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# The synthesis of chlorine-terminated telechelic polyisobutylene
## II. Investigation of the chain transfer reaction

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Abstract

This paper deals with chain transfer reactions, primarily to monomer and to inifer (p-DCC/$BCl_3$) in the carbocationic polymerization of isobutylene (IB). It is found that the MW and functionality of the polymer depend very much upon chain transfer to inifer. $Ctr,_I$, $Ctr,_M$, $Ctr,_S$, in $CH_2Cl_2$ are calculated; they are 1.09(-40℃), negligible, and $5.6\times10^{4}$(-40℃) respectively.

## Introduction

In conventional cationic polymerization of isobutylene, chain transfer to monomer usually determines MW and MWD, and very often extremely low temperatures are required to obtain commercially useful polymers. In contrast, inifer systems first proposed by Kennedy functioning both as initiator and chain transfer agent [1] can play predominant role in determining MW, MWD of the polymer and introduce functional groups at both ends of the polymers forming telechelic products at relatively high temperature. Kennedy and coworkers also reported that chain transfer to isobutylene in polar media such as $CH_2Cl_2$ and $CH_3Cl$ with a p-DCC/$BCl_3$ inifer system was insignificant, and that chain transfer to initiator was almost unaffected by the temperature [2, 3]. These are somewhat in contradiction to conventional situations, thus a systematic investigation was carried out to verify the inifer concept.

## Experimental

The purification and synthesis of reagents, and the chlorine terminated telechelic polyisobutylene have been described in the previous paper of this series.

## Results and Discussion

### 1. Chain transfer to isobutylene [IB]

The effect of [IB] on $\overline{Mn}$ of the polymer is listed in Table I.

Assuming $[\overline{IB}]=\{[IB]_0-[IB]\}/\{\ln([IB]_0/[IB])\}$ [3] and $[I]=[I]_0/2$, since the binifer is used, $1/\overline{DP}=k_t/kp[\overline{IB}]+k_{tr,m}/kp+k_{tr,I}[I]/kp[\overline{IB}]$. If we keep all variables except $[\overline{IB}]$ constant and by plotting $1/\overline{DP}n$ vs. $1/[\overline{IB}]$, We obtain Ctr,m=$3.36\times10^{-4}$ in pure $CH_2Cl_2$ at -40℃. This value suggests insignificant chain transfer to monomer under given condtions.

Table I. The effect of [IB] on $\overline{Mn}$ of the polymer

| $[IB]_0$M | conv. C(%) | Mn | $1/[IB]M^{-1}$ | $1/DPn\times10^3$ |
|---|---|---|---|---|
| 0.7 | 73.0 | 3950 | 2.56 | 14.2 |
| 1.1 | 70.1 | 5940 | 1.56 | 9.43 |
| 1.5 | 74.6 | 8430 | 1.22 | 6.64 |
| 1.9 | 72.0 | 10400 | 0.93 | 5.38 |

[p-DCC]=$8.8\times10^{-3}$M, $[BCl_3]$=0.1M, -40℃, $CH_2Cl_2$, 20 min.
Correlation coeffieient r=0.99

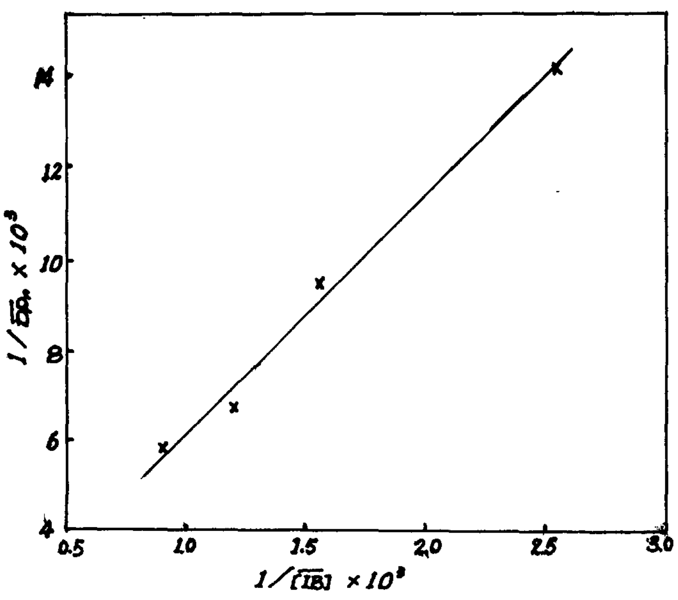



Fig. I Plot of $1/\overline{DP}n$ vs. $1/[\overline{IB}]$

2. The effect of temperature on $C_{tr,I}$

Kennedy and coworker showed insignificant temperature effect on $C_{tr,I}$. in the range -40℃～-70℃ [3].

