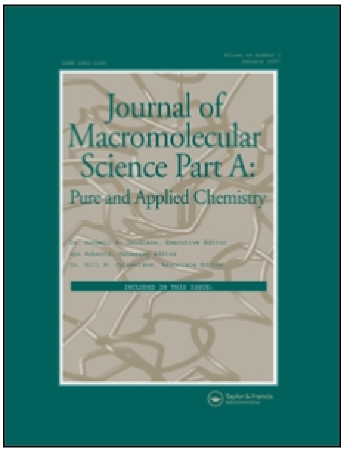

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The Kinetics of Donor-Acceptor Complex Polymerization. I. Introduction and Theory

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The Kinetics of Donor-Acceptor Complex Polymerization. I. Introduction and Theory

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ABSTRACT

A general reaction pattern is proposed for donor-acceptor complex polymerization. The explicit solution of polymer yield as a function of time is obtained for three limiting cases of reactant concentration.

INTRODUCTION

In recent years, there has been considerable research into polymerization reactions involving donor-acceptor (A-D) complexes (sometimes called charge-transfer complexes) [1-16]. Much of the

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most recent work in these systems has been in copolymerization studies, but similar reactions have been noted in salt-catalyzed homopolymerizations [17-22].

In general these reactions are typified by the following scheme.

$$\text{Acceptor monomer (A)} + \text{Donor monomer (D)} \rightleftharpoons \underset{\substack{\downarrow \\ \text{to polymeric product,} \\ \text{usually 1:1 alternating} \\ \text{copolymers.}}}{[\text{A-D}]} \ \begin{array}{l}\text{donor-acceptor} \\ \text{complex}\end{array}$$

This type of reaction is exemplified by the furan-maleic anhydride system [7].

If the acceptor-donor pair does not spontaneously form such an A-D complex, then the formation of the latter may be "catalyzed" by the addition of a Lewis acid to the monomer pair. In this case, the acceptor monomer form an adduct with the Lewis acid:

$$\text{Lewis acid (Z)} + \text{A} \rightleftharpoons [\text{Z-A}]$$

The acceptor monomer-salt adduct ([Z-A]) may now be an entity of sufficient electropositivity to attract a donor monomer and form the donor-acceptor complex.

$$\text{Z-A} + \text{D} \rightleftharpoons \underset{\substack{\downarrow \\ \text{to polymer as before}}}{[\text{ZAD}]}$$

Exemplary of this catalyzed reaction is the formation of 1:1 alternating copolymer from the zinc chloride catalyzed acrylonitrile-styrene monomer-pair [5].

Typically, acceptor monomers tend to be those with polar side-groups (acrylates, nitriles) while donor monomers contain nonpolar or weakly-polar side-groups (ethylene, 1,3-butadiene, styrene). To date, those Lewis acids most studied are zinc halides and ethyl aluminum chlorides.

One important feature of these reactions is that the A-D (or ZAD) monomer pair propagates as a "monomeric" unit, for the most part excluding the addition of either of the free, uncomplexed monomer.

The resulting copolymer is of necessity composed of equimolar amounts of the two monomers and is of a highly regular, alternating structure [6, 13, 23-27].*

The rates of propagation are higher than would normally be expected (1, 2, etc.) but as yet there is no definitive statement as to the electronic structure of the propagating species. Initiation of the polymerization has been accomplished thermally [28, 29] with free-radical initiation [30], by UV irradiation [16, 31, 32], by γ-irradiation [18, 19], and by electrolysis [8-11].

In this paper we have derived general equations connecting the yield of polymer with the time of polymerization from a kinetic scheme which appears to fit the experimental facts most closely. These equations have been derived specifically for copolymerization reactions in the presence of "catalyzing" salts. Nonetheless, they may be modified to take into account uncatalyzed copolymerizations and catalyzed homopolymerizations.

THEORY

We have envisaged a kinetic scheme which includes the experimentally-verified equilibria between the catalyst salt and monomers, and an optional salt regeneration step.

