JoVE: Science Education

Kinetics of a typical addition polymerization to poly(dimethylsiloxane)

--Manuscript Draft--

Manuscript Number:	10369
Full Title:	Kinetics of a typical addition polymerization to poly(dimethylsiloxane)
Article Type:	Manuscript
Section/Category:	Manuscript Submission
Corresponding Author:	Kerry Dooley UNITED STATES
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	
Corresponding Author's Secondary Institution:	
First Author:	Kerry Dooley
First Author Secondary Information:	
Order of Authors:	Kerry Dooley
Order of Authors Secondary Information:	

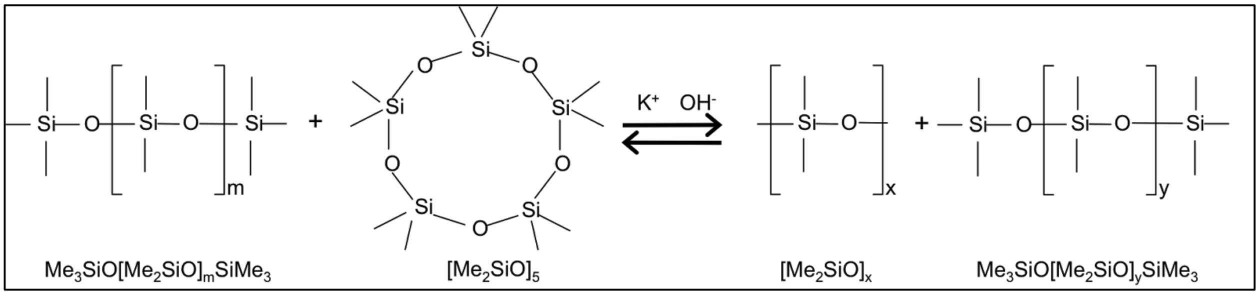
PI Name: Kerry Dooley

Science Education Title: Kinetics of a Typical Addition Polymerization to Poly(dimethylsiloxane):

Overview

The goal of this video is to show how a measured property (viscosity) from a batch polymerization reaction can be used to determine polymer molecular weight, and how molecular weight can be related to conversion of monomer.

The polymer industry manufactures thousands of raw materials used in a broad variety of commercial products.[1,2] Many polymers are made in stirred tank reactors, either batch or continuous. This polymerization to poly(dimethylsiloxane) (PDMS, aka "silicone") is:



Where "Me" is a methyl group. The potassium hydroxide is the catalyst. The $[Me_2SiO]_5$ is a 5-membered ring which is opened to form the basic building block (the "link") of the polymer. The second product represents finished polymer (it reacts with something called an "endblocker" to stop growth), the first one is a still-growing ("living") polymer. All growth takes place while the chain is attached to the catalyst.

The system is controlled by running control sequences PS1-PS5 on the Emerson DeltaV® control system. This is a standard industrial distributed control system (similar to Siemens Wonderware®, Honeywell Experion® or ABB Symphony®), that can be operated from PCs. These sequences open/close/adjust valves in the proper sequence and inform you when and how to add ingredients to the reactor. After sequence PS3, the reactor is full and ready for polymerization. PS4 is started and once the reactor temperature reaches >105 °C, liquid samples are collected to determine kinematic viscosity, which leads to molecular weight after calculations. The polymerization proceeds until near equilibrium. Once done, the "RXN COMPLETE" pushbutton is set to neutralize the KOH catalyst with CO_2 (the K_2CO_3 product is inert). The neutralization completes PS4. After this, the low boilers (unreacted material) are stripped out under vacuum (PS5). PS5 takes a long time to complete as, after the stripping, the reactor cooling is slow. Hit the "STRIPPING COMPLETE" pushbutton in PS5 when done stripping; cooling is unattended.

Principles:

This is a type of addition polymerization. Such polymerizations are discussed in many kinetics[3] and all basic polymer-science textbooks.[4] The reaction is almost thermoneutral, and is usually run between 110-140 °C and atmospheric pressure.

