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Step growth polymerization molecular weight

KP2. Kinetics of Step-Growth Polymerization It is important to understand how reactions continue over time. This information can tell us how long it takes for the polymer to reach the optimal length. It can also give an insight into how encoding occurs, just as kinetics can provide insight into other response mechanisms. The presentation polymer grows through the process of growth measures. Reaction generally involves a replacement in carboxylic acid. For example, the formation of polyester often involves the replacement of alcohol function groups on carboxylic acid, making ester. The drawings below show that the actions use ethylene glycol and oxalic acid, to use common names common in the industry. Oxalic acid is usually not used in making polyesters, but it is drawn here as a very simple example structure. If you know some basic kinetics, you know that we can express the response rate as the rate of change in product concentrations per change in time. In this case, the product is polymer, abbreviation P. Alternatively, we can express the response rate as the rate of change in monomer concentrations per change in time. Just by looking at the equation of the reaction, we expect that every time a polymer molecule is made, the monomer molecules are used. In this case, we have a joint polymer, made of two different monomers, so that is why we can express the response rate as the rate of change either monomer concentration. The negative sign in rates shows we see the rate of monomer loss; like polymers appear, monomers disappear. If you know something about organic reaction mechanisms, you probably know that the first step in esterification is the contribution of lonely couples from alcohol oxygen on diol to carbon carbonyl on contributed acid. (It can actually be the second step, but we'll get to later.) The first step in the mechanism is a fundamental response. All the other steps you will draw in the mechanism are also basic reactions. The great thing about the underlying reaction is that we always know each other's rate laws: it's a constant time rate of concentration of all species leading into the move. In this case, this first step is also a rate-determination measure, so the entire reaction is governed by that first step rate law. It takes both monomers, so we get simple rate laws. Note that, based on stoichiometry (monomers ratio in the reaction equation), we will probably carry out these polymerizations with the same amount of diol and dicarboxylic acid. Instead of worrying about the M1 and M2 separately, we can call them both [M]. so what we have here is a simple second order rate law. The legal form of this rate is called the differentiation rate law, as it is stated in terms of the rate of change of one thing with the rate of change to another. Other. That's not what you're interested in, and you just want to see what happens to the focus over time, you might want to integrate this phrase to get integrated from rate law. If we are to periodically measure the concentration of monomer during polymerization and inverse plots over time, we will get a straight line. The slope of the line will be a constant rate, and the bypass will reflect the inverse monomer concentration for which we have initiated a reaction. At this point, we need to pause and talk about what we actually mean by monomer concentration. Because of its very specific feature of conducive polymerizations, it is not really an ethylene glycol concentration or oxalic acid. Look at this drawing of the growth process of this step and we'll discuss why that is. Remember that, in step-growth empowerment, the majority of molecules may respond at the same rate. Two monomers link together to form dimers, two dimers form tetramers, two tetramers forming octane, etc. It won't go perfectly as we see it in this picture; inevitably would be some stragglers throwing the average off. But note what that means: monomers disappear immediately. No one is really interested in how quickly the monomer turns into an inspector. They want to know how a polymer chain gown is in progress. So, in the above expression, [M] does not refer to the concentration of both monomers at all. It refers to the concentration of reactive function groups in the monomers. After all, when the monomers disappear, the same esterification reaction continues to occur, and it is really an important concentration of alcohol and carboxylic acid groups, whether they are found on monomers, dimers, tetramers, or whatever. In these rate expressions, sometimes people will use [OH] and [CO2H] in rate expressions, stressing that they really follow the loss of the working groups. And note what happens to the groups that work. Their concentration is smoothly down over time. Furthermore, the concentration of ester, which represents a new pool of functions in polymers, is growing at the same rate. [OH] and [CO2H] were down by 8 (or half) in the first step; [CO2R] increased by 8, etc. SO the re-functional group usage rate is equivalent to the product's functional group appearance rate. The other thing we're interested in here is the level of polymerization: the number of monomers put in the chain. Polymers grow at a certain rate, but how long does it get? Just look at the simple scheme of polymer growth above, we see the average level of polymerization rising (written as a DP or as Xn; bar over the symbol signals we see on average). If you look closely, you will that the level of polymerization is always the concentration of the original monomer divided by the balance of monomer concentrations. That turns out to be a very important relationship. Note that this relationship only inverts the remaining monomer breakdowns (or, really, a fraction of the abandoned monomer function group). The opposite quantity is a fraction of the converted monomer. That depicts a functional group that has been converted into esters. Because we are dealing with a breakdown, the converted breakdown is just one minus the remaining breakdown. If we do a little algebra, we get variations on that piece of information. Why do we do that the last part? Because now we have arrived back at the expression for polymerization levels. So, now we have an equivalent way of expressing polymerization levels in terms of converted fractions. The relationship was called the Carothers equation, in honor of Wallace Carothers, the DuPont chemist who