New telechelic polymers and sequential copolymers by polyfunctional initiator-transfer agents (inifers)

LV. Tert.-chlorine capped polyisobutylenes by aliphatic inifers

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Summary

The unsaturated aliphatic dichlorides <u>cis</u> and <u>trans</u> $Cl(CH_3)_2C-CH=CH-C(CH_3)_2Cl$ in conjunction with BCl_3 have been found to be excellent binifers and yield tert.-Cl capped poly-isobutylenes PIB in CH_3Cl at -30°C. Intramolecular cyclization is absent and terminal chlorine functionality is $\overline{F}_n = 2.0\pm0.1$. The normalized inifer constants have been determined: $C_{I_{trans}} =$ 1.05, and $C_{I_{cis}}$ = 3.8 and 1.05, respectively, for the first and second allylic chlorines in the <u>cis</u> isomer. The inequality of the chlorines have been analyzed. The <u>cis</u> and <u>trans</u> isomers have identical relative termination constants ($\overline{k}_t/\overline{k}_p$ = 6X10^{-3}). The structure of the PIBs obtained has been analyzed by a variety of techniques. Model experiments with isobutylene/Cl-$(CH_3)_2C-CH=CH-C(CH_3)_2$ Cl = 2/1 in the presence of BCl_3 gave the expected <u>trans</u> $Cl(CH_3)_2CCH_2-(CH_3)_2C-CH=CH-C(CH_3)_2-CH_2C(CH_3)_2-Cl$. The end groups of polymers have been quantitated. The central position of the -CH=CH- residue in polymers has been demonstrated by molecular weight determinations i.e., the $\overline{M}_n$ of PIB has decreased by a factor of two after oxidative cleavage. The uniform distribution of -CH=CH-group across all polymeric species has also been established.

Introduction

Telechelic polyisobutylenes (PIB) are of interest for a variety of potential applications (1,2,3). The synthesis of tert.-Cl capped PIB is now carried out semicommercially (4) using aromatic inifers (5,6), e.g., $pClC(CH_3)_2C_6H_4C(CH_3)_2$ Cl/ BCl_3, in CH_3Cl at -78°C. Low temperatures are necessary to "freeze out" undesirable intramolecular aromatic alkylation leading to chain transfer (7,8). Cyclization can be avoided by the use of an "hindered" aromatic binifer, (8) or trinifer. In the latter systems indanyl ring formation is prevented by steric hindrance and perfectly telechelic linear ($\overline{F}_n$ = 2.0 ± 0.1) or three-arm star ($\overline{F}_n$ = 3.0 ± 0.1) PIBs can be prepared at much higher temperatures.

By the use of aliphatic inifers the risk of indanyl ring formation would be eliminated and telechelic PIBs close to the reflux temperature of CH_3Cl (-27°C or higher) could be obtained. Initial efforts in this direction has included the use of $Cl(CH_3)_2C-CH_2CH_2-C(CH_3)_2Cl$, however, this compound was not an inifer but a conventional cationogen whose ionization occurred

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by cyclic chloronium ion formation (10). Subsequently Cl(CH$_3$)$_2$C-C≡C-C(CH$_3$)Cl was shown to be of very low reactivity (11). The present paper concerns the synthesis of α,ω-di-tert.-Cl capped PIBs by the use of Cl(CH$_3$)$_2$C-CH=CH(cis and trans)-C(CH$_3$)$_2$Cl/BCl$_3$ systems in CH$_3$Cl diluent at -30°C (i.e., very close to the reflux temperature of this solvent)). Kinetic experiments demonstrate that these dichlorides are excellent binifers and structure characteriztion indicate perfectly telechelic products.

Experimental

Syntheses

2,5-Dichloro-2,5-dimethyl-3-hexyne (DClDMeHy)   2,5-Dimethyl-3-hexyne-2,5-diol (Aldrich) was chlorinated in CH$_2$Cl$_2$ by excess dry HCl gas at 0°C for 24 hr to produce the corresponding dichloride. The CH$_2$Cl$_2$ was removed by rotovap and the product was purified by distillation under reduced pressure. Yield: 43.7%, ^{1}H-NMR(CCl$_4$): δ(ppm): 1.9(s,12H).

Cis-2,5-dichloro-2,5-dimethyl-3-hexene (cisDClDMeH$_6$)
This compound has been obtained from 2,5-dimethyl-3-hexene-2,5-diol by catalytic hydrogenation in the presence of Lindlar's catalyst (6) under atmospheric pressure at room temperature followed by chlorination as described above for DClDMeHy. The product was purified by distillation, yielding a colorless liquid. Yield: 32%, ^{1}H-NMR(CCl$_4$) δ(ppm): 5.3(s,2H), 1.3 (s, 12H). This compound is rather unstable, it readily loses HCl; therefore it should be stored in a refrigerator or preferentially in Dry Ice.

