Complexation of the propagating chain-end in living cationic polymerization

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Summary

Kinetics of polymerization has been studied in the system isobutylene/dicumylmethylether/BCl_3 (CH_2Cl_2, $-80°C$) in the presence of dimethyl sulphoxide added as electron donor in a broad concentration range. The apparent propagation rate constant showed a DMSO concentration dependence typical for complex equilibria.

At a given DMSO concentration, the apparent rate constant decreases with increasing initial monomer concentration showing a seemingly zero-order propagation. A possible explanation of this phenomenon is the formation of a chain-end/monomer complex. Equilibrium and propagation rate constants have been determined.

Introduction

The living carbocationic polymerization of isobutylene (IB) [1,2] is a very important preparative method to obtain well defined polyisobutylenes (PIB). In our earlier work [3,4], to get insight into the mechanism of polymerization in general and of initiation in particular, we investigated the 1,3,5-tri-(2-methoxy-2-propyl)-benzene (TCME)/BCl_3/IB system in the presence and abscence of dimethyl sulphoxide (DMSO), a strong electron donor, to detect the complexes formed during the ion-generation step of the initiation. The B^{11} NMR investigations clearly show that between the TCME and BCl_3 an exchange reaction takes place (Scheme 1) yielding 1,3,5-tri-(2-chloro-2-propyl)-benzene and BCl_2OMe. Both BCl_3 and BCl_2OMe give molecular complexes with DMSO demonstrating their Lewis acidic

Scheme 1:

Ether/chloride exchange reaction
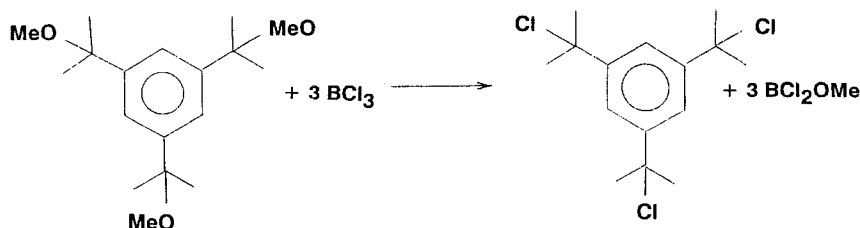
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character. However, we were not able to detect any ions or ionic complexes which are supposed to be involved in the cationation step of initiation. Based these results and on earlier observations about the addition of electron donors [5], we decided to study the effect of electron donors in detail. Another subject of this work is the study of the effect of monomer concentration on the apparent reaction order of propagation in living cationic polymerizations.

Experimental
Materials: The source and purity of materials, solvents used
      in this research have already been published [3].
Polymerization: The polymerizations were carried out under dry
      nitrogen atmosphere in a dry box. Both large culture
      tubes and 300 mL round bottom reaction flasks served as
      reactors.
Kinetic investigations:
   A.) Parallel experiments were run with the same
      reaction mixtures and the polymerizations were
      terminated by fast introduction of 2 mL precooled
      MeOH at a given time. From the reaction mixtures
      samples (a few mL) were taken out and injected
      into the injecting port of a gas chromatograph
      (GC) equipped with FID detector.
   B.) From the reaction mixture 1 mL samples were taken
      and transferred into a culture tube containing
      1 mL precooled MeOH at a given time. From the
      culture tube the GC investigation were carried
      out as described in paragraph A.
The instruments and methods of NMR and GPC investigations have been reported [3].

Results and Discussion
1. Effect of electron donor
The TCME has been proved to be a good initiator of living polymerization of isobutylene in the presence of BCl_3 [2]. The TCME/BCl_3/IB system yields quite broad molecular weight distributions (MWD) but in the presence of DMSO a significant MWD narrowig can be observed [5]. This initiating system seems to be a good model for kinetic investigations because by using it, undesirable side reactions and problems, e.g. indanyl-skeleton formation and slow initiation, can be avoided. In this work the progress of polymerization was monitored by GC, determining the concentration of the remaining monomer directly. To obtain information about the kinetics of polymerization, first we determined ard estimated values of the apparent rate constant of propagation (k_p^A) using the following equation:

$$k_p^A = \frac{1}{t} \ln \frac{M_o}{M} \qquad (1)$$

where   t = polymerization time
          M_o = starting monomer concentration
          M = actual monomer concentration at time t.