created the nylon. KP2.1 problem. Predict polymerization levels if 75% of the final batch of monomers have been converted into polymers. So, what does the relationship look like? Here are some data from Paul Flory, another DuPont and nobel laureate chemist, obtained in the intermediate period between World Wars when such chemistry had just begun (Flory, P. J. Am. Chem. Soc. 1937, 59, 466-470). That's a breakdown changed on x axes and expressions for polymerization levels on the y axis. This is exponential growth. Polymerization levels start shooting upwards dramatically. We already know that from our introduction to stepping in growth, but what stands out from the data is how higher levels of polymerization are, and high molecular weight, not really happening until it's too late in reaction. If we need a polymer of heavy confinement of high molecules, chemicals are better reliable; otherwise, if things go wrong, we will be left with some short chain goo rather than long chain material. Now let's take this new relationship and see them in the kinetic context of our second order. We started with the same integrated rate laws, but we've multiplied everything on both sides of the equation with the starting monomer concentration. That's a fair game in the algebra, remember. The reason for doing so is to get a term that resembles our relationship that depicts polymerization levels. So far, we have taken the ratio we gained in the first row and worked out its relationship with the changed fraction, which we replaced in the last lineup. Now we bring carothers in common to remember that this really tells us how the level of polymerization changes over time. Relationship indicates the polymerization stage should increase linearly over time. This relationship suggests the polymerization stage should increase linearly over time. Again, we will use Flory data to describe relationships, using fractional conversion data. He can measure that data easily, and know how it relates to polymerization levels. It should be linear. But don't worry; Flory knows what's wrong. You probably know also, if you remember some things about replacements on carbonyls. The problem is, we deal with neutral nucleophile and electrophyls that are quite inactive. That reaction should be really slow. It's not very slow, thorough, because it's self-cited. One monomer of carboxylic acid can activate the other, making it a better electrophile. This means that coupling alcohol with carboxylic acid is not the first basic step of the reaction, but the second. Before alcohol acids and carboxylic acid can come together, two carboxylic acids need to collide already. This means we have a third order reaction. As it happens, the legal form of third-order rates is not all the more complicated, and we can do some of the same algebra with it to see how polymerization levels will vary with time given this new information. We can take Flory data again and provide this new treatment. This time, we got a linear relationship. The correction illustrates one of the basic uses of kinetic, which is a tool that allows us to investigate how the reaction occurs. In this very specific case, kinetics indicate that there are additional measures (pre-rate determination) in response. In addition, we found that it is a square degree of polymerization that is increasingly linear with time. KP2.2 problem. Given the concentration of early alcohol groups [M]0 = 17 M, determine the constant rate from Flory data in L2mol-2s-1. Flory also established a statistical basis for predicting molecular weight and heavy distribution of molecules in polymers. For example, when we have a level of polymerization, it is an easy step to calculate the weight of the estimated molecules. That's just the polymerization level of times the heavyweight of monomer molecules; in other words, the number of monomers in the time of each other's heavyweight chains. (This approach ignores any small molecules such as lost water during conveyor reactions.) $M_n = DP \times M_0$ $M_w = M_0 / (1 - p)$ This is called the average molecular weight number. It is based on taking an average value for the length of the chain and converting it into the molecular weight of the chain. Of course, some chains may be far shorter (Flory actually points out, based on the probability, that there will be some monomers left) and therefore they contribute less to the overall sample. The second way to approach the average weight of the chain molecule is to assess a fraction of the amount of weight contributed by each chain's length. Weight the average chain will then be given by: $M_w = \sum \pi_x M_0$ where the π_x is the breakdown of the long chain x. What is Breakdown of long chain x? This approach begins by considering the probability that the chain will x units long. As mentioned above, the long chain x unit has an ester x-1 relationship and 2 ends of the non-reacted chain. We know the probability of chain endings converted to polymer relationships is p, and in chain x long units that need to occur x-1 times, for the probability of px-1. We also know that the probability of a functional group left unreacted is 1-p, and that needs to happen twice here, for probability (1-p)2. The probability of having a long chain x is: $\pi_x = x \cdot p^{x-1} \cdot (1-p)^2$ This means: $M_w = \sum x \cdot p^{x-1} \cdot (1-p)^2 \cdot x M_0$ $M_w = (1-p)^2 M_0 \sum x^2 \cdot p^{x-1}$ Series on the right can be redirected to: $\sum x^2 \cdot p^{x-1}$ Series on the right can be redirected to: $\sum x^2 \cdot p^{x-1} \cdot (1 + p) / (1 - p)^3$ So that: $M_w = (1-p)^2 M_0 (1 + p) / (1 - p)^3$ $M_w = M_0 (1 + p) / (1 - p)$ That provides a simple forecast of average molecular weight based on the breakdown changed in the mapping Although Mn and Mw are essentially predictions of molecular weight theory, this quantity can also be measured experimentally using different methods. The ratio between these two quantities is always used as an expression of the breadth of molecular weight distribution, called the polydispersity index or simply an imbalance: $D = M_w / M_n$ In case of conversion, $D = [M_0(1 + p) / (1 - p)] / [M_0 / (1 - p)]$ $D = 1 + p$ Because p always breakdown, the result is that the inequidity of condemnation polymerization is statistically expected to be less than 2.0. KP2.3 problem. Given the 99% monomer conversion with an average molecular weight of 120 g/mole, counting Mw, Mn and D. D.

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