

GROUP TRANSFER POLYMERIZATION OF ETHYL ACRYLATE WITH LEWIS ACID CATALYST

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ABSTRACT

This paper reports the kinetics of group transfer polymerization (GTP) of ethyl acrylate (EA) with zinc iodide catalyst in 1,2-dichloroethane using dimethyl ketene methyl trimethylsilyl acetal (MTS) as initiator at 0 °C and above 0 °C. The amount of catalyst used was studied. When zinc iodide catalyst used is more than 10 mol% relative to monomer, the rate of polymerization is proportional to the concentration of monomer, whereas zinc iodide catalyst used is less than 10 mol% of the monomer, the rate of polymerization is independent of the monomer concentration.

In the GTP of EA an induction period was observed when the zinc iodide contents are less than 10 mol%. If the reaction temperature is over 0 °C, living species become unstable and diminish, leading to incomplete monomer conversion. The reaction curves equations are obtained. The polymers have narrow molecular weight distributions which are not changed as decreasing zinc iodide contents. The polydispersity is about 1.2.

INTRODUCTION

In 1983 Du Pont reported a new type of living polymerization, termed group transfer polymerization (GTP)^[1]. Polar monomer, especially acrylate and methacrylate may be polymerized by using ketene silyl acetals as initiators at ambient temperature in the presence of anion catalysts (e.g. HF_2^- , CN^- , F^- , N_2^-) or Lewis acid catalysts to living polymers with controlled molecular weights and end group configurations^[2-5]. According to a report^[6], zinc halide catalyst should be present at levels of about 10 — 20 mol% of monomer in order to achieve complete conversions of acrylates. Müller^[7] reported the kinetics of GTP to MMA in THF by TASHF_2 catalyst. But the kinetics of polymerization by zinc halide catalysts has not been demonstrated yet. This paper presents the kinetics of polymerization of ethyl acrylate (EA) with zinc iodide catalyst in 1,2-dichloroethane with dimethyl ketene methyl trimethyl silyl acetal (MTS) as initiator at 0 °C and above 0 °C. The amount of catalyst used was investigated and the influence of reaction temperature on polymerization discussed.

EXPERIMENTAL PART

1. Synthesis of dimethylketene methyl trimethylsilyl acetal (MTS)

MTS was prepared according to Ainsworth^[8], from α -anions of acetates and trimethylchlorosilane (TMCS) with lithium diisopropylamide. Methyl isobutyrate was added at 0 °C followed by the addition of TMCS. The products were obtained by

distillation and stored in ampules at room temperature.

bp. 51 °C /17mm, n_D^{20} 1.4135

Anal. Calcd: C 55.12%, H 10.41%.

Found: C 55.02%, H 10.44%.

The product was confirmed by ^1H NMR and Infrared spectrum.

2. Polymerization

1,2-dichloroethane (analytical grade) was dried over 4 Å molecular sieves and calcium hydride for several days and then distilled. Ethyl acrylate was dried over 4 Å molecular sieves 2 days, and distilled under dry N_2 by vacuum distillation and stored over calcium hydride in refrigerator. The pure nitrogen used was dried by passing through two 80 cm long columns of silica-gel drier and two 80 cm long columns of 4 Å molecular sieves.

All glassware and syringes were dried at 120 ° — 130 °C at least 24 hours before use.

The ZnI_2 catalyst was heated to 300 °C in vacuo for 30 min and then allowed to cool under dry nitrogen before use.

Polymerizations were carried out in rigorously cleaned and dried glass reaction flasks with a magnetic stirrer under dry nitrogen using syringe techniques for introduction of initiator.

At different time intervals during polymerization aliquots were taken and analysed for the determination of unreacted monomer concentration by pyridine sulfate dibromide method^[9].

After the reaction completed a few amount of methyl alcohol was added to terminate the reaction, the reaction mixtures were washed with water several times to remove ZnI_2 , then dried, filtered, concentrated and cooled. By adding petroleum ether the products were precipitated.

3. Molecular weights

Molecular weights and molecular weight distributions were measured by GPC with THF as eluent at 30 °C. The column set was calibrated with polystyrene standard (from E. Merck, Darmstadt, F. R. Germany).

RESULTS AND DISCUSSION

1. Influence of amount of catalyst used on GTP of EA

According to the report^[6] zinc halide catalyst should be present at levels of about 10 — 20 mol% relative to monomer to achieve complete conversions of acrylates. In our studies MTS was used as initiator, the polymerization of ethyl acrylate was performed in 1,2-dichloroethane solvent at 0 °C in the presence of ZnI_2 catalyst.

