Polymer Chemistry

COMMENT

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Reply to the comment on "synthesis of cyclic polymers and flaws of the Jacobson-Stockmayer theory" by R. Szymanski

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In a recent publication the authors[1] have presented theoretical and experimental results indicating that the Jacobson–Stockmayer (JS) theory[2,3] does not provide a correct description of reversible polycondensations for all polymers and for high conversions (*e.g.* polycondensation in bulk). In this context reversibility means that all condensation step whether resulting in chain growth or in cyclization are reversible and thus, part of an equilibrium. The first two sections of that paper were focused on the demonstration that small, and above all, large cycles can be formed by end-to-end (ete) cyclization in reversible like in irreversible polycondensations. A significant contribution of ete-cyclization to the course of reversible polycondensations was denied by J + S apparently as a contribution to Florýs dogma,[4,5] that the end groups of long polymer chains will never meet. To avoid critique that the authors over-or misinterpret Flory and J + S, the original statements should be cited here:

Flory ref. 4, p.137: However, in ordinary bifunctional polycondensation (no diluent) the primary product of monomers (or dimers) of fifteen or more members is almost exclusively linear polymer. This results from the statistical improbability that the ends of long chains of atoms connected by valence bonds about which there is free rotation, will meet".

Jacobson and Stockmayer in ref. 2, p. 1607: "Formation of rings occur here primarily by ester interchange, very few of the chains present being small enough to give rings directly by intermolecular esterification".

However, Florýs dogma was proven wrong by mathematical simulation of irreversible step-growth polymerizations published by Gordon *et al*.[6,7] and Stepto and coworkers[8,9] in the years 1972–1975. The experimental evidence was later contributed by Kricheldorf and coworkers.[10,11]

The existence of ete-cyclization in reversible polycondensation was not only proven by numerous experiments,[1] it is a consequence of straightforward logic. Firstly, when the end groups of oligomers and polymers are reactive enough to undergo intermolecular condensation (*i.e.* chain growth), they are also reactive enough to undergo intermolecular condensation. In this regard, there is no difference between reversible and irreversible polycondensations, because the equilibration reactions typical for reversible polycondensations do not change the reactivity of end groups. The only parameter which can prevent ete-cyclization is extreme chain stiffness, but this property also hinders cyclization by back-biting, and stiff chains are excluded from the JS theory as outlined by J + S themselves.[2] Secondly, Kricheldorf *et al*. have demonstrated by MALDI-TOF mass spectrometry[1,12] that cycles up to a degree of polymerization (DP) of 90 exist in nylon-6 prepared by reversible polycondensation of ε-aminocaproic acid or its mixtures with ε-caprolactam. In poly(l-lactide)s prepared *via* ring-opening polycondensation combined with simultaneous polycondensation (ROPPOC) cycles up to DP 120 were identified. Now consider formation of cycles having DP = 80. The nucleophilic end group can react with a group in the polymer chain at DP = 80 (back-biting) or with the electrophilic end group of chains having a DP of 80. When the electrophilic end group is more reactive than an amide or ester group in the chain (as it is typical for the experiments in ref. 1 and in almost all successful polycondensations), the vast majority of cycles will then be formed by ete-cyclization. When the reactivities of electrophilic end groups and bonds in the chain are similar at least part of the cycles will be formed by ete-cyclization. In summary, the existence of ete-cyclization in reversible polycondensation is a matter of fact (not denied by Szymanski) and leads to an important conclusion for the proper understanding of irreversible polycondensations. Whenever a step-growth polymerization involves ete-cyclization, it can theoretically reach 100% conversion. The last section of ref. 1 was dedicated to the discussion, what is the meaning of 100% conversion

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and what are the consequences for the understanding of reversible polycondensations.

In his "Comment" Szymanski criticizes part of our previous paper[1] with the following description of reversible polycondensations: "There is one but important reason supporting the statement, that the commented paper cannot be regarded correct for the equilibrated system. Namely reversibility of the studied polycondensations implies reformation of linear structures containing functional end groups even in conditions when linear polymer is not observable using the available methods The concentration of these groups and the relevant linear polymers at the system equilibrium can be very low, may be even undetectable, but nevertheless cannot be neglected. Consequently, the linear polymers exist in all systems discussed by the authors..."

This statement deserves three comments.

(1) The authors have emphasized the importance of ete-cyclization for the proper understanding of reversible polycondensations and for the formation of large cycles. However, the authors have never stated that ete-cyclization is irreversible, and linear chains are, of course, regenerated from cycles. It is a trivial consequence of a reversible step-growth polymerization that any cyclization is reversible and linears are always present below 100% conversion. Furthermore, the authors have never concluded that their polycondensations have reached 100% conversion and 100% cyclization. Such an expectation is not realistic for any real polycondensation.