In a series of experiments, the M_O was kept constant and the DMSO concentration was varied in a very broad range. The k_p^A versus lg[DMSO] curve shows a characteristic shape (Fig.1) indicating complexation equilibria between the propagating chain-end and the DMSO or DMSO.BCl_3.
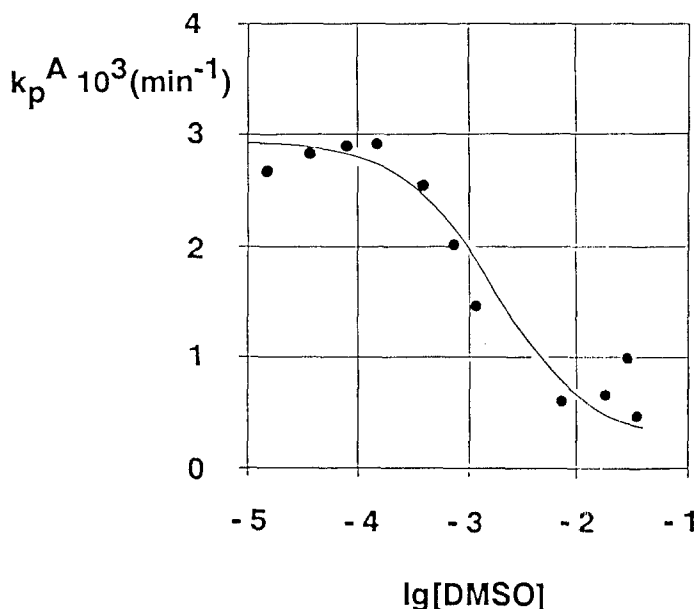

Figure 1
The effect of [DMSO] on apparent rate constant of polymerization. [[IB]=0.443 mole/L, [BCl_3]=0.05 mole/L, [TCME]=$5.4.10^{-3}$ mole/L, [DMSO]= varied, -30°C, AMI, 25 mL,30 mins, CH_2Cl_2. Analytical method: GC(FID).]
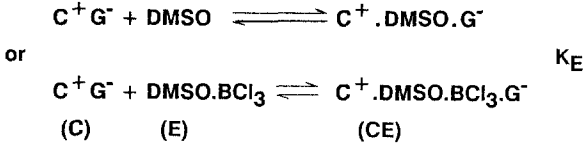
To describe the change of k_p^A with [DMSO] we proposed and found to be valid the kinetic model for the electron donor complexation shown in Scheme 2.
A computer curve fitting resulted in K_E = 560 L/mole, $k_{p,C}$ = 6.6 min^{-1} and $k_{p,CE}$ = 0.55 min^{-1} indicating that the complexed chain-end (CE) has a lower reactivity than the uncomplexed (C). The solid line in Fig.1 was calculated by using Eq. (2).
According to this model, the chain-end complexation gives rise to two propagating chains, C and CE. Indeed, the molecular weight distribution (MWD) of PIB-s prepared from the polymerization mixtures proved to be higly affected by [DMSO] (Fig.2). At low DMSO concentrations the MWD is slightly broad but unimodal, while at medium [DMSO] it gets broader and bimodal clearly showing the coexistence of two propagation chains. At high DMSO concentrations the MWD is narrow and unimodal.
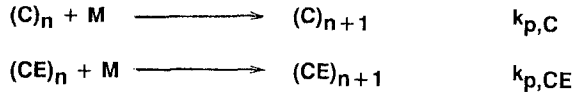
Scheme 2:

Model for electron donor complexation

Complexation equilibria:

$$C^+G^- + DMSO \rightleftharpoons C^+.DMSO.G^-$$

or $$K_E$$

$$C^+G^- + DMSO.BCl_3 \rightleftharpoons C^+.DMSO.BCl_3.G^-$$

(C)   (E)   (CE)