When ZnI_2 catalyst used was more than 10 mol% of EA, ZnI_2 catalyst was dissolved thoroughly and homogeneous systems were obtained. Curve 1 and curve 2 in Fig. 1 show the relationship of monomer concentration $[M]$ with reaction time at 0 °C and the plots of $-\ln [M]$ against t show the linear relationship as shown in Fig. 2. It clearly indicates that the polymerization rate is the first order with respect to concentration of monomer, the kinetic rate equation may be written as

$$-\frac{d[M]}{dt} = K_x [M] \quad (1)$$

where $[M]$ is the concentration of EA, K_x is the rate constant of polymerization at $[ZnI_2] > 10$ mol% of EA, $K_x = 0.089$ (min^{-1}) and 0.079 (min^{-1}) obtained from curve 1 and curve 2 in Fig. 2 respectively.

When ZnI_2 catalyst used was less than 10 mol% of EA at 0°C the dependence of EA concentration on reaction time was measured as shown in Fig. 1 curve 3. It can be seen that GTP of EA has also a complete conversion in this condition. It is interesting that the rate of polymerization is independent of monomer concentration, the kinetic equation may be described as

$$-\frac{d[M]}{dt} = K'_x \quad (2)$$

where K'_x is the rate constant at $[ZnI_2] < 10$ mol% of EA, $K'_x = 0.014$ ($\text{mol} \cdot \text{Kg}^{-1} \cdot \text{min}^{-1}$) or $K'_x = 0.016$ ($\text{mol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$) obtained from curve 3 in Fig. 1.

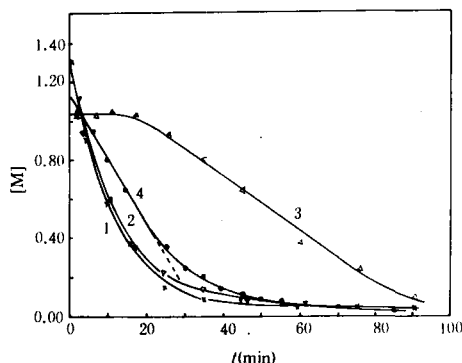


Fig. 1 Relationship of EA concentration with reaction time t at 0°C

Curve 1	×	[MTS]	9.9×10^{-3} mol/kg,	[ZnI ₂]	0.20 mol/kg.
Curve 2	∇	[MTS]	10.0×10^{-3} mol/kg,	[ZnI ₂]	0.10 mol/kg.
Curve 3	Δ	[MTS]	10.5×10^{-3} mol/kg,	[ZnI ₂]	0.028 mol/kg.
Curve 4	●	[MTS]	10.3×10^{-3} mol/kg,	[ZnI ₂]	0.056 mol/kg.

The kinetics of polymerization of EA was also studied for the system with the amount of ZnI_2 between the above two experiments. The relationships of monomer concentration and $-\ln[M]$ with time are shown in Fig. 1 curve 4 and Fig. 2 curve 3 respectively. It can be found obviously that the reaction order changes from zero order to first order with respect to monomer concentration. At zero order the rate constant K'_x is 0.033 ($\text{mol} \cdot \text{Kg}^{-1} \cdot \text{min}^{-1}$) or 0.039 ($\text{mol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$) and at first order the rate constant K_x is 0.058 (min^{-1}). The turning point represents the following relations:

$$-\frac{d[M]}{dt} = K'_x = K_x [M]_{\text{turn}} \quad (3)$$

Replacing (3) with K_x and K'_x , we obtain

$$[M]_{\text{tum}} = 0.57 (\text{mol} \cdot \text{Kg}^{-1})$$

Hence ZnI_2 concentration is:

$$\frac{[\text{ZnI}_2]}{[M]_{\text{tum}}} \times 100\% = 9.8\%$$

i.e. at the turning point the concentration of ZnI_2 is 9.8 mol% of EA. This value is in agreement with the value "10 mol% of monomer" reported by Du Pont.