A small amount of molecular weight modifier ("endblocker") is used to stop chain growth, but the catalyst then starts a new chain. Common endblockers are dimethylsiloxanes with trimethylsiloxy end-groups. A "living" chain reacts with the endblocker, forming an end-capped "dead" polysiloxane product with a trimethyl end group.

$$\mathrm{Me_3SiO[Me_2SiO]_mSiMe_3} + \mathrm{KO[Me_2SiO]_n}\text{-----} \longrightarrow \mathrm{Me_3SiOK} + \mathrm{Me_3SiO[Me_2SiO]_{m+n}}\text{-----}$$

The Me_3SiOK will react with another polysiloxane to create another trimethylsiloxy end-group. As seen from the above reaction, the overall effect is not only the endcapping, but also control of the chain length. Average chain lengths (m+n) between 43-205 are typical for industrial PDMS; several different grades are made. Because the monomer addition rate >> reaction rate with endblocker (otherwise you would never get to a high molecular weight), the endblocker doesn't influence the reaction kinetics, only the molecular weight distribution.

In analyzing polymerization kinetics, the most difficult step is going from a physical property (*e.g.*, kinematic viscosity) to molecular weight (MW). The next most difficult is to get from MW to fraction conversion. The viscosity-average molecular weight, which is measured here, is intermediate between number-average and weight-average molecular weights. The number average means 50% of the chains are below this weight, 50% above. The weight average means 50% of the sample weight is in chains of lower weight, 50% in chains of higher weight.

Dividing the number average MW by a monomer weight gives the number average degree of polymerization. This is related to fraction conversion as shown below. Then the fraction conversions vs. time can be used to determine the order of the reaction in the normal ways learned in PCHEM or Reactor Design classes.

Procedure:

1. Open the N_2 cylinder. Run control sequence PS1 which tests the equipment, and PS2 which tests the system for leaks and fills it with N_2 for both safety and kinetics reasons (O_2 inhibits many polymerizations, and can lead to explosions).

2. Run PS3 to add monomer to the reactor. PS3 prompts the addition of smaller ingredients (catalyst solution and endblocker) through a small funnel called the "adder tank".

3. Start PS4 and once the temperature reaches >105 °C, frequently take liquid samples (at least every 8 min) from the sample draw point (caution: HOT, wear a thermal glove).

4. Continue the polymerization until near equilibrium, getting at least 7 samples. Reaction progress can easily be monitored from the product of volts x amps of the agitator (power). Once power has stopped increasing, then the reaction is close to equilibrium.

5. When done, set the "RXN COMPLETE" pushbutton to neutralize the catalyst with CO_2. The neutralization using the CO_2 cylinder is part of sequence PS4; open the cylinder and follow the instructions in PS4.

6. Proceed with the stripping sequence (PS5). When it gets to the step that says, "You are stripping now", strip for 15 min. Then hit the "STRIPPING COMPLETE" pushbutton in PS5. Collect the low boilers from the low boilers tank in a flask.

7. Cooling of the reactor is automatic and unattended. Pumpout is done much later.

8. The kinematic viscosity of the liquid samples is measured with the appropriate Cannon-Fenske viscometer. If the viscometer efflux time is too short (<60 s), use a viscometer of a lower number rating. Size 200 works for the first couple of samples, size 500 for the last few samples, and the sizes 300 and 400 for the in-betweens.

Representative Results

The molecular weight is determined by empirical relationships, such as Barry's relationship for polydimethylsiloxanes with molecular weights **above ~2,500**.[5]

$\mathrm{Log}_{10}\,(\mu_{cSt}) = 1.00 + 0.0123\,M^{0.5}$

This gives the "viscosity-average molecular weight". When the Barry relationship predicts M < 2,500, you should instead interpolate experimental data found in Kuo,[6] remembering to also use the kinematic viscosity of the DC-245 monomer for chain length 1. Multiply the measured efflux time (in s) between the 2 marks by the viscometer constant to get the kinematic viscosity in cSt. Divide the viscosity average MWs by 1.6 (empirical factor for PDMS) to get the number average molecular weight. Divide that by the monomer molecular weight to get the average chain length, $(P_N)_{avg}$, which includes the unreacted monomer.