This scheme can be written symbolically as

$$Z + mA \overset{K_0}{\rightleftharpoons} ZA_m$$

$$ZA_m \underset{k_{-1}}{\overset{+mD \;\; k_1}{\rightleftharpoons}} Z(AD)_m \xrightarrow{k_p} P_mZ \xrightarrow{k_r} Z + mP$$

$$Z \rightarrow \text{recycled}$$

*The existence of alternate A-D units, as indicated by NMR studies has not been completely conclusive using conventional techniques. However, the recent work by Schaefer [25] using high resolution pulsed ^{13}C NMR on 1:1 styrene-acrylonitrile copolymers does considerably strengthen the evidence of alternating structures in these systems.

For the sake of clarity, we have omitted the use of square brackets to denote units of concentration throughout this treatment. Thus symbols denoting reagents or polymeric products will carry the assumption of a self-consistent set of concentration units.

The following is a description of the symbols used.

- Z: the free catalyst salt.
- A: the acceptor monomer.
- D: the donor monomer.
- ZA_m: the adduct formed between the acceptor monomer, A, and the catalyst salt, Z, of variable stoichiometry, m.
- $Z(AD)_m$: the donor-acceptor complex of the salt and both monomers of variable stoichiometry, m.
- P_mZ: the catalyst-containing macromolecular product formed from the polymerization of $Z(AD)_m$.
- P: the macromolecular product formed after the regeneration of catalyst from P_mZ.
- K_0: equilibrium constant defined as

$$K_0 = ZA_m/(Z)(A^m) \tag{1}$$

- k_1, k_{-1}: the forward and backward rate constants for the complex formation, respectively.
- k_p, k_r: rate constants for the propagation and regeneration reactions, respectively.

It should be noted here that the rate constant, k_p, is a composite of the true propagation constant and the rate constant of the initiation and termination reactions. It could also be a function of the catalyst concentration, or the number of photons passed in UV initiation or the number of Faradays passed in electrolytic initiation. The use of such an "apparent" rate constant, k_p, serves to describe the actual monomer-consuming step at this stage, and its internal complexity does not detract from the validity of the scheme.

The initial concentrations of the components are, at any time t, defined by the conservation equations

$$Z_0 = Z + ZA_m + Z(AD)_m + P_mZ \tag{2}$$

$$D_0 = D + mZ(AD)_m + mP_mZ + P \tag{3}$$

$$A_0 = A + mZA_m + mZ(AD)_m + mP_mZ + P \tag{4}$$

where P_mZ is defined as the concentration of $Z(AD)_m$ units existing as polymer and where P is the concentration of catalyst-free AD units existing as polymer.

We denote the total concentration of AD units existing as polymer, regardless of the presence of catalyst units, to be P_t, such that

$$P_t = mP_mZ + P \tag{5}$$

In order to solve this problem, we have to make the over-all assumption of a "steady state" of $Z(AD)_m$ existing in the system.

From the basic assumption of the steady state, that, for first-order consumption of $Z(AD)_m$

$$\begin{aligned} dZ(AD)_m/dt &= 0 \\ &= k_1D^mZA_m - (k_{-1} + k_p)\,Z(AD)_m \end{aligned} \tag{6}$$

we have,

$$Z(AD)_m = \frac{k_1}{k_{-1} + k_p}\,D^mZA_m \tag{7}$$

Three different extremes of reactant concentration make this possible. They are as follows:

I: $D_0 \gg Z_0$

$A_0 \gg Z_0$, so that $D \simeq D_0$ and $A \simeq A_0$

II: $Z_0 \gg D_0$

$A_0 \gg D_0$, so that $ZA_m \simeq (ZA_m)_0$

III: $D_0 \gg A_0$

$Z_0 \gg A_0$, so that $D \simeq D_0$ and $Z \simeq Z_0$

We can now take each case (I, II, and III) in turn, perform the necessary substitution, and evaluate the integral involved to find the total polymer yield, P_t, as a function of time, t.

