

Modeling of Polymerization Reactions. I. The Cationic Polymerization of Isobutylene by Aluminum Organic Compounds

G. MASCHIO, F. ARTIGIANI, M. DI MAINA, and P. GIUSTI, *Istituto di Chimica Generale, Facoltà di Ingegneria, Università di Pisa, Via Diotisalvi 2, 56100 Pisa, Italy*

Synopsis

This paper describes the development of a mathematical model for the polymerization of isobutylene initiated with $\text{Et}_2\text{AlCl} + \text{Cl}_2$. Previous experiments have shown that this polymerization is "kinetically living." A computer analysis based on our mathematical model permits the calculation of the theoretical conversion-time curves, the molecular weight averages, and polydispersity. The good agreement between experimental and theoretical results suggests that the reaction mechanism proposed and the mathematical model derived are quite correct.

INTRODUCTION

The modeling of polymerization reaction has been fairly extensively described in the literature, and many reviews have appeared quite recently.¹⁻⁸

Most of the work has been developed for classical stepwise polycondensation reactions and for radical chain reactions. Very little work has appeared on ionic polymerization, especially for cationic polymerization where the steady-state approximation often cannot be applied.

In this series of publications some of the mathematical modeling procedures already described in the literature and some new procedures will be applied to cationic polymerization systems that we have extensively investigated in the past as far as kinetics and reaction mechanism are concerned.

For the polymerization of many vinyl-aromatic or oxygen-containing cyclic monomers we have been able to measure accurately the time-conversion curves, the time-conductivity curves, the molecular weight, and the molecular weight distribution of the polymers obtained in ionic processes initiated with various cationic catalysts (I_2 , $\text{BF}_3\text{Et}_2\text{O}$, AlCl_3 , $\text{Cl}_2 + \text{Et}_2\text{AlCl}$, etc.).⁹⁻¹⁶

Reaction mechanisms which well explain most of the features of these systems have been proposed, and according to them some kinetic models have been derived.¹⁷ The aim of this series of papers is the treatment of these kinetic models in order to derive, through mathematical or statistical methods, the theoretical time-conversion and time-conductivity curves as well as the theoretical molecular weight and molecular weight distribution which may be compared with the experimental ones.

The utility of this work is not only to check the validity to the model proposed, but even the possibility of modifying the experimental reaction conditions to obtain some special characteristics of the polymerization system or of the polymer product.

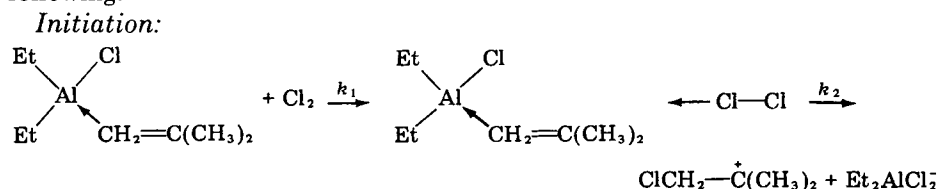
Finally this analysis will be quite useful in understanding the effect of reactor type on the characteristics of the polymer produced.

EXPERIMENTAL RESULTS

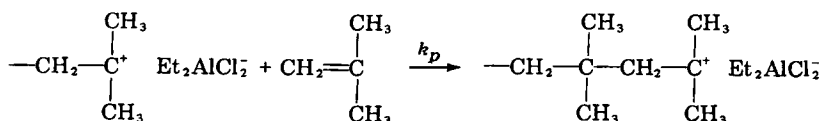
Previous experiments carried out in our laboratories^{9,10} have shown that the polymerization of isobutylene initiated with $\text{Et}_2\text{AlCl} + \text{Cl}_2$ is characterized by S-shaped curves for the variation both of the conductivity and of the conversion with time. Complete conversion is always achieved, and a second addition of monomer polymerizes completely without acceleration while the conductivity remains fairly constant during the polymerization.

Such polymerization presents kinetic characteristics similar to those belonging to "living polymerizations": further additions of monomer, in fact, polymerize completely at a speed which decreases only slightly along the series of subsequent monomer additions; transfer reaction with monomer is also absent.