Assuming Ctr.m can be neglected as mentioned above we plot 2× [IB]/$\overline{DP}$n against [I]$_o$/2. The results are given in Table II through V. in the temperature range of -10～-50℃ in $CH_2Cl_2$/n-$C_6H_{14}$ 70/30 (v/v).

It is seen that a set of straight lines are drawn as shown in Fig.II. From the slopes of these lines, the Ctr,I values at defferent temperature are obtained.

Table II. The effect of [p-DCC] on PIB Mn at -10℃

| $[I]_o/2\times10^3$M | Mn$\times10^{-4}$ | C(%)(conv.) | $2[M]/\overline{DP}n\times10^3$ |
|---|---|---|---|
| 9.5 | 0.56 | 44.5 | 19.2 |
| 7.65 | 0.69 | 38.1 | 16.0 |
| 4.75 | 0.91 | 33.7 | 12.8 |
| 2.4 | 1.39 | 16.9 | 9.3 |
| 0.475 | 1.86 | 5.8 | 7.47 |

$[IB]_o$=1.27M, $[BCl_3]_o=8.2\times10^{-2}$M, $CH_2Cl_2$n-$C_6H_{14}$ 70/30(v/v), 10 min.
Correlation coefficient r=0.998

Table III. The effect of [p-DCC] on PIB $\overline{Mn}$ at -30℃

| $[I]_o/2\times10^3$M | Mn$\times10^{-4}$ | C(%)(conv.) | $2[M]/\overline{DP}n\times10^3$ |
|---|---|---|---|
| 9.5 | 0.69 | 58.4 | 9.41 |
| 7.65 | 0.92 | 52.2 | 7.48 |
| 4.75 | 1.12 | 38.8 | 6.87 |
| 2.4 | 1.59 | 30.75 | 5.13 |
| 0.475 | 2.33 | 6.1 | 4.05 |

$[IB]_o$=0.87M, $[BCl_3]_o=9\times10^{-2}$M, $CH_2Cl_2$/n-$C_6H_{14}$ 70/30 (v/v), 10min.
Correlation coefficient r=0.983

Table IV. The effect of [p-DCC] on PIB Mn at -40℃

| $[I]_o/2\times10^{3}$M | $Mn\times10^{-4}$ | C(%)(conv.) | $2[\bar{M}]/\overline{DP}n\times10^{3}$ |
|---|---|---|---|
| 7.65 | 1.06 | 60.2 | 5.45 |
| 4.75 | 1.40 | 57.7 | 4.24 |
| 2.4 | 1.83 | 41.85 | 3.73 |
| 0.48 | 2.92 | 21 | 2.70 |

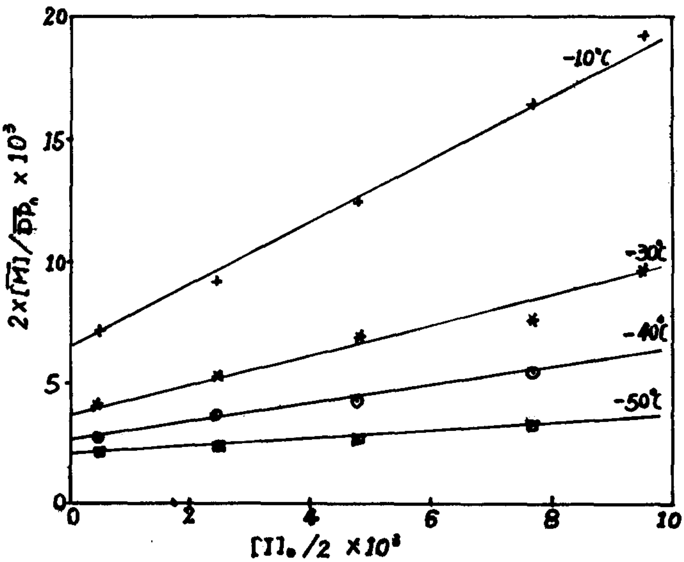
$[IB]_o$=0.79M, $[BCl_3]_o=8.5\times10^{-2}$M, $CH_2Cl_2/n\text{-}C_6H_{14}$ 70-/30 v/v, 10min.
Correlation coefficient r=0.989

Table V. The effect of [p-DCC] on PIB Mn at -50℃

| $[I]_o/2\times10^{3}$M | $Mn\times10^{-4}$ | C(%)(conv.) | $2[\bar{M}]/\overline{DP}n\times10^{3}$ |
|---|---|---|---|
| 7.65 | 1.02 | 85.1 | 3.14 |
| 4.75 | 1.33 | 81.4 | 2.61 |
| 2.4 | 1.75 | 71.5 | 2.33 |
| 0.475 | 2.94 | 21.8 | 2.16 |

