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ROMP of COD under equilibrium conditions : the turning point concept

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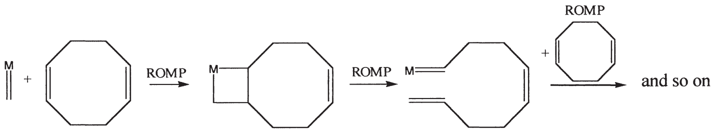
SUMMARY: ROMP of COD under equilibrium conditions leads to a complex system of coupled sub-equilibria. Concerning the ring/chain equilibrium, a new concept is introduced for the description of the course of the ring equilibrium concentration as a function of the feed concentration. At the center of this concept is a new specific mark. It is the turning point of the first derivative of the feed-concentration-dependent ring equilibrium concentration (integral as well as individual).

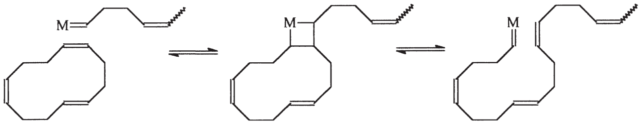
Introduction

Conventional cyclic olefins except cyclohexene undergo ring opening polymerization by addition of metathesis catalysts (ROMP) [1]. The focus of our interest is ROMP of 1Z,5Z-cyclooctadiene (COD) under equilibrium conditions. Using COD, the chain start as well as the chain growth process occur in an irreversible manner (Eq. 1a). The irreversibility is based on the ring strain in COD. If secondary reactions are hindered, the polymerization proceeds only this way, known as living ROMP [2,3].



Eq. 1a

If secondary reactions are not hindered, several competing processes take place. The back-biting reaction is illustrated from the right to the left in Eq. 1b.



Eq. 1b

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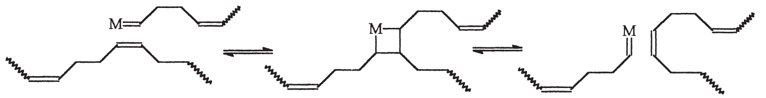
The active species reacts intramolecularely with a double bond in the chain. Eq. 1a and 1b demonstrate that a reversibility between chain build up and chain degradation is only possible in the case of higher cyclic oligomers, which are generated from the chain via back-biting. The substrate COD does not take part in the polymerization/depolymerization equilibrium.

In Eq. 1c an additional secondary reaction is presented - the cross metathesis step between two chains, also called chain transfer reaction.

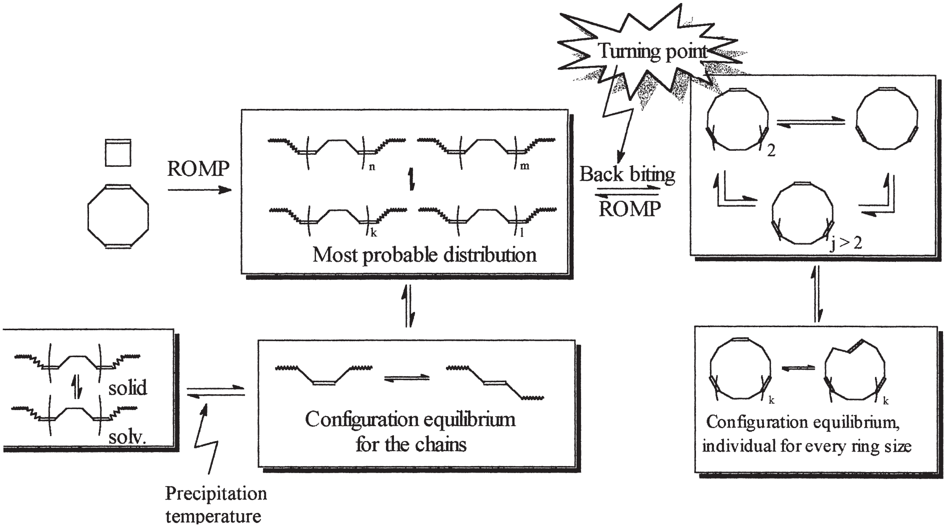


Eq. 1c

The occurrence of the secondary metathesis steps leads to a complex product spectrum.