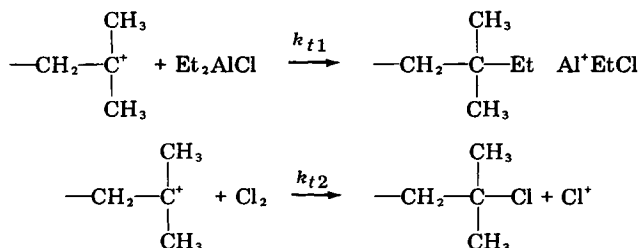
It has been demonstrated, however, that the molecular weight of the polymer obtained through the subsequent additions of monomer to the same system, increased only slightly with each successive addition. This indicated that the molecular weight of the polymer was regulated by transfer reactions with substances and concentrations of which are proportional mainly to the concentration of chlorine and aluminum compound. The reaction mechanism proposed is the following:



Propagation:



Transfer:



Starting from the analysis of the experimental results, obtained for the polymerization of isobutylene in CH_3Cl at -45°C , the reaction rate constants for the various elementary reactions have been obtained:

$$k_p = 8 \times 10^3 - 15 \times 10^3 \text{ L/mol}\cdot\text{s}$$

$$k_i \simeq 300 \text{ L/mol}\cdot\text{s}$$

$$k_{t1}/k_p \simeq 0.027$$

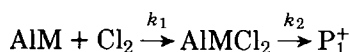
$$k_{t2}/k_p \simeq 0.33$$

MODEL DEVELOPMENT

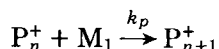
Mathematical Model

Starting from the kinetic reactions proposed above for this polymerization, we have developed a mathematical model, which will be used for the following purposes: check of the kinetic scheme proposed by a comparison between theoretical and experimental results; determination of more appropriate values of the rate constant of the elementary steps; optimization of the experimental reaction conditions in order to achieve some peculiar results as far as the characteristics of the polymer are concerned. The already proposed reaction scheme may be rewritten as follows:

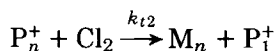
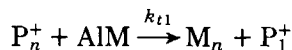
Initiation:



Propagation:



Transfer:



where $\text{AlM} + \text{Cl}_2$ represent the catalytic system, M_1 is the monomer (isobutylene), P_n^+ is the propagating species, and M_n is the dead polymer chain.

In order to obtain the average molecular weight and its distribution, it is important to calculate the moments of the molecular weight distribution both for the growing chains and for the dead polymer.

With this aim the generating functions of the distribution moments must be introduced:

$$G(s,t) = \sum_{n=1}^{\infty} s^n \text{P}_n^+(t) \quad \text{for the growing chains} \quad (1)$$

$$F(s,t) = \sum_{n=1}^{\infty} s^n (\text{P}_n^+(t) + \text{M}_n(t)) \quad \text{for the total polymer chains formed} \quad (2)$$

By the application of these definitions to the kinetic system proposed, the following transforms are obtained:

Rate of formation of the growing chain:

$$r_G = \sum_{n=1}^{\infty} s^n r_{\text{P}_n} = s(k_2 \text{AlMCl}_2 + (k_{t1} \text{AlM} + k_{t2} \text{Cl}_2)G(1,t)) - (k_p \text{M}_1(1-s) + (k_{t1} \text{AlM} + k_{t2} \text{Cl}_2))G(s,t) \quad (3)$$

Rate of formation of dead polymer chain:

$$r_M = \sum_{n=1}^{\infty} s^n r_{M_n}(t) = -s k_p M_1 G(1,t) + (k_{t1} AIM + k_{t2} Cl_2) G(s,t) \quad (4)$$

Rate of formation of the total polymer:

$$r_F = r_G + r_M = \sum_{n=1}^{\infty} s (k_2 AIM Cl_2 + (k_{t1} AIM + k_{t2} Cl_2) G(1,t) - k_p M_1 G(1,t)) + (s-1) k_p M_1 G(s,t) \quad (5)$$

By the use of the generating functions the moments of molecular weight distribution of j th order are obtained:

$$\lambda_j = \left(\frac{\partial^j G(s,t)}{\partial s^j} \right)_{s=1} \quad (6)$$

$$\epsilon_j = \left(\frac{\partial^j F(s,t)}{\partial s^j} \right)_{s=1} \quad (7)$$

The physical significance of each of the leading moments is very helpful in forming the modeling equations. The average molecular weights, the polydispersity, and the variance of the MW distribution can be determined from these moments without the use of partial differential equations.