$[IB]_o$=0.64M, $[BCl_3]_o=9\times10^{-2}$M, $CH_2Cl_2/n\text{-}C_6H_{14}$ 70-/30 v/v, 10min.
Correlation coefficient r=0.989

Fig. II Plot of $2[\bar{M}]/\overline{DP}n$ vs. $[I]_o/2$



Since $C_{tr,I}=k_{tr,I}/k_p$ and both $k_{tr,I}$ and $k_p$ are functions of temperature, so it is logical that $C_{tr,I}$ could also be described by the Arrhenius equation $C_{tr,I}=A\cdot\exp(\triangle E/RT)$ and $\ln C_{tr,I}=\ln A-[E_{tr,I}-E_p]/RT$. By plotting $\ln C_{tr,I}$ vs. $1/T$ (Fig. Ⅲ), we obtain $\triangle E=E_{tr,I}-E_p=26$ KJ/mole. From these data, it is seen that temperature also has considerable effect upon $C_{tr,I}$ under given conditions .

Table VI. the Effect of temperature on $C_{tr,I}$

| T | $C_{tr,I}$ |
|---|---|
| -10 | 1.32 |
| -30 | 0.47 |
| -40 | 0.37 |
| -50 | 0.14 |

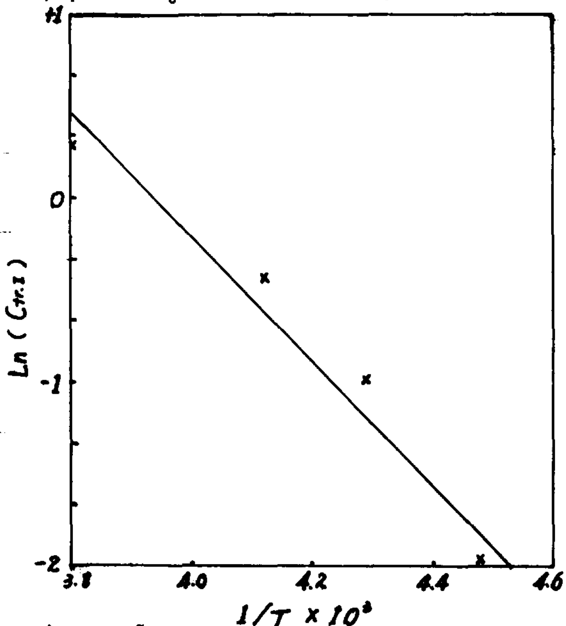



Fig. Ⅲ Polt of $\ln C_{tr,I}$ vs. $1/T$

3. The effect of medium polarity on $C_{tr,I}$.

The change of medium polarity was achieved by mixing $CH_2Cl_2$ and n-hexane in different proportions. The apparent effect may be due to both the effect of medium polarity and chain transfer to $CH_2Cl_2$.

Table Ⅶ The effect of [p-DCC] on $\overline{Mn}$ in $CH_2Cl_2/n\text{-}C_6H_{14}=80/20$(v/v)

| $[I]_o/2\times10^{3}$M | $\overline{Mn}\times10^{4}$ | C(%)(conv.) | $2[M]/\overline{DPn}\times10^{3}$ |
|---|---|---|---|
| 9.1 | 0.719 | 78.2 | 10.4 |
| 7.3 | 1.01 | 59.8 | 9.46 |
| 4.55 | 0.93 | 81.6 | 7.5 |
| 2.28 | 1.33 | 57.1 | 7.39 |

$[IB]_o=1.3$M, $[BCl_3]_o=9\times10^{-2}$M, -40℃ 10min

Correlation coeffieient r=0.96

Table VIII The effect of [p-DCC] on $\overline{Mn}$ in $CH_2Cl_2$/n-$C_6H_{14}$=60/40(v/v)

| $[I]_o/2\times10^{4}M$ | $\overline{Mn}\times10^{4}$ | C(%)(conv.) | $2[M]/\overline{DPn}\times10^{4}$ |
|---|---|---|---|
| 9.1 | 1.62 | 51.2 | 7.01 |
| 7.3 | 1.98 | 51.4 | 5.71 |
| 4.55 | 2.53 | 36.7 | 5.04 |
| 2.28 | 2.75 | 33.5 | 4.75 |
| 0.455 | 3.20 | 24.4 | 4.34 |

$[IB]_o$=1.42M, $[BCl_3]_o=9\times10^{-2}M$, -40℃ 10min
Correlation coefficient r=0.95