Propagation:

$$(C)_n + M \longrightarrow (C)_{n+1} \qquad k_{p,C}$$

$$(CE)_n + M \longrightarrow (CE)_{n+1} \qquad k_{p,CE}$$

Propagating center concentrations:

$$\alpha = 1/(1 + K_E \cdot E)$$
$$C = \alpha \cdot I_0$$
$$CE = (1-\alpha) \cdot I_0$$

Apparent rate constant:

$$k_p^A = k_{p,C} \cdot C + k_{p,CE} \cdot CE =$$
$$= (k_{p,C} + k_{p,CE} \cdot K_E \cdot E) \cdot I_0 /(1 + K_E \cdot E) \qquad (2)$$

Thus, to prepare PIB-s with narrow MWD we have to add a certain ammount of electron donor to complex the propagating chain-end, i.e., to reduce its reactivity (its hardeness [6]), to filter out side reactions.
From the K_E value obtained, the distributions of C and CE can be calculated:

$$C/I_0 = \frac{1}{1 + K_E[DMSO]} \qquad (3)$$

$$CE/I_0 = \frac{K_E[DMSO]}{1 + K_E[DMSO]} \qquad (4)$$

where C/I_0 an CE/I_0 are the molar fraction of the uncomplexed and complexed chain-ends, respectively (Fig. 3). Fig.3 shows that close to 100 % complexation can be achieved around [DMSO] ≈ 0.1 mole/L. This value is, however, higher than the concentration of BCl_3, and can not be used because the BCl_3:DMSO = 1:1 complex immediately precipitates from the solution and the polymerization stops.
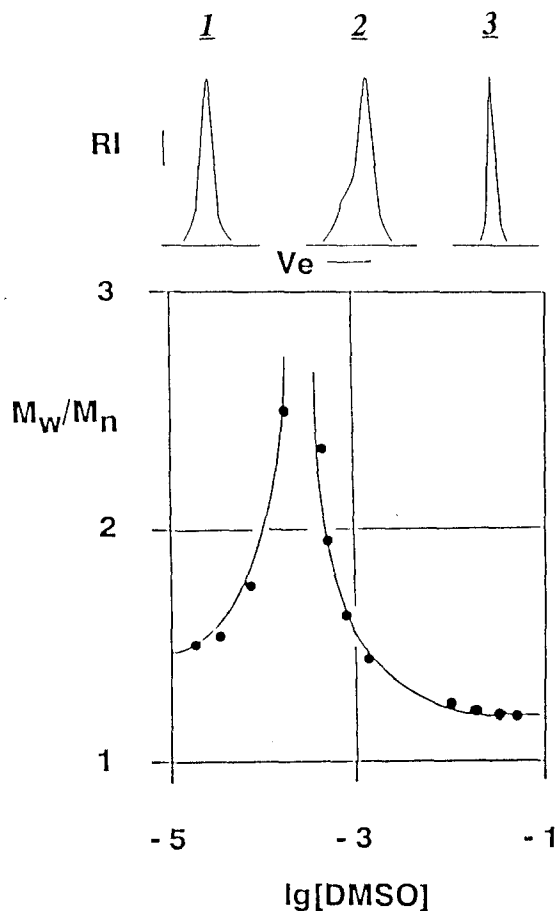
Figure 2
Dependence of M_w/M_n on [DMSO]. (Experimental details see with
Fig.1.) 1 lg[DMSO]=4.81, 2 lg[DMSO]=-3.42, 3 lg[DMSO]=-1.42

On the other hand, our experiments give an orientation: if the
DMSO concentration approximately equals to the chain-end
concentration ([DMSO]) $\approx 3 \times [I_0]$) then the extent of complexa-
tion is about 94 % and the MWD is sufficiently narrow.