To get the fraction conversion (f_m), start with the mass balance for the average of P_N (polymer only): [7]

$$\overline{P_N} = \frac{f_m}{\int_0^{f_m} df / P_N} \qquad (1)$$

The left-hand side is the average of P_N (polymer only) up to time t, where $f = f_m$. But the average P_N that you measure includes the monomer. To account for monomer in $(P_N)_{avg}$, recall that by definition:[3-4]

$(P_N)_{avg}$ = [Σ (monomer moles + moles polymer groups] / [moles monomer + moles polymer]

and therefore:

$$(P_N)_{avg} = \left[\frac{f_m}{\overline{P}_N} + (1 - f_m) \right]^{-1} \qquad (2)$$

There is one point at which the average <u>polymer</u> P_N (the one with the overbar) and $(P_N)_{avg}$ for the entire batch are almost equal, and that is the last one, where f_m approaches 1. Compute f_m for the last point by mass balance, using the amount of low boilers collected. Solve for $\overline{P}_N$ at this point. For many addition polymerizations, we treat $\overline{P}_N$ as constant for the entire batch. This allows you to compute f_m at all other times from **Equation 2.** Also compute the equilibrium constant K (first-order reversible kinetics model) for the reaction by mass balance.

Once f_m has been determined as a function of time, assume irreversible kinetics and determine the reaction order with respect to monomer. Use statistical analysis to determine the quality of your fits and the confidence limit on the rate constant k_p. Also determine the fit for first-order kinetics (expected from theory).[3-4] Test the hypotheses that the two fits actually differ (null hypothesis: they don't). If they do, discuss possible reasons why.

At similar conditions, others have reported a first-order rate constant of 10^{-3} s^{-1} for the DC-245 monomer, and a K > 60.

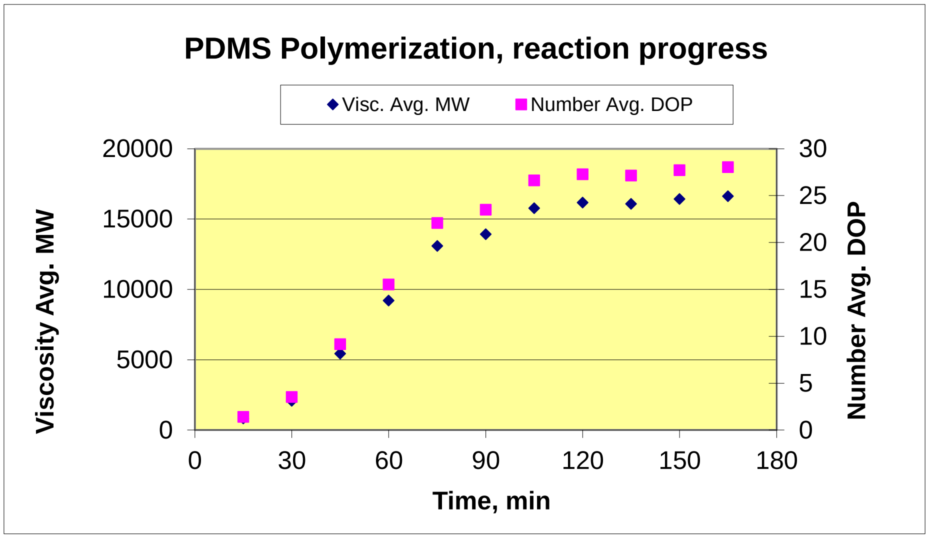


Figure 1. Typical polymerization results. "DOP" = degree of polymerization. The MW's were computed from Dow Corning data (see last page) or Barry's equation (>2500).[5]

The workup of some raw data is shown in **Figure 1**. These data are for the polymerization of Dow Corning DC-245 monomer. The reaction conditions were: 0.04 wt% catalyst solution, 12 wt% endblocker (modifier), 130 °C and 1 atm pressure. Note that this is a relatively large amount of endblocker to use, thus the low final degree of polymerization (DOP).

Here 11.36 L of monomer were reacted and only 15 mL low boilers were recovered, so the data should follow irreversible kinetics. The fit to first-order (in monomer) kinetics is shown in **Figure 2** below. The fraction conversions (f) were determined using **Equations. 1 and 2** with the assumption that the polymer produced is at constant chain length (P_N). Note that the fit is reasonable but not perfect. Slight deviations from the theoretically expected first-order kinetics can arise for several reasons, among them diffusional effects (when the viscosity increases, the diffusivities can decrease significantly), and several other reasons discussed in specialized texts on polymer science. Two other reasons are suggested by the raw reaction temperature data (temperature oscillations affect the rate constant), and by the small leaks in the pumps, reactor, and heat exchangers (some O_2 will get into the system, gradually inhibiting the reaction).

