

Kinetics of living polymerisations

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Summary

By means of a simple kinetic analysis of living polymerisations it is shown how both the concentration of growing ends and the rate-constant of propagation can be determined, provided that both the yield and the degree of polymerisation are given as functions of time.

Introduction

Since PEPPER (1974) first identified explicitly the polymerisation of styrene by perchloric acid in methylene dichloride at -73° and -45°C as a living cationoid polymerisation, many more reports of such systems have appeared. Although of course the kinetics of living anionic polymerisations have been explored extensively since SZWARC first identified and named this category of reactions, it seems appropriate to put together the relevant equations in a manner which is new and more useful for cationoid (cationic and pseudo-cationic) polymerisations, although no novel principle is involved, see esp. BOEHM *et al.* (1972). The main reason for doing this is that in most earlier treatments the time-element was rather neglected, and that most of the results of recent researches are presented in the form of the dependence of molecular weight on conversion or yield. This form of presentation eliminates the independent variable, time, and thus immediately curtails the scope and usefulness of the study. The reason can be made clear very easily: In the general rate-equation (1) below, there are two unknowns: the rate-constant and the concentration of growing centres. In order to measure these, we need two dependent variables to measure, and in the studies with which we are concerned these are the yield as a function of time and the molecular weight as a function of time. One purpose of this paper is to show that, given this information, the kinetic problem can be solved completely. However, if the time is eliminated, the problem is not soluble; so a second purpose of this paper is to plead that in all studies on living

polymerisations both conversion and molecular weight should be reported as time-dependent variables.

Algebraic treatment

Consider a polymerisation without transfer and termination with a stationary state of the Second Kind, i.e. one in which $k_i = k_t = 0$ throughout the reaction after its instantaneous start. Assume further that the rate of propagation is of order z with respect to the monomer concentration at any time, and that $z \geq 0$.

Then

$$-dm/dt = k_x m^z [P_n^*] \quad (1)$$

where $[P_n^*]$ is the concentration of growing chains, which is constant, k_x is the experimental rate-constant. Under the assumed conditions, the Degree of Polymerisation n will be the ideal DP, so that

$$n = (m_0 - m)/[P_n^*] \quad (2)$$

Therefore the variation of n with time is given by

$$dn/dt = (-dm/dt)/[P_n^*] \quad (3)$$

From (1) and (3):

$$dn/dt = k_x m^z \quad (4)$$

and if $Y = (m_0 - m)/m_0$ and therefore $dY/dt = -(dm/dt)/m_0$,

then from (3):

$$dn/dY = m_0/[P_n^*] \quad (5)$$

Consequences

1. Most results on allegedly living polymerisations are presented as plots of n against Y . The eqn. (5) shows -

(i) why many of these plots are rectilinear: $[P_n^*]$ is constant;

(ii) that when the plots start to curve, at least one of the underlying assumptions ceases to be valid;

(iii) that the all-important concentration of growing chains, $[P_n^*]$, can be calculated from the slope of the n vs. Y plot;

and (iv) that this is valid, whatever may be the value of z .

2. If $z = 1$, $k_x = k_p^*$, which can be obtained from a plot according to eqn. (4). This method of obtaining k_p^* is unambiguous. It is, however, obvious that this k_p^* cannot be assigned to any particular mode of propagation

without further chemical information about the system. If, for example, one has a dieidic polymerisation carried by paired and unpaired cations, the rate-equation takes the form

$$-dm/dt = (k_p^+[P_n^+] + k_p^\pm[P_n^+A^-])m \quad (6)$$

The k_p^* is a weighted mean of k_p^+ and k_p^\pm , and of course the $[P_n^*]$ determined as indicated above is a weighted mean of $[P_n^+]$ and $[P_n^+A^-]$. Additional evidence from experiments with common-ion salts, from the dependence of the DPD on the reaction conditions, etc. is required to resolve such ambiguities. Nevertheless, the order of magnitude of the k_p^* obtained and the manner in which it varies with reaction conditions, e.g. the dielectric constant of the medium, can give useful clues as to whether one is dealing with an eneidic or monoeidic system, and if monoeidic whether it is, for example, cationic or pseudocationic.

3. If $z = 1$, eqn. (1) can be rewritten as

$$-d \ln m / dt = k_p^*[P_n^*] \quad (7)$$

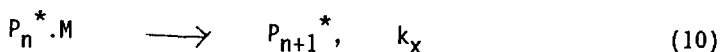
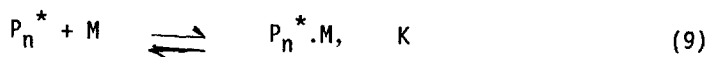
The corresponding plot has slope $k_p^*[P_n^*]$, and this should agree with the product of the values of k_p^* and $[P_n^*]$ obtained separately as indicated above.

4. If $z \neq 1$, a more useful form of eqn. (4) is eqn. (8):

$$\ln(dn/dt) = \ln k_x + z \ln m \quad (8)$$

Both z and k_x can be found from the plot of $\ln(dn/dt)$ against $\ln m$. Actually, many published polymerisations appear to be of zero order with respect to m , so that $z = 0$, and for such systems the plot of n against t is also rectilinear and its slope is k_x .

The simplest interpretation (though not the only one) of a zero-order polymerisation is in terms of the Fontana-Kidder mechanism (Fontana 1948) in which the growing centre is a partner in an associative equilibrium with the monomer, and the rate-determining propagation step is the isomerisation of the resultant complex:



The rate equation for such a reaction is

$$-dm/dt = k_x Km([P_n^*] + [P_n^* \cdot M]) / (1 + Km) \quad (11)$$

This is, of course, a well-known type of kinetic equation. If dt/dm is plotted against $1/m$, a straight line is obtained with slope S and intercept I , where

$$S = 1/k_x K([P_n^*] + [P_n^* \cdot M]) \quad (12)$$

$$I = 1/k_x ([P_n^*] + [P_n^* \cdot M]), \quad (13)$$

so that $K = I/S$ (14)

Since k_x can be obtained as shown earlier in this section, values of $[P_n^*] + [P_n^* \cdot M]$ can be found from both I and S . At very low m , the order of the reaction should change from zero to first with respect to m .

5. It is evident from our treatment and discussion, that it would be of great advantage if in all future publications on allegedly living systems both the Y and the DP were to be reported as functions of time and the values of k_x and $[P_n^*]$ derived from them were given. This cannot entail any extra work, since in all such researches the time must be known at which samples are taken for analysis; the gain in information, however, would be considerable.

Acknowledgments

My thanks are due to Prof. D.C. PEPPER and Dr. S. BYWATER for helpful discussions and to the Leverhulme Foundation for help with the production of this paper.

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Accepted November 17, 1987 K