2. *Effect of monomer concentration*
The use of the IMA and AMI methods (1) to investigate the
livingness of polymerization frequently leads to controver-
sial data [7], i.e., the monomer consumption seems to be zero
order in IMA experiments (if the conversion in an IMA step is
less than 100 %, the monomer accumulates but the rate does not
increase), but first order in AMI experiments [the $\ln(M_0/M)$
versus t plots are linear]. In order to analyze the role of
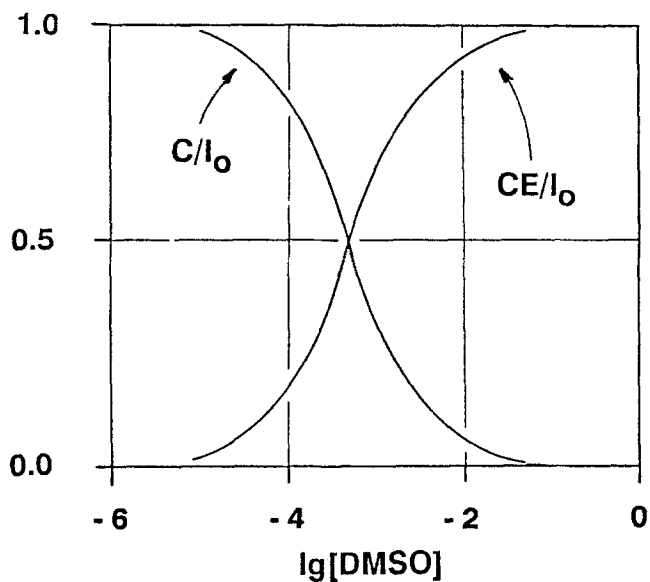monomer concentration, we investigated the kinetics of poly-

Figure 3
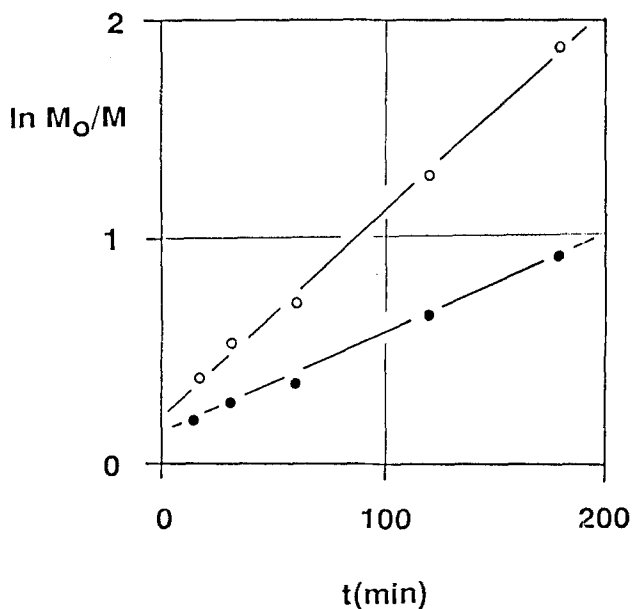Molar fractions of C/I_O and CE/I_O (K_E = 560 L/mole)

t(min)

Figure 4.
First order plots of isobutylene polymerization.
[[IB] = varied, [BCl$_3$] = 0.05 mole/L, [TCME] = 5.4.10^{-3}
mole/L, [DMSO] = 1.6.10^{-2} mole/L, -30°C, AMI, 200 mL, sample
volume 1 mL, CH$_2$Cl$_2$. Analytical method: GC (FID)]
- o - o - M_O = 0.135 mole/L, - o - o - M_O = 0.449 mole/L

merization at constant $[DMSO] \approx 3 \times [I_o]$, and varied the M_o in AMI experiments. If we plot $\ln(M_o/M)$ as a function of t, we obtained straight lines as expected, indicating that the rate of propagation is first order in monomer (Fig.4). The presence of the small intercepts can be explained by the fact that during the addition of BCl_3 to the isobutylene/DMSO/CH_2Cl_2/TCME mixtures a significant heat evolvement takes place. The apparent rate constants (k_p^A) have been obtained from the slope of the straight lines. Plotting $1/k_p^A$ versus M_o, we obtained a straight line (Fig.5) indicating that the k_p^A decreases with increasing M_o., i.e.,
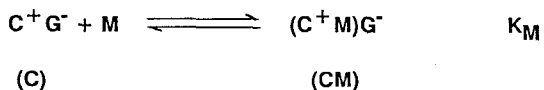
$$1/k_p^A = A + BM_o \tag{5}$$