Trans-2,5-dichloro-2,5-dimethyl-3-hexene (trans-DClDMeH$_6$)
Dimethyl-3-hexyne-2,5-diol was reduced by lithium aluminum hydride to the corresponding trans-hexene diol (12) and the product was chlorinated by the above procedure used for the preparation of the cis-isomer. Purification by distillation gave a 42% yield; ^{1}H-NMR(CCl$_4$): δ(ppm) 5.8 (s,2H), 1.9 (s,12H).

Polymerization   Polymerizations were carried out at -30°C under dry N$_2$ in a dry box (5).

Characterization(s) ^{1}H-NMR spectra were taken by a Varian T-60 spectrometer using CCl$_4$ solutions and a TMS standard. GPC was performed using a Waters Associates 6000A high-pressure GPC equipped with dual ultraviolet and refractive index detectors and five ultra µ-Styragel columns. Chain-end functionality was calculated from elementary chlorine analysis carried out by Galbraith Laboratories. Melting points were determined by a Laboratory Devices Mel-Temp. instrument.

Results and Discussion

A) Kinetic Studies: Demonstrating and Quantifying Inifer Activity

Experimentation started by establishing that both cis- and trans-DClDMeH$_6$ in conjunction with BCl$_3$ are initiators for IB polymerization. Thus the addition of BCl$_3$ to IB/DClDMeH$_6$/CH$_3$Cl charges at -30°C resulted in immediate polymerization.

Table I summarizes representative data. Conversions rapidly
(∿10 mins) reached ultimate values and tended to be < 100%.
Increasing both the cis- or trans-DClDMeH$_6$ concentrations in the
charge resulted in a proportional decrease in $\bar{M}_n$ ($\bar{M}_n$ = f(1/I$_o$)),
a clear sign of chain transfer (inifer) activity. The molecu-
lar weights obey the relationship $\overline{DP}_n$ = ([M$_o$]-[M$_t$])/[I$_o$], where
[M$_o$] and [I$_o$] are initial monomer and inifer concentrations and
[M$_t$] is the final monomer concentration. Initiation efficien-
cies (i.e., (100X(gPIB/$\bar{M}_n$)/I$_o$) were ∿100% within experimental
error. In regard to $\bar{M}_w$/$\bar{M}_n$ values, in view of the relatively
high conversions (changing [M]) the values for the trans-
DClDMeH$_6$ are not too far from the theoretical, whereas the rel-
atively high values for the cis compound are due to structural
peculiarities (see below).

TABLE I

Polymerization of Isobutylene by the cis or transDClDMeH$_6$/BCl$_3$

  System (MeCl, -30°C, [BCl$_3$] = 0.256 mole/L, 30 min, V=25 mL)

DClDMeC$_6$	I$_o$ x 10^2 mole/L	i-C$_4$H$_6$ mole/L	Conv. %	$\bar{M}_n$ g/mole	$\bar{M}_w\bar{M}_n$
	-	0.938	< 5.0	1340	-
cis	5.60	0.704	81.2	490	1.4
	5.60	0.938	70.1	570[a]	2.2
	2.80	0.938	55.2	1240	2.6
	1.40	0.938	49.1	2050	2.7
	0.56	0.938	40.4	4220	2.1
trans	6.04	0.957	66.9	1010	1.4
	3.25	0.957	57.6	1410	1.7
	1.32	0.957	46.4	2900	1.8
	0.98	0.957	42.3	3250	2.0
	0.40	0.957	32.0	4340	2.9

[a]by VPO

Experiments have been carried out to quantify the inifer
activity by inifer plots and thus to determine C$_I$ for both cis
and trans-DClDMeH$_6$. In view of the rather high conversions
(i.e., >30%), the integrated inifer equation was used (13).
Figure 1 shows the inifer plots whose slope and intercept,
respectively, yield C$_I$ (i.e., k$_{tr,I}$/k$_p$) and k$_t$/k$_p$. Accord-
ing to the slopes C$_{Icis}$ = 4.8 and C$_{Itrans}$ = 2.1, however,
these values must be corrected in light of the following con-
siderations: the much higher inifer reactivity of the
cisDClDMeH$_6$ as compared with the trans compound is most likely
due to steric strain in the former. Ionization causes strain
relief by isomerization so that the second chlorine in the cis
compound will have the same reactivity as that in the trans
compound (see scheme top of next page). Thus the Cls in the
trans compound are equivalent and their normalized C$_I$ values
per Cl site are 2.1/2 = 1.05. The reactivities of the two Cls
in the cis isomer are not identical, the first Cl is more re-
active than the second: After ionization of the first Cl the
remaining allylic Cl becomes a trans Cl with C$_I$ = 1.05, thus
the C$_I$ for the first cis Cl is 4.8-1.05 ∿3.8. Thus, the first