The relevant equations are

$$\bar{M}_n = (\epsilon_1/\epsilon_0) W \quad (8)$$

$$\bar{M}_w/\bar{M}_n = \epsilon_2 \epsilon_0 / \epsilon_1^2 \quad (9)$$

$$\bar{M}_w = (\epsilon_2/\epsilon_1) W \quad (10)$$

$$\sigma^2 = \epsilon_2/\epsilon_0 - (\epsilon_1/\epsilon_0)^2 \quad (11)$$

Well-Stirred Batch Reactor

In order to apply the model to the reactor used for the polymerization experiments, the following material balances for a stirred batch reactor are derived:

$$\frac{dG(s,t)}{dt} = r_G \quad (12)$$

$$\frac{dF(s,t)}{dt} = r_F \quad (13)$$

By the use of eqs. (3) and (5) the desired moments of distribution are derived. By the use of eqs. (12) and (13) in a dimensionless form, a set of ordinary differential equations has been obtained and integrated with the Runge-Kutta method (at variable step) using a computer program in CSMP III.

This system of differential equations has been integrated with the following initial conditions:

$$\lambda_0 = 0, \quad \lambda_1 = 0, \quad \epsilon_0 = 1, \quad \epsilon_1 = 1, \quad \epsilon_2 = 0$$

By integrating these equations the following information is obtained: the conversion-time curve, the variation with reaction time of the following entities,

the concentration of the components of the catalytic system, the rate of polymerization, the number of both dead and living polymer chains, the number and weight average molecular weight, the polydispersity, and finally, by a successive data elaboration, the molecular weight distribution.

COMPARISON OF MODEL PREDICTIONS WITH EXPERIMENTAL DATA

The experimental data available for the polymerization of isobutylene at -45°C , in CH_3Cl solution and with $\text{Cl}_2 + \text{AlEt}_2\text{Cl}$ as catalytic system are the conversion-time curve, the conductivity-time curve, and the weight average molecular weight. The analysis of these experimental results allowed us to determine tentative values of the rate constants for the propagation, initiation, and transfer processes.

The computer analysis based on our mathematical model allowed us to determine: the theoretical conversion-time curve which can be compared with the experimental one; the theoretical curve relating the concentration of living chain carriers, which may be compared with the experimental conductivity-time curve if we assume that the only relevant contribution to the conductivity is due to the living cations; the theoretical weight average molecular weight, which can be compared with the experimental one.

The first use of this computer analysis has been to obtain more reliable values of the rate constants which follow:

$$k_p = 7500 \text{ L/mol}\cdot\text{s}$$

$$k_1 = 100 \text{ L/mol}\cdot\text{s}$$

$$k_2 = 0.05 \text{ s}^{-1}$$

$$k_{tr1} = 100 \text{ L/mol}\cdot\text{s}$$

$$k_{tr2} = 500 \text{ L/mol}\cdot\text{s}$$

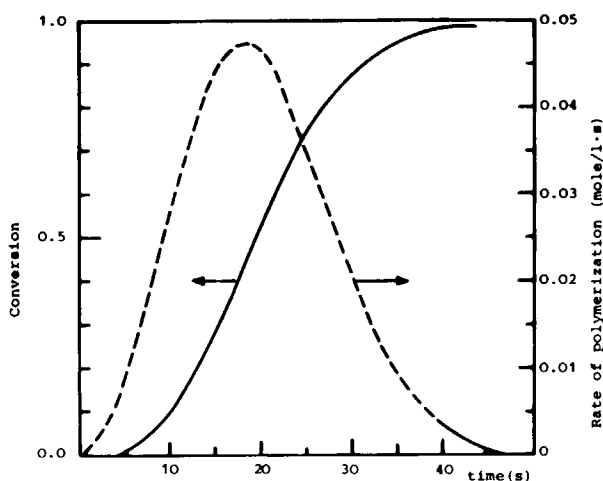


Fig. 1. Conversion-time and rate of polymerization-time curves $t = -45^{\circ}\text{C}$; $[\text{M}]_0 = 0.1 \text{ mol/L}$; $[\text{AlM}]_0 = 1.8 \times 10^{-4}$; $[\text{Cl}_2]_0 = 1.2 \times 10^{-4}$.

