Living carbocationic polymerization
XV. Telechelic polyisobutylenes
by the CH$_3$O(CH$_3$)$_2$C-pC$_6$H$_4$-C(CH$_3$)$_2$OCH$_3$ · TiCl$_4$ initiating system

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Summary
        The synthesis of symmetrical linear telechelic polyiso-
butylenes (PIB) carrying -CH$_2$C(CH$_3$)$_2$Cl end groups (^{t}Cl-PIB-Cl^t)
has been accomplished by living isobutylene (IB) polymerization
using the CH$_3$O(CH$_3$)$_2$C-pC$_6$H$_4$-C(CH$_3$)$_2$OCH$_3$·TiCl$_4$ initiating system
in CH$_3$Cl/n-C$_6$H$_{14}$ (40/60 v/v) at -80°C. The living nature of
the polymerization was demonstrated by linear $\overline{M}_n$ versus amount
of PIB formed (W$_p$) plots starting at the origin. Polymers with
up to $\overline{M}_n$ = 126,000 and $\overline{M}_w/\overline{M}_n$ = 1.1 have been prepared. The
effect of temperature on the polymer structure has been inves-
tigated. Undesirable indanyl end groups which form in poly-
merizations even at -80°C can be eliminated by preparing the
initiating di-tert.-ether·TiCl$_4$ complex in the presence of
monomer.

Introduction
        The clean synthesis of tert.-chlorine capped polyisobu-
tylenes ^{t}Cl-PIB-Cl^t by living carbocationic polymerization
using various initiating systems has recently been demonstra-
ted (1-10). In the course of these investigations it was of
interest to determine whether and under what conditions would
the CH$_3$O(CH$_3$)$_2$C-pC$_6$H$_4$-C(CH$_3$)$_2$OCH$_3$ · TiCl$_4$ complex lead to well-
defined ^{t}Cl-PIB-Cl^t. This initiating system was of particular
interest because of its relatively low cost, high stability,
and advantageous solubility characteristics (11). The follow-
ing ·schematic equation summarizes the ingredients used and
anticipated products in these investigations:
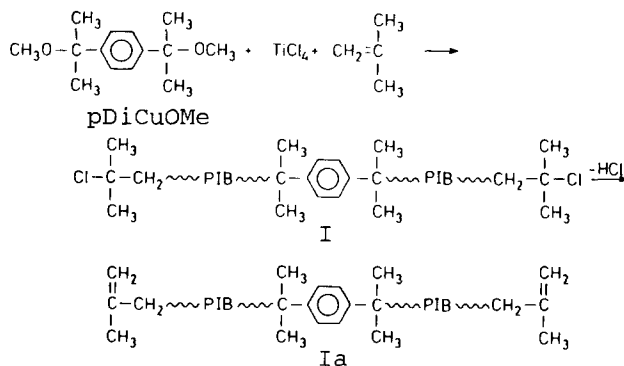
Experimental

Materials and procedures have been described (1,2,6,10, 12). Experiments were carried out by the IMA technique (1) in culture tubes and in 250 mL round bottom flasks with mechanical stirrer. The preparation of 1,4-di-(2-methoxy-2-propyl)benzene (p-dicumyl methoxy, pDiCuOMe) has been described (6). The purity of the chemicals was ascertained by ^{1}H NMR spectroscopy and GC analysis.

Results and Discussion

A) Preliminary Experiments, Key Observations

Polymerization of IB with the pDiCuOMe·TiCl$_4$ initiating system was carried out in CH$_3$Cl/n-C$_6$H$_{14}$ 40/60 v/v solvent mixture at -40°C. Figure 1 shows representative GPC traces. The
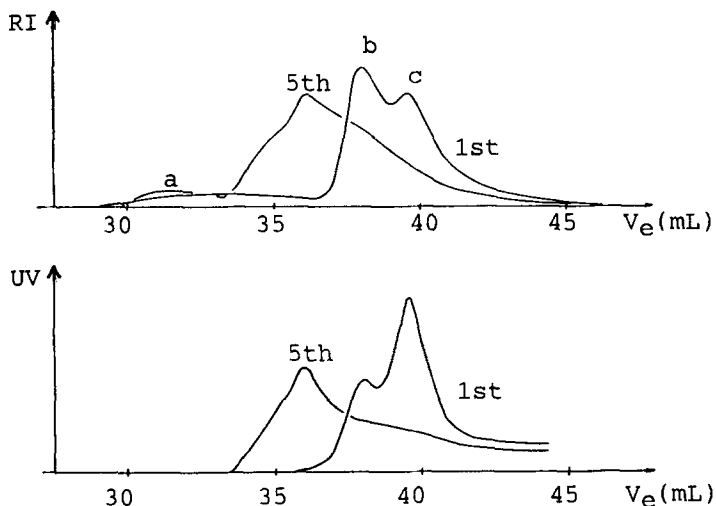