The zero-order case, n = 0, is soluble for each of Case I, II, or III to give the same answer

$$dP_t/d_t = mk_p\left(Z(AD)_m\right)^0 \tag{8}$$

$$P_t = mk_pt \tag{9}$$

CASE I

In this system (low concentration of Z_0 relative to A_0 and D_0) it is possible to derive the final kinetic expression for P_t as a function of t. Combining Eqs. (1) and (2) we can write

$$ZA_m = \frac{K_0A^mZ_0 - K_0A^mZ(AD)_m - K_0A^mP_mZ}{1 + K_0A^m} \tag{10}$$

At <u>low</u> conversions Eq. (7) becomes

$$Z(AD)_m = QZA_m \tag{11}$$

where

$$Q = \frac{k_1}{k_{-1} + k_p} . D_0^{\,m} \tag{12}$$

Combining Eqs. (10), (11), and (12), we then have the instantaneous concentration of $Z(AD)_m$ as

$$Z(AD)_m = \frac{QK_0A_0^{\,m}}{(1 + K_0A_0^{\,m})\left(1 + Q\ \dfrac{K_0A_0^{\,m}}{1 + K_0A_0^{\,m}}\right)} .(Z_0 - P_mZ) \tag{13}$$

Equation (13) simplifies to

$$Z(AD)_m = R(Z_0 - P_mZ) \tag{14}$$

where

$$R = \frac{QK_0A_0^{\,m}}{(1 + K_0A_0^{\,m})\left(1 + Q\ \dfrac{K_0A_0^{\,m}}{1 + K_0A_0^{\,m}}\right)} \tag{15}$$

In order that we may find $Z(AD)_m$ as a function of only one variable (time), we must also find P_mZ as a function of time. The rate of formation of P_mZ is

$$\frac{dP_mZ}{dt} = k_pZ(AD)_m - k_r(P_mZ) \tag{16}$$

Substituting for $Z(AD)_m$ in Eq. (16) (from Eq. 14), we have

$$\frac{dP_mZ}{dt} = k_pRZ_0 - (k_pR + k_r)P_mZ \tag{17}$$

which may be integrated to give

$$P_m Z = \frac{C_1}{C_2}\ (1 - \exp(-C_2 t)) \tag{18}$$

where

$$C_1 = k_p R Z_0 \tag{19}$$

$$C_2 = k_p R + k_r \tag{20}$$

Now, taking into account Eq. (5), the rate of polymer formation can be written as

$$\frac{dP_t}{dt} = \frac{m dP_m Z}{dt} + \frac{dP}{dt} \tag{21}$$

which simplifies to

$$dP_t/dt = mk_p Z(AD)_m \tag{22}$$

Combining Eqs. (14), (18), and (22) and separating variables, we have

$$dP_t = m\left[k_p R Z_0 - k_p R \frac{C_1}{C_2}\right] dt + mk_p R \frac{C_1}{C_2} \exp(-C_2 t)\ dt \tag{23}$$

This integrates to

$$P_t = Et + F(1 - \exp(-C_2 t)) \tag{24}$$

where the boundary condition for integration is that $P_t = 0$ when $t = 0$ and where

$$E = mk_pR\left[Z_0 - \frac{C_1}{C_2}\right] \tag{25}$$

and

$$F = \frac{mk_pRC_1}{C_2{}^2} \tag{26}$$

CASE II

In this case the donor monomer, D, is initially in low concentration relative to the acceptor monomer, A, and the catalyst, Z.

At low conversions, Eq. (7) becomes

$$Z(AD)_m = SD^m \tag{27}$$

where

$$S = \frac{k_1}{k_{-1} + k_p} (ZA_m)_0 \tag{28}$$

(This is analogous to Eqs. (11) and (12) in Case I.) Then, from Eqs. (3), (5), and (27), we have the following expression for $Z(AD)_m$

$$Z(AD)_m = S(D_0 - mZ(AD)_m - P_t)^m \tag{29}$$

This can be usefully solved only when the stoichiometric constant is unity, such that