(2) The authors fully agree with the scenario described by Szymanski as a general description of reversible polycondensations, in as much, as it supports the critique of the authors. Given a polycondensate containing 1.0 or 0.1 weight % of linear chains, the remaining 99.0 or 99.9% of the reaction product comprises cyclic species. Although this is a reasonable result for the authors, it is incompatible with the JS theory for the polycondensation of monomers far below their critical concentration. This aspect is even sharpened by the third point.

(3) In the scenario described by Szymanski the role of ete-cyclization is ignored. The existence of ete-cyclization enables a reversible polycondensation (like an irreversible one) to reach theoretically (!) 100% conversion.

The meaning of 100% conversion and the consequences for the understanding of reversible step-growth polymerizations have been discussed[1] and are here discussed on the basis of eqn (1)–(3). Eqn (1) is the definition of the conversion (p) for normal step-growth polymerizations. 100% conversion is defined as total consumption of end groups, what necessarily means total absence of linear chains. Hence, it is a simple logic that in the absence of side reactions all reaction products are cycles at 100% conversion. Eqn (2) and (3) carry the same message. Eqn (2) represents the most probable molar (number) contribution of linear chains, an equation originally elaborated by Flory for irreversible polycondensations.[4] When Flory became aware of the JS theory, he calculated that eqn (2) is also valid for the fraction of linear chains in reversible polycondensations, a calculation, which was later confirmed by

Niehaus and Jackson *via* SEC analyses of nylons and poly (ethylene terephthalate). According to eqn. (2) all linear chains have disappeared at 100% conversion. Eqn. (3), the law of self-dilution, which correlates the molar concentration of all linear species (incl. monomers) with the conversion, yields the same result.

$$p = (N_0 - N_t)/N_0 \qquad (1)$$

with N_0, N_t = number of functional groups at the beginning and at any later time of the polycondensation

$$n_x = p^{x-1}(1 - p) \qquad (2)$$

with x = degree of polymerization of linear chains

$$[\text{La}]_t = [\text{La}]_0 \ (1 - p) \qquad (3)$$

with $[\text{La}]_0$, $[\text{La}]_t$ = molar concentration of all linear species at the beginning and after a certain reaction time t.

It is decisive for the critique of the JS theory, that eqn. (1)–(3) are independent of monomer structure, monomer concentration and reversibility of the step-growth polymerization. Gordon *et al.*[6,7] and Stepto and coworkers[8,9] have calculated this scenario for irreversible polycondensations already more than 50 years ago. Yet, in the presence of ete-cyclization, also reversible polycondensations will yield 100% cycles at 100% conversion. This conclusion was confirmed by J + S themselves, because they calculated, that for initial monomer concentrations below the critical concentration 100% conversion yields a reaction product exclusively consisting of cycles.

Most of Szymanskís comment is concerned with the calculation of the critical concentration of polylactides and the correct understanding of the critical concentration. Szymanskís calculation indicate, that the critical concentration of polylactide in bulk may be above the real concentration of L-lactide in bulk, so that formation of >95% of cyclic polylactide, incl. high molar mass species, is in agreement with the JS theory, in as much, when part of the cycles are the result of the initially kinetically controlled ROP. The authors agree with this conclusion, and concede that that their assumption, the ROPPOC-type polycondensation of lactide in bulk proceeds above the critical concentration, was not justified. Yet, for the following reasons, this point and the entire results of Szymanskís calculation are not relevant for the critique of the authors.

(A) The experiments with lactide had the purpose to prove the existence of ete-cyclization in reversible polycondensations and Szymanskís calculation does not negate the existence of ete-cyclization.

(B) Calculations and conclusions of Szymanski do not cover the experiments and conclusions presented by the authors for syntheses of nylons.

(C) Eqn (1)–(3), and definition and consequences of 100% conversion are valid for all kinds of monomers and all possible monomer concentrations and not confined to the chemistry of lactide.

The main problem of the JS theory is the calculation that certain (and technically important) classes of monomers, such as aliphatic α,ω-diols, α,ω-diamines, α,ω-dicarboxylic acids, ω-hydroxy acids and ω-amino acids, can only yield less than 10 weight % of cycles at 100% conversion, when they were polycondensed above the critical concentration. This calculation is in total contradiction to the definition of conversion (1) and to the message of eqn (2) and (3).

In summary, the authors consider the "Comment" of Szymanski as a useful contribution to the proper understanding of the JS theory, and, as he has mentioned himself, it is mainly a complementary piece of work. However, the authors cannot see that it devaluates or even disproves our critique of the JS theory. Therefore, the authors repeat their final conclusion. First, ete-cyclization also exist in reversible step-growth polymerizations with the consequence that they can theoretically reach 100% conversion. Second, 100% conversion results in formation of 100% cycles regardless of monomer structure and reaction conditions, and thus, the JS theory does not provide a correct description of the course of reversible step-growth polymerizations up to 100% conversion for all kinds of monomers at all possible monomer concentrations.

Conflicts of interest

There are no conflicts to declare.

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