The overall equilibrium for the 1,4-polybutadiene (resp. cyclobutene) system consists of several coupled sub-equilibria, like the polymerization/depolymerization equilibrium between ROMP of cyclic oligomers (from trimers upwards) and back-biting of 1,4-polybutadiene, an equilibrium between all ring sizes, one between the chains of different length, moreover a configuration equilibrium for the chains and one for every individual ring size. Additionally, we found a new precipitation/solution equilibrium for the polymeric chains (Scheme 1).

Scheme 1



Recently, we succeeded in describing this complex equilibrium system quantitatively, varying the feed concentration, the temperature and the solvent [4-6].

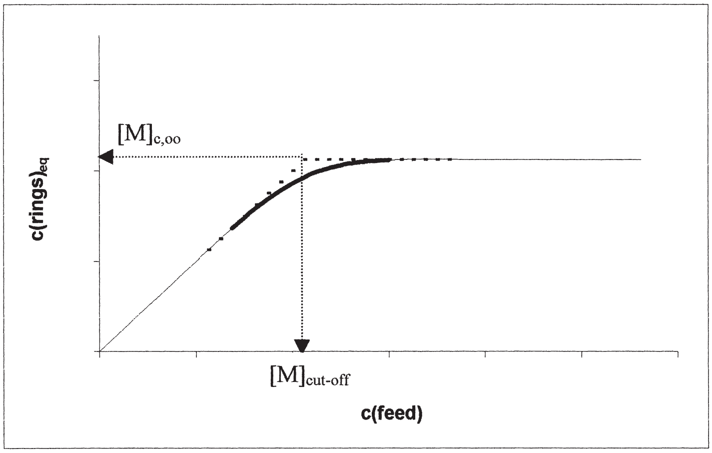
In this contribution we focus on the ring/chain (back-biting/ROMP) equilibrium. The turning point as a specific mark for the ring/chain equilibrium will be introduced and explained.

The turning point concept

Theories describing the ring/chain equilibrium are based on an entropic control of the reactions. This leads to a most probable distribution for the chains of different lengths [7] at equilibrium. Their existence at equilibrium state depends on the concentration of the smallest repeat unit (feed concentration) in the system. At a low concentration the back-biting reaction is dominant and almost only rings are present at the equilibrium. At a high concentration the rings run into saturation and an additional amount of smallest repeat units yields in a polymeric chain fraction (Scheme 2) [8,9]. In the saturation area the ring distribution is described through the Jacobson-Stockmayer theory [10]. This is valid for not too small rings without ring strain or other peculiarities resulting in enthalpic influences.

Until now, literature offers two terms as a characteristic mark for the ring/chain equilibrium resp. for the polymerizability - the „cut-off point“ $[M]_{cut\text{-}off}$ [8] and the „critical concentration“ $[M]_{c,oo}$ [11].

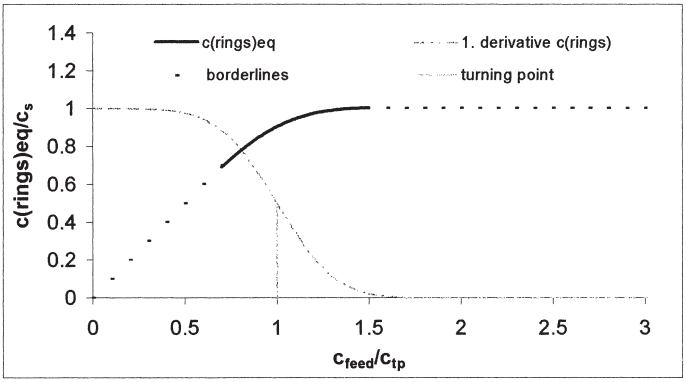
Even if there is a difference between their definitions (Scheme 2), their values are equal. Both correspond to the integral saturation concentration of the rings.



Scheme 2

The knowledge of $[M]_{cut-off}$ resp. $[M]_{c,oo}$ is important for the polymer chemist to choose the correct reaction conditions for a polymer synthesis. The determination of the specific marks is based on the borderlines of high and low feed concentrations.