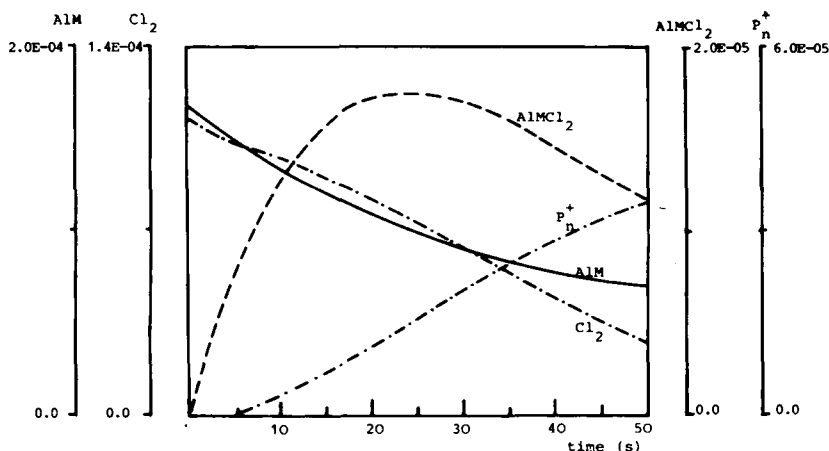


Fig. 2. Theoretical concentrations of the components of the catalytic system and of the active centers vs. time; relevant to the experimental conditions reported in Figure 1.

By the above-mentioned values of the rate constants, the conversion-time and velocity-time curves reported in Figure 1 are obtained. These curves clearly confirm the acceleration present in these polymerizations as the conversion-time curve is S-shaped and the velocity-time curve has a maximum.

In Figure 2 the predicted concentration of the components of the catalytic system and of the active centers vs. time are given. It is interesting to notice the typical behavior of consecutive reactions with a maximum of the intermediate species concentration and the S-shaped curve of the active centers concentration vs. time, which closely resembles the experimental conductivity-time curve.

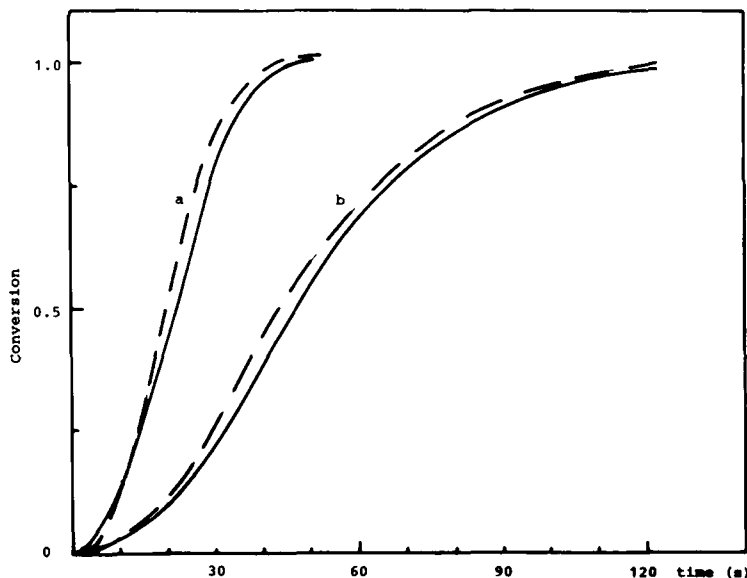


Fig. 3. Comparison of experimental and theoretical conversion-time curves obtained at -45°C : (—) experimental; (---) theoretical; (a) $[\text{M}]_0 = 0.1 \text{ mol/L}$; $[\text{AlM}]_0 = 1.8 \times 10^{-4} \text{ mol/L}$; $[\text{Cl}_2]_0 = 1.2 \times 10^{-4} \text{ mol/L}$; (b) $[\text{M}]_0 = 0.1 \text{ mol/L}$; $[\text{AlM}]_0 = 1.1 \times 10^{-3} \text{ mol/L}$; $[\text{Cl}_2]_0 = 5.0 \times 10^{-6} \text{ mol/L}$.