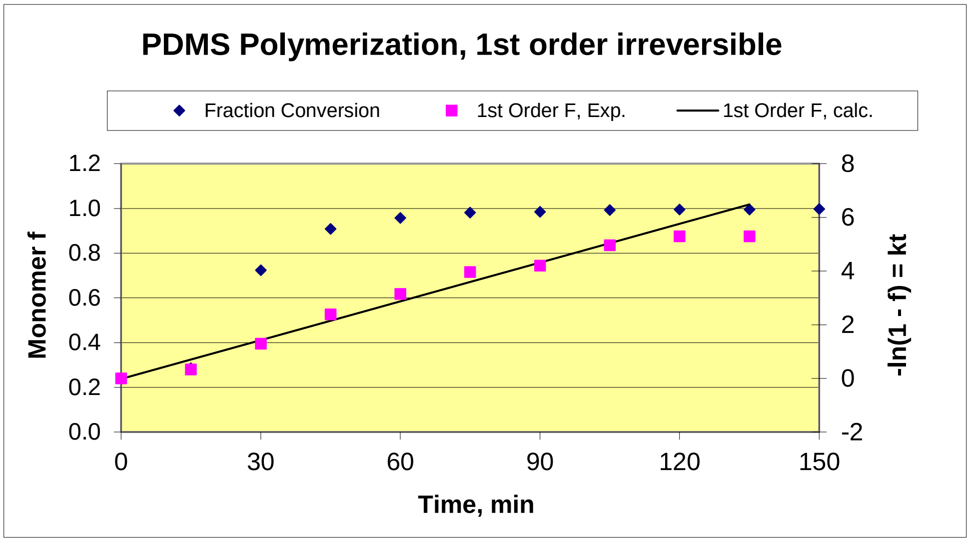


Figure 2. Kinetics analysis of the data in Figure 1. "F" is the 1st order function, i.e., the solution of the batch reactor mass balance for a 1st order irreversible reaction.

Summary

Polymer science provides many examples of the basic principles of chemical kinetics and reactor design. Simple rate expressions can describe fairly complex chemical processes, as in this experiment. Reactor system design must find the optimal reactor type (batch, stirred tank, plug flow, or hybrid) considering kinetics, capital costs, and molecular weight distribution. In particular, the last factor is usually the most important, because it largely defines the product. Depending on this factor alone the product can often range from a hard brittle solid to a rubber to a liquid. A bulk (no solvent) polymerization such as this one has the advantage that subsequent processing to obtain a pure polymer is simple – just strip out the low boilers and filter out the neutralized catalyst. But the disadvantage of bulk polymerization is that if one loses control of temperature (too high), even in a thermoneutral polymerization such as this one, other reactions will predominate and these can lead to "runaway", an uncontrolled exothermic reaction that may result in explosion. Polymerizations with higher heats of reaction than this one are reacted either in solution, suspension (a continuous water phase is present, and the monomer is in droplet form), or in the gas phase.

The major takeaways from the experiment are how one can process raw data of an easily measurable physical property (viscosity) to ultimately determine the monomer fraction conversions and the kinetics of the reaction. Many other physical properties, *e.g.*, density and particle light scattering, are used for this purpose in other polymerizations.

Applications[8]

Polymers made by ring-opening polymerizations include Nylon-6 from caprolactam (used for everything from wire harness connectors to auto air intake manifolds), acetal copolymers with ethylene oxide and dioxolane (used for everything from fuel tanks to sprinklers), poly(ethyleneimines) (used in detergents and cosmetics), and many other silicon-backbone polymers. Except for Nylon-6, these are made commercially by anionic or cationic living polymerizations. Other polymers made similarly include copolymers of styrene (especially with isoprene), isobutene-isoprene (butyl) rubber and its halogenated variants, and poly(alkyl vinyl ethers) (used in paints and adhesives). For some such polymerizations, the chain terminations are so controllable that an almost homogeneous (very narrow molecular-weight distribution) is possible. But except for certain specialty grades, it has been found that such narrow distributions present other problems, such as difficulties in extrusion.