We were interested in a general description (physically and mathematically) of the feed-concentration-dependent ring equilibrium concentration, taking into account not only the behaviour of the rings as a sum, but also the analogous one for every individual ring. To describe this behaviour, we have focussed on the transition region between high and low feed concentration because the decisive change takes place in this area. At a low feed concentration a change of the feed concentration almost only results in a change in the ring equilibrium concentration. Polymeric chains are not existent. At a high feed concentration a change of the feed concentration almost only leads to a change in the concentration of polymeric chains. The equilibrium concentration of the rings remains mainly constant. We state that between these borderline cases in the transition area a turning point must be passed regarding the change of the ring equilibrium concentration (1. derivative of the ring equilibrium concentration as function of the feed concentration) (Scheme 3).



Scheme 3

The change of the equilibrium concentration of every individual ring in dependence on the feed concentration shows an analogous behaviour. Thus, we propose to use the feed concentration at the turning point $[M]_{tp}$ as specific mark.

In the integral case, the ring saturation concentration is equal to the turning point. Our experimental results for the 1,4-polybutadiene system at 25°C in toluene confirm this (Fig. 1).

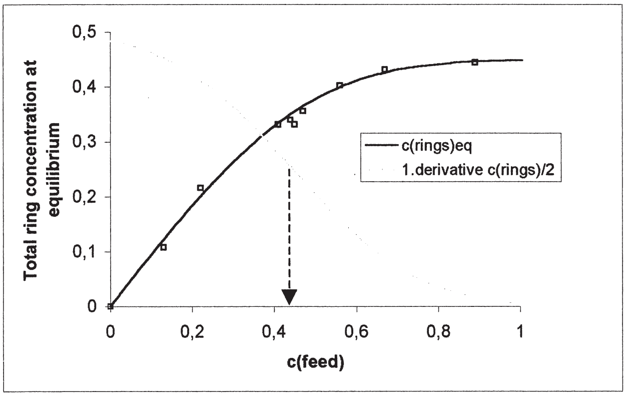


Fig. 1: Equilibrium ring concentration (3- to 6-mers) as a function of the feed concentration in the 1,4-polybutadiene system; additionally the 1. derivative and the turning point (arrow) are given

Considering every individual ring size, the ring saturation concentrations differ from the turning points. The individual saturation concentration is expected to decrease to zero according to the Jacobson-Stockmayer theory, while the individual turning point should increase infinitely in accordance with the amount of smallest repeat units necessary to build the rings, and with the fact that infinitely large rings should behave like polymeric chains. Both aspects are verified experimentally (Fig. 2).

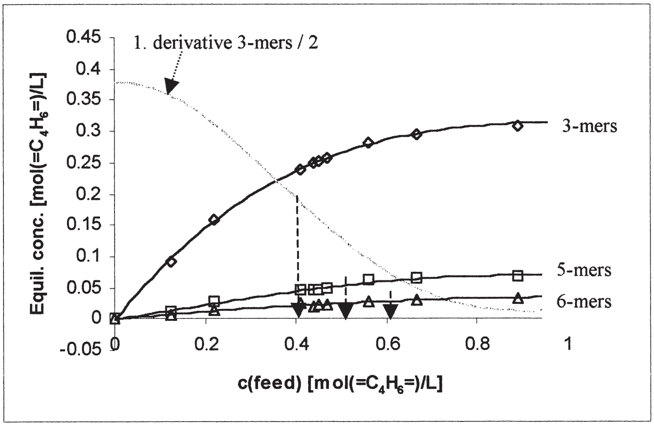


Fig. 2: Individual ring equilibrium concentration and turning point (marked by arrow) of the trimers, pentamers and hexamers; additionally the 1. derivative for the trimers is shown

To sum up, the turning point describes exactly what occurs in the transition area. It can be expressed mathematically and it is valid not only for the integral case but also for the individual one.

Additionally, for the integral case, its value $[M]_{tp}$ corresponds to the cut-off point $[M]_{cut\text{-}off}$ and the critical concentration $[M]_{c,oo}$. Thus, it can be used analogously as a measure for the polymerizability.

Conclusion

The turning point concept has a relevance not only for ROMP but also for other polymerization/depolymerization processes that include ring/chain equilibria like ROP, ADMET and conventional polycondensation.

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