacobson and Stockmayer in their original papers. It is doubtful that any real polymer would have the flexibility needed, with an effective Kuhn chain stiffness of about or less than one bond-length. However, polyethers and polysiloxanes may not be far off, allowing for large cyclic concentrations under moderately concentrated conditions.

Kricheldorf asserted that "neither Stockmayer or Flory have ever presented any experimental evidence supporting their theory". However, just following the original theoretical paper[2] by Jacobson and Stockmayer is an excellent paper by these authors with experimental evidence on ring−chain equilibria in poly(decamethylene adipate) which fits their theory (using the chain stiffness as the only adjustable parameter),[4] and Flory and co-workers have used his modification of the J−S theory to account for the experimental distribution of cyclic poly(dimethylsiloxane)s and polyamides[5,6] (on the basis of the experimental results of other groups). It should also be noted that other researchers that have compared the J−S theory (or Flory's RIS modification) to experiment generally finding good agreement.[7,8] Semlyen alone has published 16 papers in this area.[9] Kricheldorf has indicated that the J−S theory does apply in the formation of smaller cyclic oligomers at low conversion but not at high conversion, when he thinks just cyclics are formed. However, it is not clear from his paper where exactly this crossover comes, and in any case, it is hard to see what suddenly changes to make the J−S theory inapplicable. Kricheldorf does not state why he thinks this happens, apart from mentioning the need for incorporating "cyclic−cyclic distributions" and the effect of "infinite dilution". However, the J−S theory automatically generates and allows for cyclic−cyclic distributions (as well as linear−linear and linear−cyclic distributions). As well, it takes in to account the "infinite dilution" effect and predicts that the concentration of cyclics does rise significantly on increasing conversion, up to 100% depending on chain stiffness and concentration.

The Kricheldorf paper criticized the existence of a critical concentration in the J−S paper. This is the concentration (at 100% conversion) below which the polymer mixture consists purely of cyclics, only above which can infinite linear chains or rings exist. In particular, he objected to the statement in the J−S paper "there is a critical concentration of below which the condensing system can be converted entirely into rings, above which it is not possible".[2] Kricheldorf says in support of his disagreement "no component of an equilibrium can ever disappear...in other words a critical concentration responsible for the appearance or disappearance of linear species does not exist in TCPs".[1] However, infinite chains or rings do not exist *in equilibria* with smaller species—conditions either favor infinite species or they do not. It is similar to the critical solubility concentration of many compounds as defined by K_{sp}—above a certain critical concentration solid forms, below it does not. (However, to complicate matters slightly, it has been postulated by another group that critical concentrations may not exist in all cases, depending on the size of the cyclization constants.[10] However, this last idea has not been verified or predicted by other theoretical treatments).

In another section, Kricheldorf states "Results for TCPs performed in the bulk yielding >95 wt% of the reaction product in the form of one (or two) giant chain(s) having high molar masses (...above 10^6 Daltons) and a polydispersity of 1.0 have never been published". What is being implied is that as chain lengths becomes infinite the polydispersity should tend toward 1.0, as at this limit, we will only have one (infinite) chain or ring. This trend is of course wrong. For any condensation reaction involving equal amounts of bifunctional monomers, below any conversion of 100% (even at say 99.9999%),

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any sample will contain a mixture of chains. These chains, even at molecular weights of 10^{10} Da or above, will obey the Carothers–Flory distribution (ignoring cyclics in the first instance). Only at a conversion of exactly 1.0 will the predicted single infinite species be formed, but the required molecular-weight measurement will of course be experimentally inaccessible. For very stiff polymers, an idealized sample at 100% conversion can consist of more than one infinite chain or ring anyway.

