# In Step Polymerization Conversion Sets the Length of the Chains; in Chain Polymerization It Sets Their Number

— In step polymerization, even with a fraction reacted $p$ of $0.99$ the number-average chain length is only $100$, and $1000$ needs $0.999$ — the separator is whether conversion and molecular weight are tied together — [Paper 660]

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*— From thinking to syncing. —*

**Abstract**

**Joining small molecules (monomers) into long chains (polymers) is called polymerization. The one word "polymerization" names two entirely different ways of building. In step polymerization, monomers join at random and short chains gather into long ones; in chain polymerization, a single chain grows in one burst by adding monomer after monomer to its active end.What the fraction reacted (conversion) sets in each is counted.No new theorem or law is claimed. First, in step polymerization, conversion sets the length of the chains——with a fraction reacted $p$, the number-average chain length is $1/(1-p)$: 10 at $p = 0.9$, 100 at 0.99, 1000 at 0.999. Even with 99 % reacted, chains are only about 100 units long** (Section 2). **Second, in step polymerization, a slight mismatch of feedstocks caps the length——if the ratio of the two feedstocks is 0.99, the number-average length stops at 199 even when everything has reacted, and at 1999 for 0.999** (Section 3). **Third, and this is the core.In chain polymerization, conversion sets not the length of the chains but their number——setting the average length of one chain (the kinetic chain length) at 1000, at 1 % conversion there were 1955 chains averaging 1023.0844, at 50 % 100513 chains averaging 994.8971, and at 90 % 180313 chains averaging 998.2657. Step polymerization at the same conversions would give 1.0101, 2.0000 and 10.0000** (Section 4). **Fourth, the separator is whether conversion and molecular weight are tied together——in step polymerization, no long chains form unless conversion rises. In chain polymerization, chains are long from the very first, and conversion only adds to their number** (Section 5). **Keywords**: polymerization, step-growth polymerization, chain-growth polymerization, degree of polymerization, Carothers equation.

**Scope of this paper (scope note)**: **No new theorem or law is claimed——the number-average length $1/(1-p)$ of step polymerization (Carothers 1936), the length distribution and weight average (Flory), the cap from the feedstock ratio, and the kinetic chain length of chain polymerization are all known in polymer chemistry.The premises are simplified ——the length of one chain in chain polymerization is set at an average of 1000 regardless of conversion. In reality it shortens as monomer runs out, and lengthens when rising viscosity delays termination (the gel effect). Termination is by disproportionation (chains stop one at a time).What is not treated——branching, cross-linking, gelation and copolymerization.Relation to earlier papers**: **Paper 279 showed that what changed the exponent of how a polymer chain spreads was self-avoidance alone——here, not how far a chain spreads but how long it becomes is separated by the way it is built.Paper 555 showed that 0.99 multiplied 100 times gives 0.366032, and that under multiplication even a stage that is not the bottleneck matters——in step polymerization too, when each bond forms with probability 0.99, the number-average chain is exactly 100.**What is added is **checking the length of step polymerization by closed form and random draws**, **deriving the cap from the feedstock ratio**, **setting the number and length of chains in chain polymerization beside step polymerization for each conversion**, and **placing the separator on the tie between conversion and molecular weight**.

## 1. Notation and the Question

**Step polymerization**: **monomers carrying an A end and a B end join A to B at random. With a fraction $p$ of the ends reacted, the number-average and weight-average chain lengths are**

$$X_n = \frac{1}{1-p}, \qquad X_w = \frac{1+p}{1-p}$$

**If the ratio of two feedstocks (molecules carrying only A and only B) is $r \leq 1$, the length stops at $X_n = (1+r)/(1-r)$ even when everything has reacted.**

**Chain polymerization**: **a single chain with an active end grows by adding monomer after monomer, stopping with some probability. The average length of one chain (the kinetic chain length) is set at 1000, independent of conversion.**

**Question**: **in each kind of polymerization, what does the fraction reacted set?**

## 2. Step Polymerization

**Computation 2.1**: **chain lengths were derived for each fraction reacted.**

| $p$ | number average | weight average | weight over number |
|---|---|---|---|
| 0.5 | 2.0000 | 3.0000 | 1.5000 |
| 0.9 | 10.0000 | 19.0000 | 1.9000 |
| 0.99 | 100.0000 | 199.0000 | 1.9900 |
| 0.995 | 200.0000 | 399.0000 | 1.9950 |
| 0.999 | 1000.0000 | 1999.0000 | 1.9990 |

At $p = 0.99$, the share of units in chains longer than $100$ was $0.732065$.Building bonds at random over $1000000$ units gave number-average lengths of $9.9838$ at $p = 0.9$ and $101.5538$ at $0.99$, agreeing with the closed form.