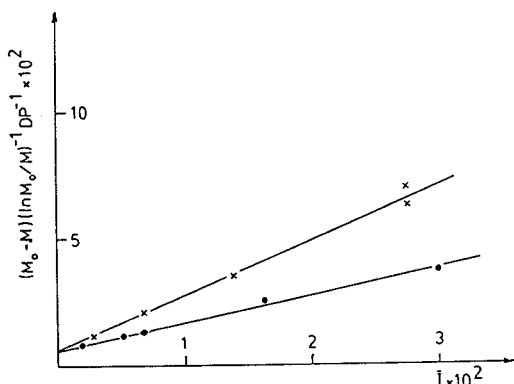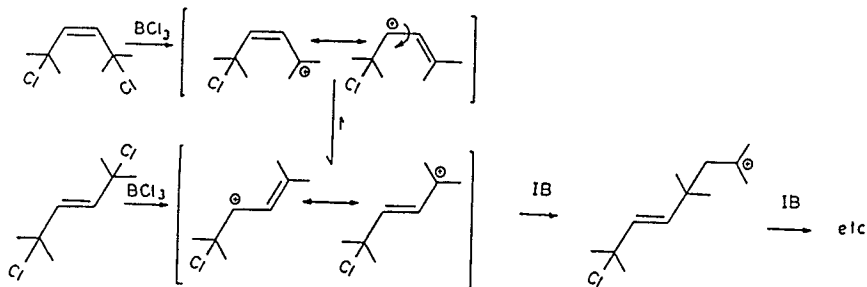Cl in the <u>cis</u> compound is almost four times more reactive than the second (However, see below).

Figure 1. Inifer plot of <u>cis</u> (X) and <u>trans</u> (O) DClDMeH$_6$

The reactivity difference between the <u>cis</u> and <u>trans</u> DClDMeH$_6$ is also reflected in their respective thermal stabilities: While the <u>cis</u> isomer is unstable and is rapidly (within hours) dehydrochlorinated to 2,5-dimethyl-1,3,5-hexatriene even when stored at -20°C, the <u>trans</u> isomer is stable and can be kept for weeks at room temperature without decomposition.

The k_t/k_p value calculated from the intercepts of the inifer plots for the two isomers are identical (6×10^{-3}) within experimental variation, i.e., the termination mechanisms are the same. This value is very similar to other k_t/k_p values determined for similar systems (14).

B) Structure Definition

The structures of the products obtained with the new binifers have been investigated. These studies were to demonstrate the -CH=CH- group in the polymer and the tert.-Cl end groups. A secondary objective was to ascertain the <u>absence</u> of intramolecular cyclization (see scheme top of next page). This process deemed unfavorable both kinetically (steric compression) and thermodynamically (tert.-C$^\oplus \rightarrow$ sec.-C$^\oplus$).