$$ZAD = S\,(D_0 - ZAD - P_t) \tag{30}$$

Equation (30) may be rearranged to give an explicit form for ZAD

$$ZAD = \frac{S(D_0 - P_t)}{1 + S} \tag{31}$$

Employing Eqs. (22) and (31) we have

$$\frac{dP_t}{dt} = \frac{k_p SD_0}{1 + S} - \frac{k_p S}{1 + S} \tag{32}$$

which may be rewritten as

$$dP_t/dt = C_3 - C_4 P_t \tag{33}$$

where

$$C_3 = \frac{k_p SD_0}{1 + S} \tag{34}$$

and

$$C_4 = \frac{k_p S}{1 + S} \tag{35}$$

Equation (33) may be integrated to give (using the boundary condition that $P_t = 0$ when $t = 0$)

$$P_t = D_0(1 - \exp(-C_4 t)) \tag{36}$$

CASE III

In this case the acceptor monomer, A, is initially in low concentration relative to the donor monomer, D, and the catalyst, Z.

Combining the conservation Eq. (4) and Eq. (1), we have for ZA_m

$$ZA_m = \frac{1}{m} A_0 - \frac{1}{m}\left(\frac{ZA_m}{K_0 Z_0}\right)^{1/m} - \frac{1}{m} P_t - Z(AD)_m \tag{37}$$

Equation (37) becomes useful for further derivation only when m is unity. Then, combining Eq. (37) with Eqs. (11) and (12), we have, for $m = 1$

$$ZAD = \frac{Q}{1 + \frac{1}{K_0 Z_0}} (A_0 - P_t - ZAD) \tag{38}$$

Then

$$ZAD = \frac{Q}{1 + \frac{1}{K_0 Z_0} + Q} (A_0 - P_t) \tag{39}$$

and utilizing Eq. (22) for the rate of polymerization we have that,

$$dP_t = C_5 - C_6 P_t \tag{40}$$

where

$$C_5 = \frac{k_p Q A_0}{1 + \frac{1}{K_0 Z_0} + Q} \tag{41}$$

and

$$C_6 = C_5/A_0 \tag{42}$$

Equation (40) may be integrated to give (when the boundary condition $P_t = 0$ when $t = 0$ applies)

$$P_t = A_0(1 - \exp(-C_6 t)) \tag{43}$$

(Note the analogy with Eq. 36 in Case II.)

Table 1 summarizes the various combinations of reaction conditions, stoichiometric constants, and reaction orders which have proved amenable to direct solution at this stage.

TABLE 1

Conditions	$P_t = f(t)$ derived when	
I		
$A_0 \gg Z_0$ $D_0 \gg Z_0$	$n = 1, 0$	$m = m$
II		
$A_0 \gg D_0$ $Z_0 \gg D_0$	$n = 1, 0$	$m = 1$
III		
$D_0 \gg A_0$ $Z_0 \gg A_0$	$n = 1, 0$	$m = 1$

FURTHER CONSIDERATIONS

The steady-state assumption that $(k_p + k_{-1}) \gg k_1$ allows the imposition of a further set of restrictions on k_p and k_{-1}, without destroying the stationary-state concentration of $Z(AD)_m$. These are that $k_p \gg k_{-1}$ and $k_{-1} \gg k_p$. It is instructive to test the effect of these restrictions on the previously derived equations for P_t against t in each of Cases I, II, and III.

First, let us consider the situation when $k_p \gg k_{-1}$ (remembering the stationary-state condition). For Case I, Eq. (24) can be supplied with new expressions for the constants E, F, and C_2 (from Eqs. (25), (26), and (20), respectively). These new expressions, when $k_p \gg k_{-1}$, are

$$E = mk_1D_0^mZ_0\left[\frac{k_r}{k_1D_0^m + k_r}\right] \tag{44}$$

$$F = \frac{mZ_0(k_1D_0^m)^2}{(k_1D_0^m + k_r)^2} \tag{45}$$

$$C_2 = k_1D_0^m + k_r \tag{46}$$

Similarly, in Cases II and III constants C_4 and C_6 (Eqs. (35) and (42)) become

$$C_4 = k_1ZA_0 \tag{47}$$

$$C_6 = k_1D_0 \tag{48}$$

It must be stressed here, that, as expected, the new constants E, F, C_2, C_4, and C_6 are <u>independent</u> of k_p. (In the above simplifications we assumed $K_0 \gg 1$, i.e., $K_0A_0^m \gg 1$ when $A_0 \gg 1/K_0$.)

