

The synthesis of chlorine-terminated telechelic polyisobutylene

I. Investigation on cycloalkylation

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Abstract

In synthesizing chlorine-terminated telechelic polyisobutylene (PIB) with a p-DCC(p-dichlorocumene)/BCl₃/CH₂Cl₂ system, it is found that cycloalkylation occurs parallel with propagation. The factors leading to cycloalkylation were investigated in detail, to clarify its origin, to define its effects upon the molecular parameters of the polymer produced and to find ways to suppress it. It is found that cycloalkylation drastically influences MW, MWD and functionality of the polymer produced. High temperature, high medium polarity, low monomer concentration and the order of addition of BCl₃ and p-DCC are the main factors favoring cycloalkylation.

Introduction

Papers published on the synthesis of chlorine-terminated telechelic polyisobutylene(Cl-TPIB) with the p-DCC/BCl₃/CH₂Cl₂ system indicate that parallel to propagation cycloalkylation also occurs[1] which would invariably affect the functionality, MW and MWD of the polymer. Therefore, systematic investigations were carried out to explore the details of this reaction and to find ways to suppress it.

Experimental

1. Reagents used and methods of purification

CH₂Cl₂ was treated with 4A Molecular Sieves for more than one week and refluxed under high purity N₂ for 12 hrs. in the presence of CaH₂ before use. n-Hexane was treated with 4A Molecular Sieves for more than a week and stored over Na wire under high purity N₂. Isobutylene was passed through CaO, CaCl₂ and KOH columns and stored as solution in

CH_2Cl_2 or n-hexane. The purity of N_2 was 99.999%. The synthesis of p-DCC has been described [2]. Elemental analysis of p-DCC,

Element	Determined	Theoretical
C%	62.3537	62.3504
H%	7.0675	7.9762
Cl%	30.61	30.6734

Its structure has been confirmed by IR and $^1\text{H-NMR}$ spectroscopy as, $\text{Cl}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{-C}(\text{CH}_3)_2\text{Cl}$. After recrystallization in n-hexane and drying under vacuum, its T_m is 67°C .

BCl_3 was prepared as reported in the literature [3]. The product was redistilled twice.

2. Apparatus and Instruments

- (1) GPC; Waters-150C with RI and UV detectors.
- (2) IR spectrometer; IR-420 (Japan) or IR-5DXC (U.S.A.).
- (3) UV spectrometer; Specord UV-VIS (German).
- (4) $^1\text{H-NMR}$ spectrometer; FT-80A(U.S.A.) or EM-360(U.S.A.)T-60.

3. Cl end-group determinations by burning in O_2

4. Procedures

Polymerization was carried out in custom made glass reactors equipped with stirrer and thermometer. The reactor was repeatedly purged with N_2 , evacuated and baked. It was then filled with isobutylene solution and initiator, and cooled to the required temperature. The charge was stirred and BCl_3 solution was added to initiate the reaction. After polymerization the system was evacuated to remove the unreacted isobutylene and BCl_3 . The polymer was precipitated with methanol, redissolved in n-hexane several times, and dried under vacuum at 40°C to constant weight.

Results and Discussion

1. The effect of reagent addition order on molecular parameters of polymer

The order of addition of initiator(p-DCC) and coinitiator (BCl_3) was investigated. The data are given in Table I. It is surprising that in C and E the results are drastically different from those of others. The GPC traces reveal some clues (Fig.1). The elution time by RI shows a singular peak at $\text{MW} \sim 300$ and a strong UV absorption band which indicates

the aromatic unit which comes from the inifer.