Figure 1. GPC traces of PIBs prepared by the pDiCuOMe· TiCl$_4$ initiating complex at -40°C; (CH$_3$Cl/n-C$_6$H$_{14}$ 40/60 v/v mixture, [pDiCuOMe]$_0$ = 1.3 x 10^{-4} mole; [TiCl$_4$]$_0$ = 2 x 10^{-3} mole; V$_0$ = 25 mL; IMA technique, 6x(1 mL/15 min))

RI (GPC) trace of the first sample in the IMA series exhibits three peaks: a UV transparent broad band at high molecular weights (a) and two UV active sharp peaks in the lower molecular weight region (b and c). On the basis of extensive earlier experience (10) it is proposed that the broad band (a) is due to a PIB fraction arising by adventitious protic initiation (i.e., by H$_2$O·TiCl$_4$), while the sharp peaks (b and c) displaying UV absorption are due to two PIB populations produced by initiation with pDiCuOMe·TiCl$_4$. Inspection of the positions of the two sharp peaks reveals that the $\overline{M}_n$ of fraction c is half of that of fraction b. (The $\overline{M}_n$s were calculated from peak positions since the MWDs are narrow).

Detailed IR and ^{1}H NMR spectroscopic analysis provided the explanation for this observation. Thus according to both IR and ^{1}H NMR spectra, shown in Figures 2 and 3, respectively, the PIBs contained indanyl end groups II and were contaminated

by "diindane" III. The sharp IR absorption at 890 cm^{-1} is characteristic of 1,3,4-trisubstituted aromatic rings and the proton resonances at δ = 6.95 and 6.6 ppm indicate mono- and diindanyl rings (13):
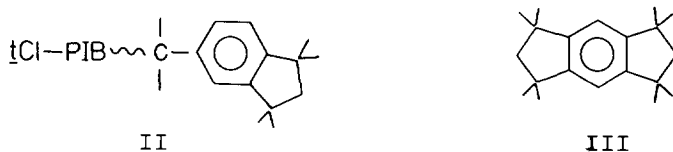

II   III

ν = 890 cm^{-1}

1000   800   ν(cm^{-1})

Figure 2. IR spectrum of PIB prepared by the pDiCuOMe· TiCl$_4$ initiating complex at -40°C, (conditions as in Figure 1, first sample by the IMA technique)

Figure 3. ^{1}H NMR spectrum of PIB prepared by the pDiCuOMe· TiCl$_4$ initiating complex at -40°C, (conditions as in Figure 1, first sample by the IMA technique)
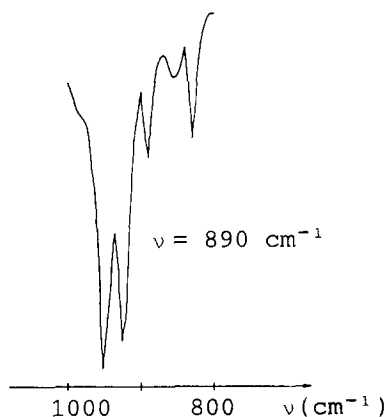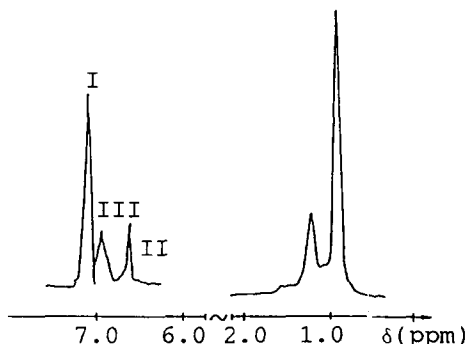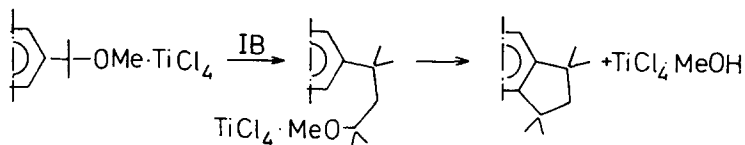