A series of experiments have been carried out by the use of both <u>cis-</u>and <u>trans</u>-DClDMeH$_6$ with charges containing 2 moles of IB relative to the dichlorides, but otherwise under conditions similar to those used in polymerizations. After 30 mins.
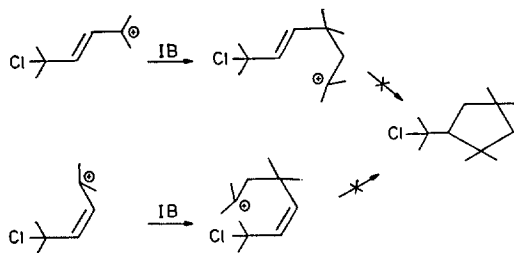
the charges were quenched with prechilled CH_3OH and the products analyzed by ^{1}H NMR spectroscopy. Figure 2 shows a representative spectrum together with assignments obtained with cis-DClDMeH$_6$. The identical product was obtained with the trans compound. Integration of the resonances indicates that both experiments yielded trans-2,9-dichloro-2,4,4,7,7,9-hexamethyl-dec-5-ene (see Figure 2). This compound (M_p = 53°C) has not been referenced in the Chemical Abstract Molecular Formula Index 1920-1986. The ^{1}H NMR of the products obtained with both the cis- and the trans-DClDMeH$_6$ exhibited a resonance at 5.4 ppm (s,2H) corresponding to the -CH=CH-group. A companion of the -CH=CH- resonances in cis (5.3 ppm) and trans-(5.8 ppm) DClDMeH$_6$ leads us to conclude that the trans product formed with both isomers. This phenomenon was also observed with higher $\bar{M}_n$ PIBs, i.e. when much higher IB/I ratios were used.
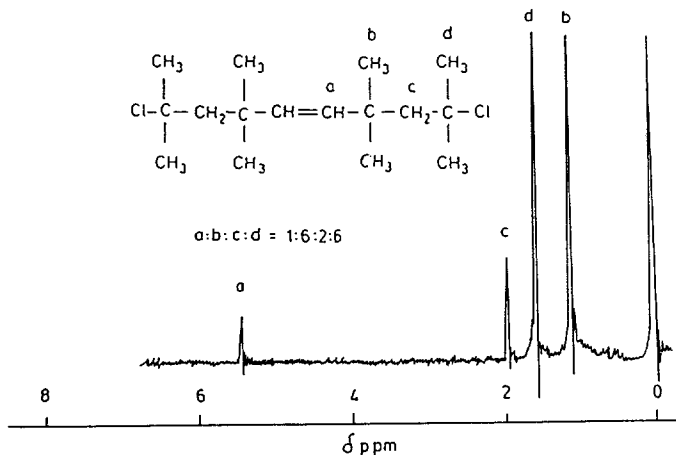

Figure 2.   ^{1}H NMR spectrum of the product formed in the cis or transDClDMeH$_6$/IB = 2/1 system in the presence of BCl$_3$ in CH_3Cl at -30°C

These experiments hold important clues as to the inifer mechanism with these dichlorides: Evidently intramolecular cyclization (see above) is absent. They also suggest that initiation (reactions 1 and 2, and 4 and 5) and chain transfer to inifer (reactions 3 and 6) are very fast. If this were not

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so and chain transfer to inifer were slow, few carbocations
would consume the entire monomer input and the final product
would contain in addition to the PIB unreacted $DClDMeH_6$ sites.
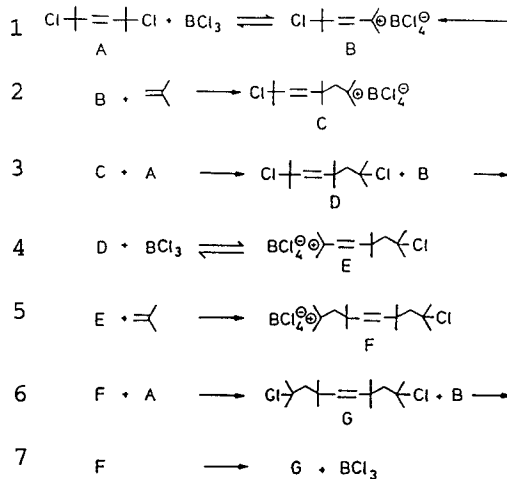
According to this analysis the inifer reactivity of the
chlorines is not the same even in the <u>trans</u> isomer because af-
ter the substitution of the first Cl by an organic group (re-
actions 1-3) the reactivity of the remaining allylic Cl is en-
hanced relative to the original allylic Cl, however, the extent
of the reactivity difference cannot be judged on the basis of
available data. Thus the C_I values are averages in systems
where the inifer sites affect each other and substitution of
one necessarily affects the remaining one.

The above results also indicate that the following ster-
ically difficult cationation is absent.
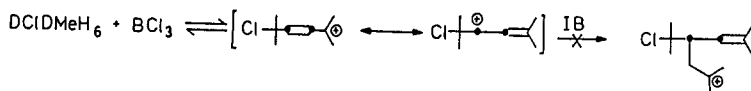
The results of these "model" experiments demonstrate
rapid initiation and chain transfer, the incorporation of
-CH=CH- groups, and the nature of the end groups arising upon
termination.

Subsequently the end groups of PIBs obtained with both
inifers have been quantitated (15). Thus representative sam-
ples have been dehydrochlorinated and the olefins so formed
analyzed (7). Integration of the terminal $-CH_2C(CH_3)=C\underline{H}_2$ pro-
tons at 4.65 and 4.85 ppm (7) relative to those of internal
-CH=CH- standards at 5.38 ppm consistently gave $\overline{F}_n$ = 2.0 ± 0.1.

These results have been independently corroborated by quantitative Cl analyses. Thus according to the Cl content of select samples, whose $\overline{M}_n$ was also determined, the samples contained 2.0 ± 0.1 atom Cl/molecule.