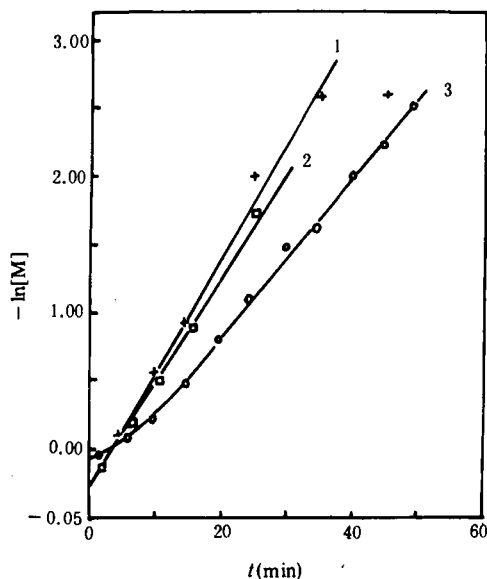


Fig. 2 - $-\ln [M]$ versus reaction time t

- Curve 1 + the same as curve 1 in Fig. 1
 Curve 2 □ the same as curve 2 in Fig. 1
 Curve 3 ○ the same as curve 4 in Fig. 1

In addition, the above three experimental results indicate that there are different induction periods with different amount of ZnI_2 used. There is no induction period in the system of $[\text{ZnI}_2] > 10$ mol% of EA (see Fig. 1 curve 1 and curve 2). However an apparent induction period was observed in the system of $[\text{ZnI}_2] < 10$ mol% of EA in which the induction period is as 17 min long (see Fig. 1 curve 3), and with the amount of ZnI_2 between above two experiments the induction period of reaction was hard to be observed (see Fig. 1 curve 4).

2. GTP of EA with ZnI_2 catalyst above 0°C

All the above experiments were performed at 0°C and below 0°C . If the reaction temperature is raised above 0°C , complete conversions of EA can not be achieved. For reactions with $[\text{ZnI}_2]$ more than 10 mol% of EA, the dependence of $[M]$ on reaction time at 17.5°C is shown in Fig. 3-a, the conversion of EA was only about 75%. Fig. 3-b shows the relationship between $-\ln [M]$ and time, the rate constant K_x (slope of curve) decreases with time and approaches zero.

We consider that these phenomena are due to living species which become unstable and diminish when the reaction temperature is raised above 0°C , leading to the incomplete monomer conversion.

Assuming that the diminishing rates of living species are proportional to their concentrations

$$-\frac{d[P^*]}{dt} = k_a[P^*] \quad (4)$$

where $[P^*]$ represents the concentration of living species, k_a is the diminishing rate constant. Integration of equation (4) gives

$$[P^*] = [P^*]_0 e^{-k_a t} \quad (5)$$

where $[P^*]_0$ represents the initial concentration of living species (i.e. initiator concentration). Equation (1) may also be written as follows:

$$-\frac{d[M]}{dt} = k[P^*]^n[M] \quad (6)$$

where k is the rate constant, n is a constant.

Replacing $[P^*]$ in (6) with (5) gives

$$-\frac{d[M]}{dt} = k[P^*]_0^n e^{-nk_a t} [M] \quad (7)$$

Integration of (7) leads to

$$\ln \frac{[M]_0}{[M]} = \frac{k[P^*]_0^n}{nk_a} (1 - e^{-nk_a t}) \quad (8)$$

Simplification of (8) gives

$$\ln \frac{[M]_0}{[M]} = A (1 - e^{-k_1 t}) \quad (9)$$

$A = \frac{k[P^*]_0^n}{nk_a}$, $k_1 = nk_a$, therefore the reaction equation may be described as formula

(9) at $[ZnI_2] > 10$ mol% of EA and above $0^\circ C$, where $[M]_0$ and $[M]$ are the monomer concentration at zero time and at t time respectively. From Fig.3-b $A=1.33$, $k=0.063$ are obtained, this reaction curve can be described by

$$\ln \frac{[M]_0}{[M]} = 1.33 (1 - e^{-0.063 t})$$

When $[ZnI_2]$ used is less than 10 mol% of EA, the reaction curve at $17^\circ C$ is shown as Fig. 4. After 90 min the conversion of EA did not increase and could not reach 100%. The kinetic equation may be written as follows:

$$-\frac{d[M]}{dt} = k'[P^*]^n \quad (10)$$

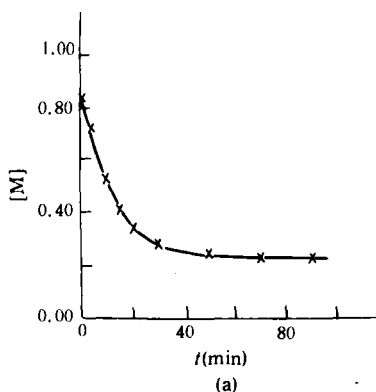


Fig. 3-a Relationship of EA concentration with reaction time. 17.5 °C
 $[\text{ZnI}_2] : 0.20 \text{ mol} \cdot \text{Kg}^{-1}$ (>10% EA)
 $[\text{MTS}] : 5.0 \times 10^{-3} \text{ mol} \cdot \text{Kg}^{-1}$