I

III

II

7.0   6.0 2.0   1.0   δ(ppm)

Additional evidence for the presence of the latter "diindane" are sharp GPC peaks at low molecular weights (∿270) exhibiting very strong UV signals. Indanyl ring formation may proceed similarly to that proposed for the pDiCuOMe·BCl$_3$ system (6):

Thus the presence of indanyl rings indicate the presence of
"half-grown" PIB molecules i.e., PIBs that have grown only in
one direction starting with only one of the cumyl groups,
whereas the growth at the second cumyl group was aborted by
intramolecular alkylation leading to indanyl end group. The
proton expelled during this alkylation may give rise to further
PIB chains and would appear as UV transparent species in the RI
(GPC) trace.

In line with this analysis, peak b in Figure 1 is due to
the PIB fraction that arose by controlled double initiation
with the pDiCuOMe· TiCl$_4$ complex (i.e., "full-grown" PIB chains
growing in both directions), peak c is due to a half-grown PIB
fraction carrying one indanyl end group, and the broad peak a,
that is due to UV-transparent PIB, mainly arose by uncontrolled
protic initiation by adventitious H$_2$O·TiCl$_4$ and perhaps by some
chain transfer involving intramolecular alkylation.

The formation of indanyl end groups is unacceptable for
the clean synthesis of telechelic products and ways to avoid
the side reactions leading to these undesirable structures have
been developed in similar systems (6,13). Thus indanyl ring
formation can be avoided in the pDiCuCl·BCl$_3$ and pDiCuOMe·BCl$_3$
(6) systems by reducing the temperature and/or the polarity of
the medium. Since the polarity of the medium used in the pre-
sent investigations has already been rather low (40/60 v/v
CH$_3$Cl/n-C$_6$H$_{14}$) and could not be further reduced for fear of
loss of initiator solubility (10), experiments were carried out
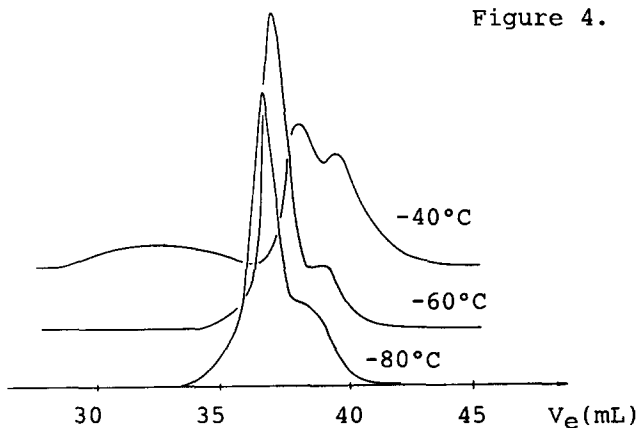by reducing the temperature. Figure 4 shows the RI (GPC)

Figure 4. GPC traces of PIBs
prepared by the
pDiCuOMe· TiCl$_4$
initiating complex at
different temperatures
(conditions as in
Figure 1, first sam-
ples by the IMA tech-
nique). Conversions:
-40°C 40%; -60°C 90%;
-80°C 100%

traces of PIBs prepared in the -40° to -80°C range. While the
extent of indanyl group formation has diminished with decreas-
ing temperatures it has not been completely eliminated even at
-80°C. Initiation due to protic impurities that occurs at
-40°C, however, was absent at the lower temperatures.

The GPC traces shown in Figure 1 also indicate that as
polymerization progresses at -40°C the active chain ends tend
to decompose (i.e., compare the sharp well-defined trace ob-
tained with the 1st sample in the series with a representative
later, in this case 5th, sample). A similar phenomenon has been

observed with ester·TiCl$_4$/IB systems (10) where decomposition occurs in the absence of monomer. In the present instance active chain end decomposition seems to proceed even in the presence of unconverted monomer. Thus the ether· TiCl$_4$ complex appears to be less stable than the ester·TiCl complexes. At lower temperatures (-60°, -80°C) sharp GPC traces were obtained during the latter stages of polymerization with the pDiCuOMe· TiCl$_4$/IB system as well, suggesting heightened complex stability with decreasing temperatures.