Although the Cls in the cisDClDMeH$_6$ are of unequal reactivities, the statistically central position of the -CH=CH- group has been established. A representative PIB has been oxidatively cleaved (16) and the molecular weights of the surviving fragments compared with that of the original sample. Figure 3 shows the GPC traces. According to these experiments exhaustive oxidation caused the $\overline{M}_n$ of the original polymer to decrease by a factor of two while the $\overline{M}_w/\overline{M}_n$ values increased. The broader than theoretical ($\overline{M}_w/\overline{M}_n = 1.5$) MWD of the original sample may be due to the different Cl reactivities in the cis binifer. It follows that the MWD of the cleaved fragments is also higher than the theoretical 2.0. These results indicate that both tert.-allylic Cls in cisDClDMeH$_6$ are active inifer sites.

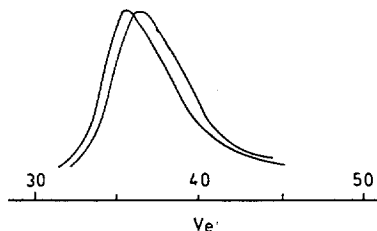30   40   50

Ve·

Figure 3. GPC trace of PIB before and after oxidative cleavage

These conclusions have been independently substantiated by -CH=CH- group distribution analysis using Kennedy-Smith-Nagy (KSN) plots (17). PIBs prepared by both DClDMeH$_6$ isomers exhibit a weak but detectable UV absorption at 254 nm (the working wave length of our detector) due to the inifer residue (-CH=CH-) in the sample. Although ethylene absorbs only in the far UV, alkyl substitution shifts its absorption to higher wave lengths and increases its molar absorption (18). Subsequently the UV and RI responses of polymer samples have been recorded and KSN plots constructed. Figure 4 shows the results. The linearity of the plot, absence of an intercept, and unity slope indicate uniform chromophore (-CH=CH-) distribution across the entire molecular weight regime of the PIB sample (17).
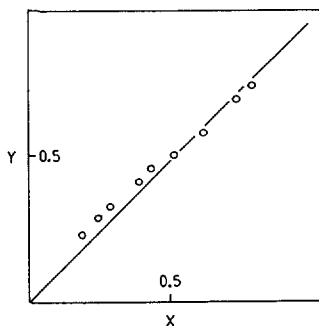

Y ⊢0.5

0.5

X

Figure 4. Kennedy-Smith-Nagy plot of a representative PIB obtained with cis or transDClDMeH$_6$

References

1.   See paper LIII in this series: K. L. Peng, J. P. Kennedy and L. Wilczek, J. Polym. Sci., in press
2.   T. Miyabayashi and J. P. Kennedy, J. Appl. Polym. Sci., 31, 2523 (1986)
3.   J. P. Kennedy and J. Lackey, J. Appl. Polym. Sci., 33, 2449 (1987)
4.   Akron Cationic Polymer Development Co., Akron, OH.
5.   J. P. Kennedy and R. A. Smith, J. Polym. Sci., Chem. Ed., 18, 1539 (1980)
6.   U. S. Patents 4,276,394; 4,316,978; 4,342,849
7.   V.S.C. Chang, J. P. Kennedy and B. Iván, Polym. Bull. 3, 339 (1980)
8.   R. Santos, J. P. Kennedy and W. Michael, Polym. Bull. 11, 261 (1984)
9.   J. P. Kennedy, L. R. Ross, J. E. Lackey and O. Nuyken, Polym. Bull., 4, 67 (1981)
10. M. Biswas and J. P. Kennedy, Macromol. Chem. Macromol. Symp. 3, 113 (1986)
11. S. Ma and J. P. Kennedy, unpublished results (1986)
12. K. Alder, H. V. Brachtel and K. Kaiser, Ann. Chem., 608, 195 (1957)
13. A. Fehérvári, J. P. Kennedy and F. Tüdős, J. Macromol. Sci. Chem., A15, 215 (1980)
14. R. Santos, A. Fehérvári and J. P. Kennedy, J. Polym. Sci. Polym. Chem. Ed., 22, 2685 (1984)
15. J. P. Kennedy, V.S.C. Chang, R. A. Smith and B. Ivan, Polym. Bull. 1, 575 (1979)
16. J. P. Kennedy and D. K. Metzler, J. Appl. Polym. Sci., Appl. Polym. Symp., 30, 141 (1977)
17. A. Nagy, Polym. Bull. 14, 259 (1985)
18. M. Hirota, Kagaku No Ryoiki, 22(3), 209 (1968)