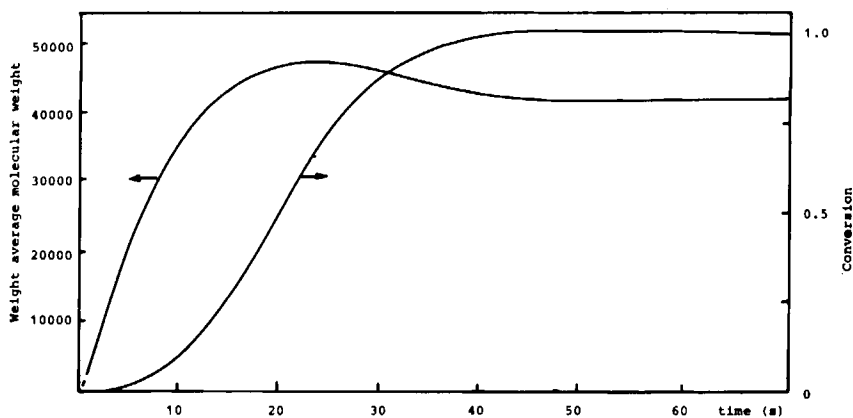


Fig. 4. Theoretical conversion-time and weight average molecular weight-time curves: $t = -45^{\circ}\text{C}$; $[\text{M}]_0 = 0.1 \text{ mol/L}$; $[\text{AlM}]_0 = 1.8 \times 10^{-4} \text{ mol/L}$; $[\text{Cl}_2]_0 = 1.2 \times 10^{-4} \text{ mol/L}$.

In Figure 3 the experimental conversion-time curves relevant to the polymerization of isobutylene in the presence of two different catalytic system concentrations are directly compared with the computed ones.

In Figure 4, the theoretical behavior of the weight average molecular weight value vs. time is given: It increases so rapidly that it gets to highest value at the same time with the inflection point of the conversion-time curve, and then it levels off to a slightly lower value.

A further comparison of the theoretical and experimental results for the weight average molecular weight is reported in Table I.

The nearly perfect coincidence between the theoretical and experimental conversion-time curves, the theoretical behaviors of the growing chains amount compared with the conductivity-time curves, as well as the good coincidence between the computed weight average molecular weight values and the experimental ones, prove that the proposed kinetic scheme and the selected mathematical model, derived therefrom, are correct.

The proposed kinetic constants values are reliable too; indeed, different values could have chosen to exactly match the theoretical and the experimental conversion-time curves, to great prejudice, however, of calculated weight average molecular weight values and vice versa.

TABLE I
Effect of Reaction Conditions on Weight Average Molecular Weight of the Polyisobutlenes
Obtained in the Presence of the Catalyst System $\text{AlEt}_2\text{Cl} + \text{Cl}_2$ at $t = -45^{\circ}\text{C}$

Run	$[\text{M}]_0$ (mol/L)	$[\text{AlEt}_2\text{Cl}]_0$ (mol/L)	$[\text{Cl}_2]_0$ (mol/L)	$\bar{M}_w \times 10^{-3}$ exptl	$\bar{M}_w \times 10^{-3}$ ^a theoret
1	0.1	1.8×10^{-4}	1.2×10^{-4}	42	44
2	0.1	1.1×10^{-3}	5.0×10^{-6}	150	150
3	0.1	3.1×10^{-3}	6.5×10^{-5}	45	41
4	0.2	3.1×10^{-3}	6.5×10^{-5}	86	76
5	0.4	3.1×10^{-3}	6.5×10^{-5}	160	140
6	0.6	3.1×10^{-3}	6.5×10^{-5}	224	250

^a These values have been determined and calculated at the highest conversions.

CONCLUSIONS

The agreement between the experimental results for the polyisobutylene polymerization by syncatalytic systems based on aluminum organic compounds and the theoretical results obtained by a computer analysis seems to suggest that the reaction mechanism proposed and the mathematical model derived are quite correct.

A further confirmation of the validity of the model proposed will be achieved if we are able to derive the theoretical molecular weight distribution and to compare it with the experimental distribution obtained by the gel permeation chromatography.

In this paper we have shown two kinds of utilization of the mathematical models; namely, (i) the control of the reaction mechanism proposed for this polymerization; (ii) the determination of more reliable values of the rate constants.

In a future publication we will show how the model proposed will be useful for the choice of the best experimental conditions in order to enhance the quasi-living character of this polymerization and to synthesize new block copolymers.

APPENDIX: NOMENCLATURE

AIM	Et ₂ AlCl
Cl ₂	chlorine
$F(s,t)$	generating function for the total polymer chains
$G(s,t)$	generating function for the growing chains
k_1, k_2	initiation rate constants
k_p	propagation rate constant
k_{t1}, k_{t2}	transfer rate constants
M ₁	monomer (isobutylene)
M _n	dead polymer
\bar{M}_n	numerical average molecular weight
\bar{M}_w	weight average molecular weight
λ_j	moment of j th order for the growing chains
ϵ_j	moment of j th order for the total polymer chains
P _n ⁺	propagating species
σ^2	variance of the molecular weight distribution

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