    B)   <u>The Synthesis of Indanyl-Free Narrow MWD ^{t}Cl-PIB-Cl^t</u>
        <u>by Living Polymerization</u>

    Observations made in the course of preliminary experiments held the clue toward the clean synthesis of narrow molecular weight distribution (MWD) ^{t}Cl-PIB-Cl^t. Usually IMA experiments have been carried out by adding IB to premixed pDiCuOMe· TiCl$_4$ complex (i.e., the time the pDiCuOMe· TiCl$_4$ was stirred in the absence of monomer at -80°C). Figure 5 shows the RI (GPC) traces of PIBs obtained in a representative series
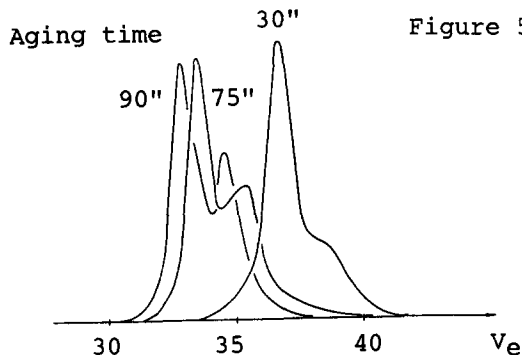

Figure 5. Effect of aging time on the polymerization of IB at -80°C: IR (GPC) traces (Conditions as in Figure 1, first samples by the IMA technique)

of aging experiments. Further, as shown by the $\overline{M}_n$ versus time plots in Figure 6, both PIB fractions corresponding to the two
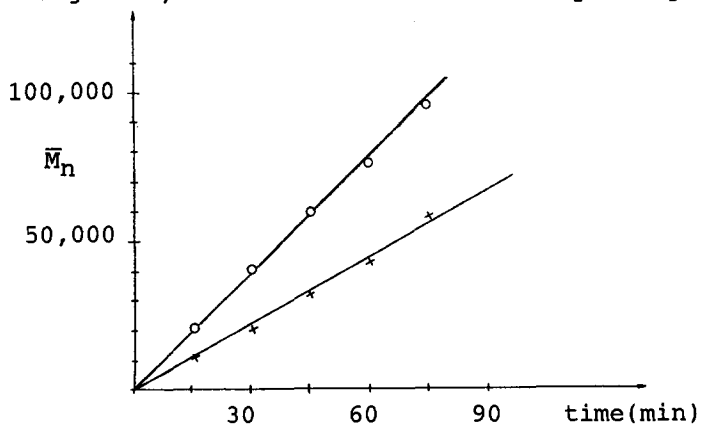

Figure 6. $\overline{M}_n$ versus time plots of PIBs prepared by the pDiCuOMe· TiCl$_4$ initiating complex at -80°C. (Conditions as in Figure 1). O: fully-grown PIB; X: half-grown PIB