Table I. The effect of the addition order on polymn. of $i\text{-C}_4\text{H}_8$

addition order	observations	\overline{M}_n	MWD	\overline{F}_n	yield
A p-DCC- BCl_3	Solution turns yellow and rapidly fades away upon BCl_3 addn. temp. rise 15°C	8940	2.2	1.9	66.9*
B p-DCC-drop-wise BCl_3	As A; intan- taneously de- coloring upon BCl_3 addn.	8610	2.6	2.1	79.3*
C BCl_3 -p-DCC	After BCl_3 addn temp. rises 1°C After p-DCC addn. temp. rise 12°C	2120	12.1	0.53	59.7*
D p-DCC- BCl_3	Same as A	8700	2.5	1.9	62.9*
E Premixing p-DCC and BCl_3 (aging)	Premixed solu- tion is yellow. Color fades after its addn. to the system. Temp. rise 9°C	3010	10.5	0.85	62.3*

$[\text{IB}]_0 = 1.43\text{M}$, $[\text{p-DCC}]_0 = 0.01\text{M}$, $[\text{BCl}_3]_0 = 0.054\text{M}$, -40°C , CH_2Cl_2 , 30min

$^1\text{H-NMR}$ spectra of the samples C and E show indanyl structure at 7.0ppm, adjacent to the aromatic resonance 7.25 ppm (Fig.II). This is approximately the same as reported by Kennedy et al. [1] who suggested cycloalkylation to explain the observations.

The experimental data here show that propagation is favored in system rich in monomer. However, systems with high concentrations of

initiating centers, locally and instantaneously, will promote cycloalkylation.

From the above results and taking into consideration that the larger the chain with terminal cations the less is the possibility of the terminal cations to attack the aromatic nucleus of the initiator. This is in line with the measured average MW of the polymer approaching ~300 and the singular effect of the addition sequence. The observed phenomena may be explained as follows. When the initiator is added last the high local initiator concentration leads to cycloalkylation and consequently affects \bar{M}_n , MW, MWD.

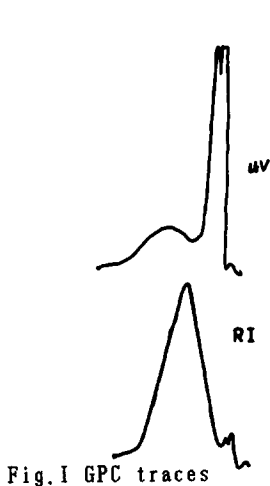


Fig. I GPC traces

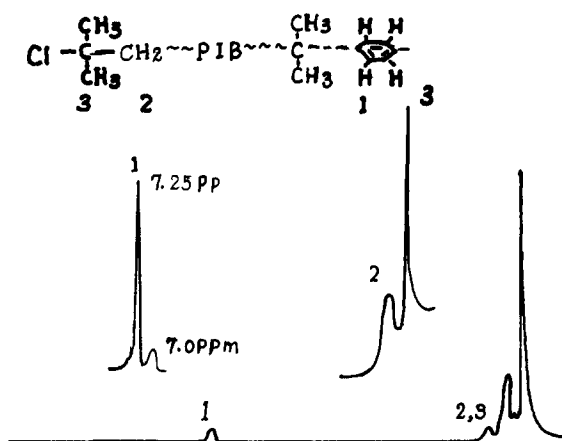
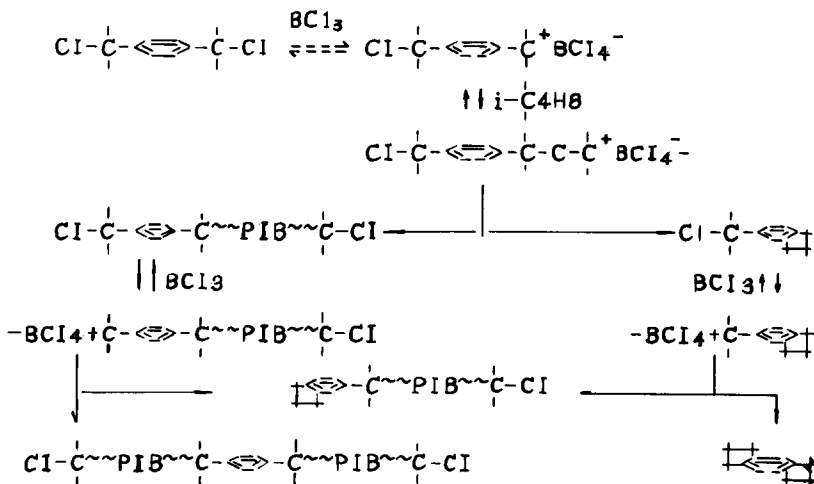
Fig. II $^1\text{H-NMR}$ spectrum of the polymer