The experimental analysis of cyclic–linear equilibria is difficult at the best of times, and there are many traps to fall into. One must be able to separate cleanly the cyclic species from the linears (which is often difficult) or have a method of collectively analyzing their respective contributions toward some measurable property. One must also make sure that during the analysis or separation that interchange between any polymer species is stopped. This last requirement is especially important as many analytic techniques (chromatography, NMR, mass spectra, GPC, intrinsic viscosity measurements) require large dilution of the samples. Thus, if the ring–chain equilibrium is not capable of being stopped, then the sample will *reequilibrate toward cyclic species* under dissolution, analysis, or separation. Most of the experimental evidence presented by Kricheldorf involves the use of alkoxytin derivatives. For instance, he shows that the intrinsic viscosity of a polymer resulting from the condensation product of poly(ethylene glycol) and a dialkoxytin compound at high conversion and high concentration is very similar to the intrinsic viscosity of the starting poly(ethylene glycol).[11] In a similar vein, he showed that the product from the condensation of a four-armed poly(ethylene glycol) and a dialkoxytin apparently resulted not in a cross-linked material as one would expect but in a material that dissolved.[12,13] Hence, he concluded that in these cases the polymers that formed were mainly low-molecular-weight cyclics and not linear or cross-linked. However, the problem with these pieces of work is that the interchange between alkoxy groups in tin compounds is very fast even at room temperature. For example, at 40 °C, $Bu_2Sn(OEt)_2$ is rapidly exchanging alkoxy groups on an NMR time scale;[14] at room temperature, it is sure to be doing so on an experimental time scale (minutes to hours). It is true that this exchange slows as the group size increases and so may or may not be occurring in the polymer examples cited, but this is just not possible to determine from the actual experimental details. Perhaps the best way to check the cyclic content under these conditions would have been a viscosity comparison on bulk materials rather than in dilute solution (as needed for intrinsic viscosity measurements or redissolution studies).

Some of the experiments involved adding thiol compounds to inhibit this equilibria by forming stronger Sn–S bonds. In principle, this might lock the distribution, as Sn–S linkages appear more thermodynamically stable than Sn–O bonds.[14] However, much less work has been done on the kinetic stability of Sn–S bonds. In one study on unhindered thiols, no exchange was seen in very pure Sn–S compounds but fast exchange was seen in the presence of (unnamed) impurities.[15] Thus, even in the thiol–tin macrocycles, exchange needs to be ruled out.

Kricheldorf cited work by Sanders and co-workers in which polymerization gave only cyclic polyester material. However, in that paper, the reactions were carried out under dilute conditions (5 mM) and so may well have been under the critical concentration.[16]

The other piece of experimental work cited to reinforce his theory was concerning polysiloxanes. Kricheldorf cited a chapter by Semlyen as saying "Around 95% of these equilibriates were identified as cycles...even when the dilution by a factor of 4 relative to neat siloxanes was taken into account".[1] However, the cited paragraph by Semlyen is unclear. It actually says "In the 5 dm^3 *(sic?)* solution equilibrate, cyclics are present as 95% of the total siloxane"[17] referring to a paper by Brown and Slusarczuk.[18] However, in the paper it is referring to, this number never appears. Instead Brown and Slusarczuk say "the macrocycle population was found to constitute...**8–10%** of the total systems equilibrated at 200–250 g/L concentration"[18] which is a completely reasonable amount for such a flexible polymer from the J–S theory. There may be a typographical error, information privately communicated to Semlyen, or a mis-citation in the Semlyen article, but this cannot be determined. It should be reinforced that the experimental polysiloxane ring–chain equilibria has been comprehensively analyzed with the J–S theory by several authors, and no anomalies have been noted.

In the final part of his paper, Kricheldorf presents an equation relating the average degree of polymerization and the ring cyclization constant. This equation might be useful where the cyclization constant is constant, but the cyclization constant would be expected to (and has been shown to[18]) change by many orders of magnitude as the molecular weight of the cycle increases. Hence, this equation is not at all useful for looking at the macrocyclization of real polymers. Indeed, this seems to be at the heart of the problem. The real conflict between the concepts and mathematical analysis presented by Kricheldorf and that by J–S is that complete ring formation at high conversion and concentration can only be found if the cyclization constants for large rings are much higher than might be reasonably expected from either theoretical treatments or if they are based on extrapolation from measured ring-cyclization constants.

In summary, there seems to be no experimental or theoretical need to attack the foundations of the J–S theory. While modifications are possible and may improve its accuracy, the basic theory seems correct and is in agreement with experimental, other theoretical treatments, and computer simulations. The evidence for very large amounts of cyclics at high initial monomer concentrations for all TCPs is limited or questionable, based qualitative evidence that can be interpreted in several ways, in disregard of the large amount of quantitative evidence supporting the J–S theory. However, large amounts of cyclics are quite possible at moderate concentrations for very flexible polymers such as polyethers and polysiloxanes, completely in accord with the J–S treatment.

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