Many polymers are vacuum-stripped as the first part of their purification to a commercial product. Among these are the poly(vinylidene chloride) copolymers, poly(chloroprene), and many grades of poly(styrene) and its copolymers such as SAN (styrene-acrylonitrile).

The uses for silicone polymers are many: lubricants, personal care products, medical devices, antifoams, sealants, waterproof coatings, and as components of detergents, electrical insulation, and paints.[9] Medical devices composed of very high molecular weight, crosslinked silicone may be approved by the FDA for implantation. More common medical uses are consumables such as catheters, tubing, gastric bags, and surgical incision drains. Commercial PDMS is non-hazardous with a flash point higher than 300 °C, minimal toxicological effects (it does not bioaccumulate), and good resistance to moderately concentrated aqueous alkali and acids.[9,10] It does not corrode most common materials. But like many polymers it can oxidatively decompose, in this case above ~150 °C.

Legend

Figure 1. Typical polymerization results. "DOP" = degree of polymerization. The MW's were computed from Dow Corning data (see last page) or Barry's equation (>2,500).[5]

Figure 2. Kinetics analysis of the data in Figure 1. "F" is the 1st order function, *i.e.*, the solution of the batch reactor mass balance for a 1st order irreversible reaction.

Materials List:

Name	Company	Catalog Number	Comments
Equipment			
Cannon-Fenske viscometers (at least 3)	Cole-Parmer	Sizes 200, 300 or 400, 500 (UX 98934)	Use to measure the kinematic viscosity of polymer samples
Stirred tank reactor	custom		20 L
Reactor Agitator	McMaster-Carr		46-460 RPM; 6-blade, flat turbine (Rushton) type, ~4" diameter.
Reagents			
Dimethlysiloxane monomer	Dow Corning	DC-245	specific gravity = 0.956 at 25 °C; viscosity = 4.2 cSt; m = average number of dimethylsiloxanes = 5
Endblock A	Dow Corning	10082-147	specific gravity = 0.88 at 25°C; m = 4.5 (not counting the two end groups)
KOH catalyst	VWR	470302-140	45 wt% solution in water
Nitrogen	Airgas	UHP grade	Used to blanket the system
Carbon dioxide	Airgas	Tech. grade	Used to neutralize the catalyst

References

1. http://www.essentialchemicalindustry.org/polymers/polymers-an-overview.html and http://www.pslc.ws/mactest/maindir.htm (both accessed 8/22/16).
2. MatWeb, Material Property Data, http://www.matweb.com/ and Plastics General Polymers Brand Name Listing, http://www.plasticsgeneral.com/BRAND-NAMES-LIST1.htm (both accessed 8/25/16).
3. Fogler, F.S., *Elements of Chemical Reaction Engineering*, 3rd Ed., Prentice-Hall, **2001**, pp. 354-382 (sections 7.1.2-7.1.5).
4. Odian, G., *Principles of Polymerization*, 4th Ed., Wiley-VCH, **2004** (ch. 3), or Rodriguez, F., *Principles of Polymers Systems*, 2nd Ed., McGraw-Hill, **1982** (ch. 4); Fried, J.R., *Polymer Science and Technology*, Prentice-Hall, **1995** (ch. 2).
5. Barry, A.J., *Viscometric Investigation of Dimethylsiloxane Polymers,* J. Appl. Phys., **1946**, 17, 1020-1024.
6. Kuo, A.C.M. *Poly(dimethylsiloxane),* in Polymer Data Handbook, Oxford University Press, **1999**, 411.

7. Or you can look at it as a simple averaging of $1/P_N$ with respect to the variable f.
8. The material in the first two paragraphs was taken from: *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2012** or the *Encyclopedia of Polymer Science and Technology*, 3rd Ed., Wiley-Interscience, Hoboken, **2003-04.**
9. http://www.dowcorning.com/content/discover/discoverchem/properties.aspx (accessed 8/25/16)
10. Shin-Etsu Silicone Fluid Technical Data, Shin-Etsu Silicones of America, Akron, 2005.
11. Dow Corning, Product Information, Silicon Fluids, http://www.dowcorning.com/applications/Product_Finder/Products.aspx (accessed 9/23/16).