Fig. III Scheme for alkylcyclization

2. Factors that affect cycloalkylation

Cycloalkylation can also be considered from a kinetic point of view. Let the rate of propagation be $R_p = K_p [P^*] [M]$ and the rate of cycloalkylation be $R_c = K_c [P^*]$. Here the K_p and K_c are rate constants of propagation and cycloalkylation, respectively.

The factors that effect K_p and K_c should be the same, such as temperature, polarity etc. The factors that affect $[P^*]$ and P^* activity will affect cycloalkylation. The effect of $[M]$ will also influence cycloalkylation and this will be discussed later.

3. The effect of temperature on cycloalkylation

¹H-NMR spectra (Fig. IV) show the effect of temperature on the variation of the indanyl structure.

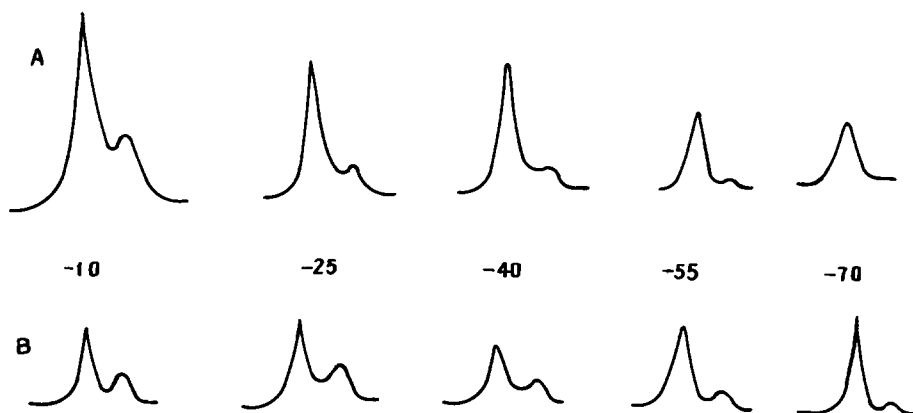


Fig. IV ¹H-NMR of polymers obtained at different temperatures
Medium, A, $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ 70/30 v/v, B, CH_2Cl_2

The relative constants of indanyl structures at different temperatures can thus be estimated. As K_c follows an Arrhenius plot, $\ln(\text{cyclic}^*)$ vs. $1/T$ (Fig. V), we have $(E_c)_{\text{app}} = 13.3 \text{ KJ/mol}$. The temperature should also affect the dielectric constant or the medium polarity, in addition.

4. The effect of medium polarity on cycloalkylation

As shown above polarity of the medium also affects cycloalkylation. ¹H-NMR spectra given in Fig. VI show different proportions of the aromatic and indanyl H due to the composition variation of solvents used. Table II shows that polymers which were prepared in different media exhibit different cycloalkyl contents. The more polar media favor

cycloalkylation. In a mixed medium e.g. $\text{CH}_2\text{Cl}_2/n\text{-C}_6\text{H}_{14}=70/30(\text{v/v})$ at -70°C , cycloalkylation is almost totally suppressed while in CH_2Cl_2 indanyl structures remain under otherwise equal reaction conditions. These findings are in line with those published by Kennedy et al. [1]