Second, we can have the situation where $k_{-1} \gg k_p$. Thus as before for Case I, the new values of E, F, and C_2 become

$$E = mk_pk_1D_0^mZ_0\left(1 - \frac{k_pk_1D_0^m}{k_pk_1D_0^m + k_r}\right) \tag{49}$$

$$F = mZ\left(\frac{k_pK_1D_0^m}{k_pK_1D_0^m + k_r}\right)^2 \tag{50}$$

$$C_2 = k_p K_1 D_0^{m} + k_r \tag{51}$$

and

$$K_1 = k_1/k_{-1} \tag{52}$$

For Cases II and III, the constants C_4 and C_6 become

$$C_4 = \frac{k_p K_1(ZA)}{1 + K_1(ZA)} \tag{53}$$

$$C_6 = \frac{k_p K_1 D_0}{1 + \frac{1}{K_0 Z_0} + K_1 D_0} \tag{54}$$

Again, as expected, the constants E, F, C_2, C_4, and C_6 all become functions, not only of k_p, but also of K_1, an equilibrium constant.

Finally, if a system exists where the two monomers, A and D, are sufficiently reactive to form a donor-acceptor complex without benefit of catalyst, then the foregoing scheme may be modified to take this into account. Thus we have

$$A + D \rightleftharpoons (AD) \xrightarrow{k_p} P$$

Similar procedures may be used to derive the yield-time relationships which will themselves be greatly simplified.

DISCUSSION OF THE SIGNIFICANCE OF THE KINETIC EQUATIONS

1. The kinetics cannot be solved for all cases. Fortunately, Case I, developed for any value of m, is the most interesting system and may be solved for a first-order reaction in "monomer."

2. Our desire to generalize the kinetic scheme made necessary the introduction of variable stoichiometry, m, in the original pre-equilibrium

$$Z + mA \overset{K_0}{\rightleftharpoons} Z(A)_m \text{ - - -}$$

This was done because of the reported ability of certain Lewis bases, e.g., acrylonitrile, to interact with catalyst salts, such as zinc halides and alkylaluminum halides, to form adducts of variable composition [33, 34]. However, because of the ability of the possible adducts to equilibrate, the value of m while being integral for discrete compounds may more properly be regarded as an average value in practice.

3. For those cases which can be solved, two main divisions occur between Case I and Cases II and III together. The principal cause of this is the effect of catalyst salt regeneration.

4. The necessary qualification of the solution of the integration steps, that a pair of the reactants had to be in excess over the third reactant, appears at first to be an insurmountable drawback to the analysis. However, because of problems in dissolving the reactants it is frequently advisable to have this excess, and in practice the qualification does not become limiting.

At this point the particular interest inherent in Case I becomes apparent. For donor-acceptor polymerizations using halides as catalyst, low Z_0 is an easily attainable and desirable condition. Thus the integration condition is a realistic goal. A glance at the final kinetic equations themselves will also indicate that Case I (Eq. 24) is the only one which has the polymer yields as a function of k_r, the catalyst regeneration constant.

5. One admitted drawback in this over-all analysis is our inability to solve the differential equations for cases other than where the reaction order, n, was unity. In the steady-state treatment herediscussed, it is, of course, quite possible to envisage polymer systems where the reaction order is unity, for instance when the rate of initiation is independent of the monomer concentration.

6. In the case where $k_p \gg k_{-1}$, it was deduced that in each case (I, II, and III) the yield of polymer as a function of time ($P_t = f(t)$) was independent of k_p, the (apparent) rate constant of propagation.

It must be stressed that "k_p" in the foregoing treatment is a function not only of the true rate constant of propagation, but also the initiation and termination steps.

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