> **Observation 2.2**
>
> in step polymerization, conversion sets the length of the chains.Long chains form only when short chains join, so no long chains exist until almost everything has reacted. With $99$ % reacted the number average is $100$, and $1000$ needs $99.9$ %——the step from $0.99$ to $0.999$ multiplies the length tenfold.

## 3. The Feedstock Ratio

Computation 3.1: with a feedstock ratio of $r = 0.99$, the number-average length even at full reaction was $199.0000$, and $1999.0000$ at $r = 0.999$.

> **Observation 3.2**
>
> in step polymerization, the precision of weighing sets the upper limit of length.The ends of the more plentiful kind are left over at the chain ends and can join no further. A $1$ % mismatch stops the length at $199$ however far the reaction goes——the length of step polymerization is bound both by how far the reaction goes and by how the feedstocks were weighed.

## 4. Chain Polymerization

Computation 4.1: chains of kinetic chain length $1000$ were built from $2 \times 10^{8}$ units of feedstock. For each conversion, the number of chains formed and their number-average length were derived and set beside step

**polymerization at the same conversion.**

| conversion | number of chains | number-average length | step polymerization |
|---|---|---|---|
| 1 % | 1955 | 1023.0844 | 1.0101 |
| 10 % | 20086 | 995.7290 | 1.1111 |
| 50 % | 100513 | 994.8971 | 2.0000 |
| 90 % | 180313 | 998.2657 | 10.0000 |

> **Observation 4.2**
>
> **this is the core: in chain polymerization, conversion sets the number of chains, not their length.A single chain adds around 1000 units in the short time between its birth and its end. So even at 1 % conversion the chains that exist are already long. As the reaction proceeds, more chains of the same length accumulate——at the same 1 % conversion, chains from chain polymerization are 1012.8536 times longer than from step polymerization.**

## 5. The Separator

> **Observation 5.1**
>
> **the separator is whether conversion and molecular weight are tied together.In step polymerization, molecular weight does not rise unless conversion does, and the feedstock ratio also binds the length. In chain polymerization, molecular weight is set by how one chain grows, and conversion only adds quantity——the one word “polymerization” hides a way of building that makes length at the end of the reaction and a way that makes it at the start.**

**Observation 5.2**

**beside Paper 279 and Paper 555.Paper 279 showed that what changed the exponent of how a polymer chain spreads was self-avoidance alone; here not spread but length was separated by the way of building. Paper 555 showed that 0.99 multiplied 100 times gives 0.366032——in step polymerization too, when each bond forms with probability 0.99, multiplying the chances that a chain continues to the next bond gives a number average of exactly 100.**

**Observation 5.3**

**what is not said.Because the kinetic chain length was held constant, changes in length from monomer depletion or the gel effect are not included. Branching and cross-linking are not treated——what is shown is that conversion sets different things in the two kinds of polymerization.**

## 6. Roll Call and Closing

1. **number average 100 at $p = 0.99$** (Computation 2.1): **step polymerization.**
2. **1000 at $p = 0.999$** (Computation 2.1): **tenfold in one step from 0.99.**
3. **share of units in chains over 100: 0.732065** (Computation 2.1): **a broad distribution.**
4. **101.5538 by random draws** (Computation 2.1): **agrees with the closed form.**
5. **199 at a feedstock ratio of 0.99** (Computation 3.1): **weighing sets the cap.**
6. **chain polymerization averages 1023.0844 at 1 %** (Computation 4.1): **long from the start.**
7. **998.2657 at 90 %** (Computation 4.1): **length does not change.**
8. **1955 to 180313 chains** (Computation 4.1): **conversion sets the number.**
9. **1012.8536 times longer at the same 1 % conversion** (Observation 4.2): **the core.**
10. **the tie between conversion and molecular weight** (Observation 5.1): **the separator; Paper 279 and Paper 555.**

**Closing**: **The one word “polymerization” names two ways of building.In step polymerization, conversion set the length of the chains: with 99 % reacted the number average was 100, and with a feedstock ratio of 0.99 it stopped at 199 even at full reaction.In chain polymerization, chains were long from the start, averaging 1023.0844 at 1 % conversion and 998.2657 at 90 %, and conversion only raised their number from 1955 to 180313——whether length is made at the end of the reaction or at its start separates the two.The separator is whether conversion and molecular weight are tied together.Placed among the earlier papers——where Paper 279 separated how chains spread, here**

**the way their length is made was separated.To be honest——this is a model with the kinetic chain length held constant, and branching and the gel effect are not included.**

## References


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