and

$$k_p^A = \frac{1/A}{1 + (B/A)M_o} \tag{6}$$

This inverse relationship provides an empirical explanation for the apparent zero order monomer consumption reported in several publications [7,8], i.e., the higher the monomer concentration the smaller the k_p^A.
This effect cannot be interpreted by the complexation of the monomer with the Lewis acid as suggested by others [8]. However, the proposition of Plesch [9], i.e., the assumption of a non-propagating complex of the chain-end and the monomer (Scheme 3) gives a possible explanation. According to this model, the monomer inserts between the carbocation and the gegenion in a sterically unfavorable way, forming an inactive
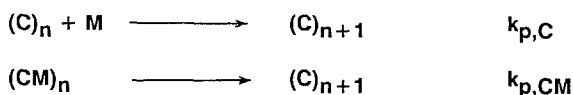
Scheme 3:

Model for monomer complexation

Complexation equilibrium:

$$C^+G^- + M \rightleftharpoons (C^+M)G^- \qquad K_M$$

$$(C) \qquad\qquad (CM)$$

Propagation:

$$(C)_n + M \longrightarrow (C)_{n+1} \qquad k_{p,C}$$

$$(CM)_n \longrightarrow (C)_{n+1} \qquad k_{p,CM}$$

Propagating center concentration:

$$C = I_o/(1 + K_M \cdot M) \quad \text{and} \quad CM = K_M \cdot M \cdot I_o/(1 + K_M \cdot M)$$

Apparent rate constant:

$$\text{Rate} = k_{p,C} \cdot C \cdot M + k_{p,CM} \cdot CM = k_p^A \cdot M$$

$$k_p^A = (k_{p,C} + k_{p,CM} \cdot K_M) \cdot I_o/(1 + K_M \cdot M) \tag{7}$$

π-complex with the propagating chain-end.
To the contrary, active monomer-complexed chain-end was proposed by Fontana and Kidder [10]. However, this cannot be kinetically distinguished from Plesch's proposition (Scheme 3 includes both possibilities).
Application of Eq.(7) [equivalent with Eq.(6)] to the experimental data provides $K_M = 6.4$ L/mole and $k_{p,C} + k_{p,CM} \cdot K_M = 3.9$ min^{-1}.
Similar dependence of the average k_p^A on the monomer concentration have been obtained in isobutylene/styrene random copolymerization experiments [10].
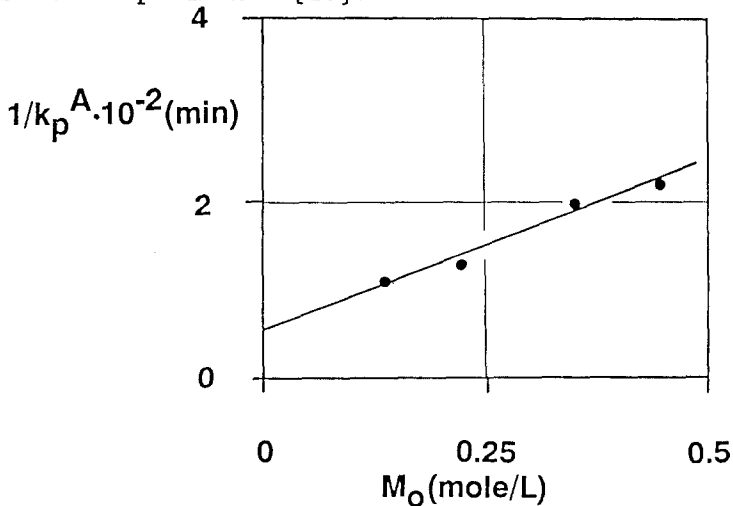

Figure 5
$1/k_p^A$ versus M_O.plot (For details see Fig.4.)

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