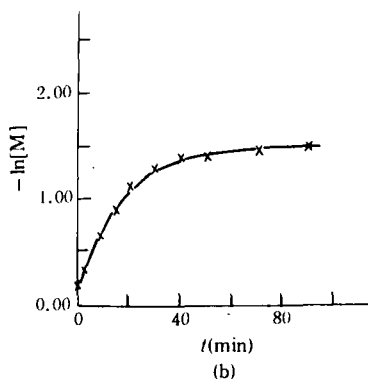


Fig. 3-b $-\ln[M]$ versus reaction time.
 × experimental points
 Curve is given by equation
 $\ln \frac{[M]_0}{[M]} = 1.33 (1 - e^{-0.063t})$ based on experimental data.

Replacing (10) with (5) gives

$$-\frac{d[M]}{dt} = k' [P]_0^n e^{-nk_\alpha t} \quad (11)$$

Integrate (11)

$$[M]_0 - [M] = \frac{k' [P]_0^n}{nk_\alpha} (1 - e^{-nk_\alpha t}) \quad (12)$$

Simplify (12)

$$[M]_0 - [M] = A' (1 - e^{-k' t}) \quad (13)$$

therefore the kinetic equation may be described as formula (13) at $[\text{ZnI}_2] < 10 \text{ mol}\%$ of EA and above 0 °C. $A' = 0.83$, $k' = 0.038$ are obtained from Fig. 4. The reaction curve can be represented by

$$[M]_0 - [M] = 0.83 (1 - e^{-0.038t})$$

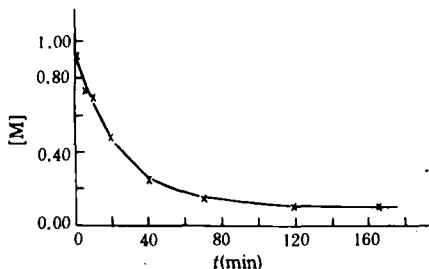


Fig. 4 Relationship of EA concentration with reaction time. 17 °C
 $[\text{ZnI}_2] : 0.026 \text{ mol} \cdot \text{Kg}^{-1}$ (<10mol% EA)
 $[\text{MTS}] : 6.3 \times 10^{-3} \text{ mol} \cdot \text{Kg}^{-1}$
 × experimental points
 The curve is given by $[M]_0 - [M] = 0.83 (1 - e^{-0.038t})$ based on experimental data.

If the amount of ZnI_2 was reduced again to make the performance in the same condition, the inductive period appeared.

3. Molecular weight and molecular weight distribution

The molecular weight and molecular weight distribution of poly-ethylacrylate prepared by GTP with ZnI_2 catalyst are listed in Table 1. The polymers have narrow molecular weight distributions which are not changed with the variation of the concentration of ZnI_2 used from $0.20 \text{ mol} \cdot \text{Kg}^{-1}$

to $0.028 \text{ mol} \cdot \text{Kg}^{-1}$. The polydispersity is about 1.2.

Table 1 Molecular weight and molecular weight distribution of polyethylacrylate

No.	1	6	3	4
$[\text{ZnI}_2] \text{ (mol} \cdot \text{Kg}^{-1}\text{)}$	0.20	0.10	0.056	0.028
$[\text{MTS}] \text{ (mol} \cdot \text{Kg}^{-1}\text{)}$	10×10^{-3}	10×10^{-3}	10×10^{-3}	10×10^{-3}
$\Delta [\text{M}] \text{ (mol} \cdot \text{Kg}^{-1}\text{)}$	1.23	1.00	1.04	0.99
$\text{Mn} \text{ (g} \cdot \text{mol}^{-1}\text{)}$	1.1×10^4	1.12×10^4	1.11×10^4	1.12×10^4
D	1.18	1.25	1.17	1.24
$\text{M}_{\text{theory}} \text{ (g} \cdot \text{mol}^{-1}\text{)}$	1.23×10^4	1.00×10^4	1.04×10^4	0.99×10^4

Note: $\Delta [\text{M}]$ is the concentration of reacted monomer.

D is the molecular weight distribution.

Keywords:

Group Transfer Polymerization, Living Polymerization, Polyethyl acrylate, Lewis acid catalyst.

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