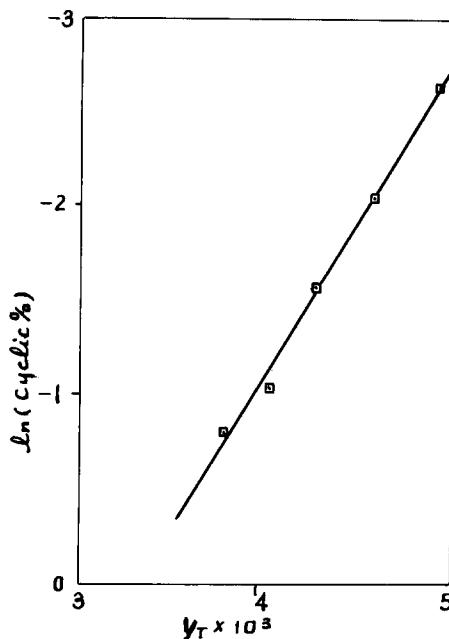


Fig.V Plot of $\ln(\text{cyclic } \%)$ vs. $1/T$

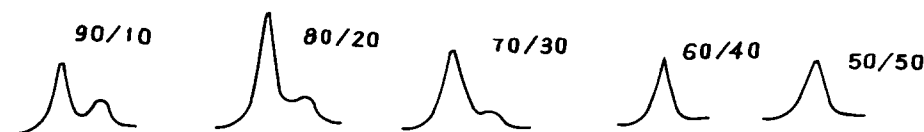


Fig. VI $^1\text{H-NMR}$ of polymers obtained in media of different polarity different $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ compositions(v/v)

5. The effect of monomer concentration on cycloalkylation

Equation $R_p/R_c = [K_p/K_c] [M]$ shows that by increasing $[M]$ cycloalkylation is suppressed. This probably arises from the dual effect of monomer; R_c is suppressed kinetically as by the equation $R_p/R_c = K_p/K_c[M]$. In addition, isobutylene may be regarded as a nonpolar medium and thus suppresses cycloalkylation. Collateral evidence can be found through the influence of $[M]$ on the functionality of the polymer.

Table III. the effect of [M] on functionality \bar{F}_n

[M]	M	\bar{F}_n
2.1		2.1
1.9		2.0
1.5		2.05
1.1		1.7
0.7		1.54

$[BCl_3]=0.1 \text{ M.}$, $[p\text{-DCC}]=8.99 \times 10^{-4} \text{ M.}$, CH_2Cl_2 , 20 min., $-40^\circ C$.

It is seen in Table III, when $[M]=1.5M$, the functionality of the polymers is close to theoretical, i.e. no or little cycloalkylation occurs. When cycloalkylation occurs, the functionality will decrease in proportion, This decrease can be regarded as an indicator. By comparing the data, we are able to estimate the influence of cycloalkylation on molecular parameters. Table IV shows the results.

Table IV The effect of cycloalkylation on functionality

Temp. C	uncyclized comp'd.(%)	\bar{F}_n		Cl-terminal(%)
		theoretical	experimental	
-10	55.6	$2 \times 0.556 = 1.11$	1.09	98
-25	64.9	$2 \times 0.649 = 1.30$	1.20	92
-40	79.6	$2 \times 0.796 = 1.60$	1.47	92
-55	87.2	$2 \times 0.872 = 1.74$	1.68	97
-70	92.5	$2 \times 0.925 = 1.85$	1.78	96

CH_2Cl_2 , $[p\text{-DCC}]=2.1 \times 10^{-3} \text{ M}$, $[BCl_3]=0.10 \text{ M}$, $[IB]=0.958 \text{ M}$. 10min

It is seen that the functionality of the uncyclized polymer approaches theoretic value (>90%).

It is shown that \overline{Mn} and conversion drop as the polarity of the medium decreases. \overline{Mn} rise supports our proposal that polar medium may play a role of chain transfer agent and conversion drop may be attributed to low activity of the initiating species formed in weak polar medium.

Conclusion

1. Among all chain transfer reactions, Ctr_{11} plays the most important role in determining molecular parameters and thus the function of inifer is verified.

2. Ctr_{11} , Ctr_{1s} for $(CH_2Cl)_2$, and Ctr_{1M} in CH_2Cl_2 have been determined. They are 1.09 ($-40^\circ C$), 5.6×10^{-4} ($-40^\circ C$), 3.36×10^{-4} (negligible at $-40^\circ C$), respectively. Various effects upon Ctr_{11} have been investigated. High temperature and more polar media favor chain transfer.

Acknowledgement

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