Table IX The effect of [p-DCC] on $\overline{Mn}$ in $CH_2Cl_2$

| $[I]_o/2$ | $\overline{Mn}\times10^{4}$ | $1/\overline{DP}\times10^{4}$ | $2[IB]/\overline{DPn}\times10^{4}$ |
|---|---|---|---|
| 9.6 | 3.47 | 16.1 | 24.8 |
| 6.6 | 4.34 | 12.9 | 19.8 |
| 3.2 | 7.4 | 8.0 | 12.28 |
| 1.6 | 11.5 | 4.87 | 7.47 |

$[IB]_o$=1.32M, $[BCl_3]_o=5.3\times10^{-2}M$, -40℃ $CH_2Cl_2$ 10min
Conversions are 70±5%.(average 70%) correlation coefficient=0.98

As shown in Tables II, IV, VII, IX their $C_{tr,I}$ values obtained in different medium polarity are listed in Table X.

Table X The effect of medium polarity on $C_{tr,I}$

| $CH_2CL_2$/n-$C_6H_{14}$(v/v) | mole fraction of $CH_2Cl_2$ | $C_{tr,I}$ |
|---|---|---|
| *100/0 | 1.19 | 2.14 |
| 80/20 | 0.89 | 0.47 |
| 70/30 | 0.83 | 0.37 |
| 60/40 | 0.76 | 0.28 |

$[p\text{-}DCC]_o=8.8\times10^{-3}M$ $[BCl_3]$=0.09M, $[IB]_o$=0.64M, -40℃ 10min.
*As described in Table II.

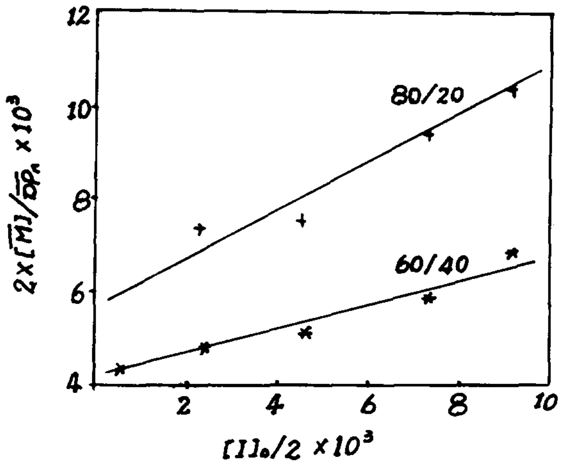



Fig. IV Plot of $2[\overline{M}]/\overline{DP}$ vs. $[I]_0/2$

These figures indicate an abrupt change of $C_{tr,I}$ with medium polarity between 100/0 and 80/20(v/v) of $CH_2Cl_2$/n-$C_6H_{14}$. This suggests that besides the ionic dependence of $C_{tr,I}$, $CH_2Cl_2$ may also act as a chain transfer agent to a certain extent under given conditions. In order to clarify this possibility further investigations will be carried out.

4. The effect of medium polarity on $\overline{Mn}$

The data of medium polarity on $\overline{Mn}$ are shown in Table XI

Table XI. The effect of medium polarity on $\overline{Mn}$

| $CH_2Cl_2$/n-$C_6H_{14}$(v/v) | Mole fraction of $CH_2CL_2$ | $Mn \times 10^{-3}$ | Conv% | $2[M]/\overline{DPn} \times 10^3$ |
|---|---|---|---|---|
| 90/15 | 0.92 | 7.8 | 51.6 | 11.2 |
| 80/25 | 0.87 | 13.7 | 4.32 | 6.87 |
| 70/35 | 0.80 | 24.5 | 28.9 | 4.28 |

$[IB]_0$=1.1M, $[p\text{-}DCC]_0$=$9.7\times10^{-3}$M $[BCl_3]$ $4.18\times10^{-2}$M, -40℃ 10min

Correlation coefficient r=0.989.

1. During the synthesis of chlorine-terminated telechelic PIB with a p-DCC/$BCl_3$/$CH_2Cl_2$ system, cycloalkylation will occur in parallel with propagation. This reaction drastically influences molecular parameters, such as MW, MWD and functionality.

2. The main factors that affect cycloalkylation are temperature, polarity of the medium and monomer concentration. High temperature, high medium polarity and low monomer concentration favor cycloalkylation.

3. The order of addition of p-DCC and $BCl_3$ influences cycloalkylation and this is attributed to the instantaneous and high local concentration of the initiating center.

Acknowledgement

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References

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(2) O. Nuyken, D.P. Stephen, Macromol. Chem., 184, 553(1983).

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