Viscosity and Density Data at Low Molecular Weight

Data originally from: Dow Corning.[11]

MW, g/mol	162	410	1250	28000
Viscosity, cs, 25 °C	0.65	2.0	10	1000
Specific gravity, 25 °C	0.760	0.872	0.935	0.970

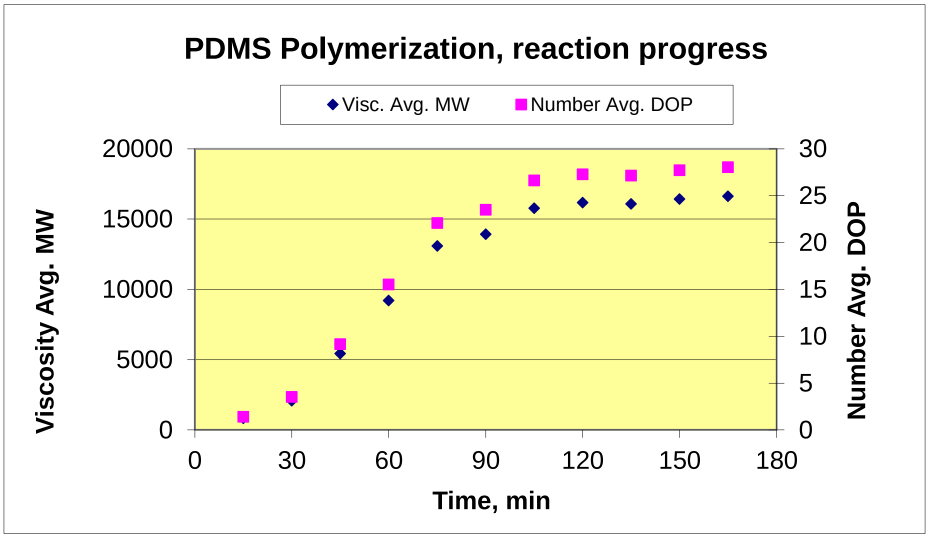


Figure 1. Typical polymerization results. “DOP” = degree of polymerization. The MW’s were computed from Dow Corning data (see last page) or Barry’s equation (>2500).[5]

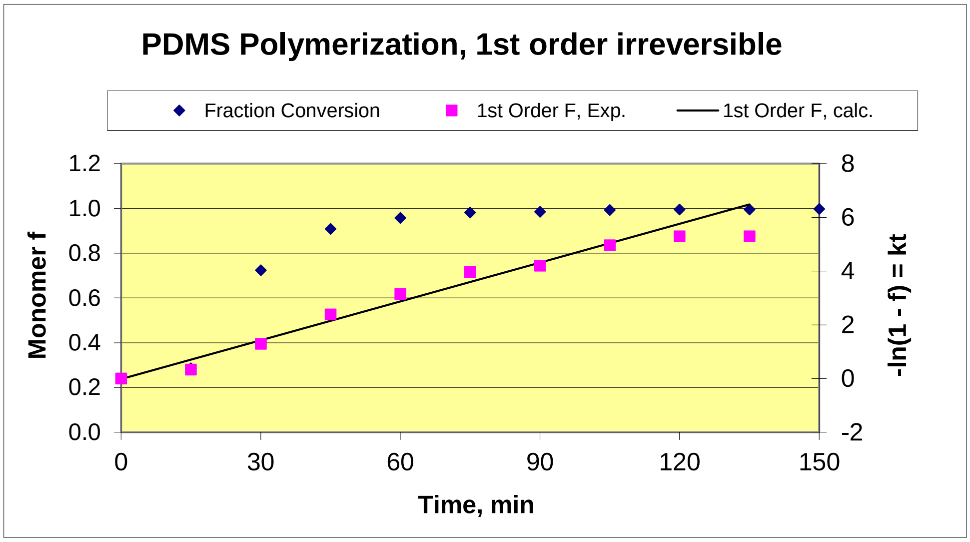


Figure 2. Kinetics analysis of the data in Figure 1. “F” is the 1st order function, i.e., the solution of the batch reactor mass balance for a 1st order irreversible reaction.