peaks in the RI traces exhibited living character with one of
the fractions growing twice as fast and having $\overline{M}_n$s exactly
twice that of the other fraction. This observation is not too
surprising since the $\overline{M}_n$ of the fully-grown PIB fraction should
be twice that of the half-grown population. (The $\overline{M}_n$ values
have been obtained from GPC peak positions since the MWDs are
narrow.) It is theorized that the half-grown PIB is due to
ionized species that form during aging. The following scheme
helps to visualize these events:
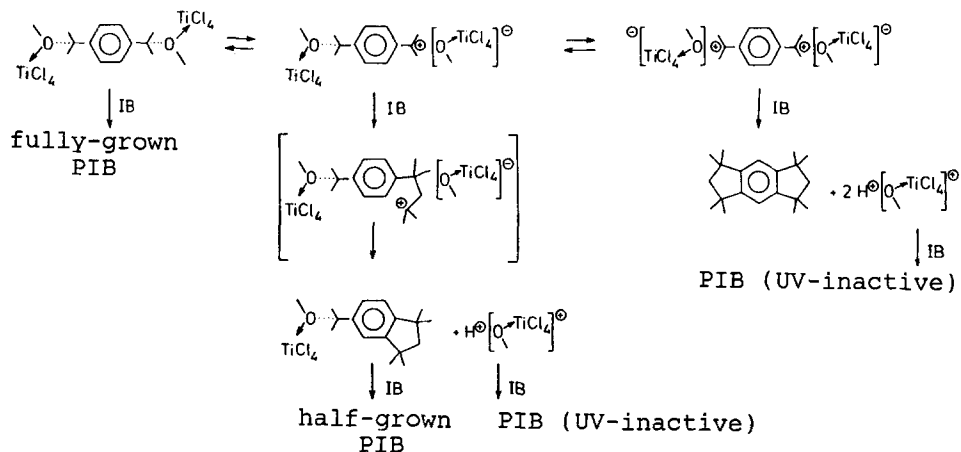
The ionized species is expected rapidly to add IB leading to
half-grown species and diindenes.
 This analysis leads to the proposition that indanyl end
group formation could be avoided by the use of unaged initi-
ating systems, in other words, with initiating systems pre-
pared in situ in the presence of monomer. Under such con-
ditions living polymerization by the desirable less-ionized(?)
species would be maximized whereas intramolecular alkylation
by the ionized species that arise during aging would be mini-
mized. Subsequent experiments carried out with in situ pre-
pared pDiCuOMe· TiCl₄ fully substantiated this analysis. In
these experiments the addition sequence of the ingredients
were:Solvent, Initiator, Monomer and lastly TiCl₄ coinitiator.
Figure 7 shows the results of a representative series of ex-
periments. The linear $\overline{M}_n$ versus W_p plot passing through the
origin and the horizontal $N/[I]_0$ versus W_p plot (insert) or-
iginating at $N/[pDiCuOMe]_0 = 1.0$ demonstrate living polymer-
izations. Initiator efficiency (I_{eff}, the moles of polymer
chains formed relative to the moles of pDiCuOMe used)were con-
sistently ∿100%. Gratifyingly, the $\overline{M}_w/\overline{M}_n$ values are 1.05-1.17,
within experimental error of Poisson MWDs. The systems are
homogeneous and M_ns in excess of 120,000 have been reached.
The narrow MWDs indicate that initiation is fast relative to
propagation.
 Direct evidence for the absence of indanyl structures
was obtained by ^{1}H NMR and IR analysis of low $\overline{M}_n$ (∿3000) sam-
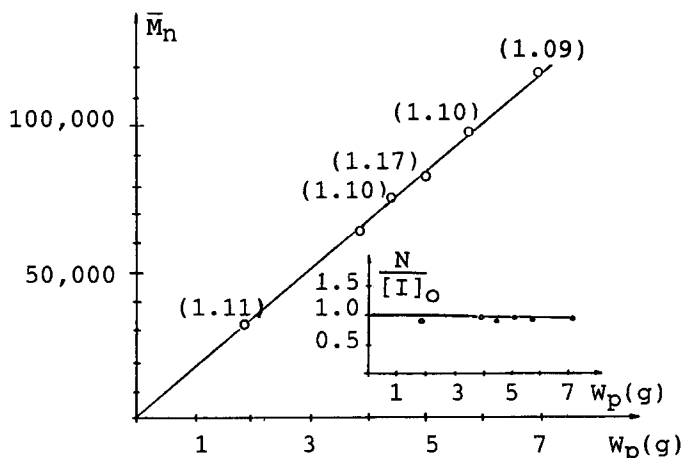ples so as to facilitate spectroscopic analysis. These samples

$$\overline{M}_n$$

Figure 7. $\overline{M}_n$ and $N/[I]_O$ (insert) versus W_p plots of a PIB prepared by the pDiCuOMe· $TiCl_4/IB/(CH_3Cl/n-C_6H_{14}$ 40/60 v/v)/-80°C system. ($[pDiCuOMe]_O = 6.4x10^{-5}$ mole; $[TiCl_4]_O = 1x10^{-3}$ mole; $V_O = 25$ mL). The numbers indicate $\overline{M}_w/\overline{M}_n$ values

were prepared by adding $TiCl_4$ to quiescent solvent + IB + pDiCuOMe mixtures at -80° in $CH_3Cl/n-C_6H_{14}$ 40/60 v/v. Figure 8 shows the results of a representative sample. In no case have we found evidence for the presence of indanyl structures in PIBs prepared by unaged initiating systems.
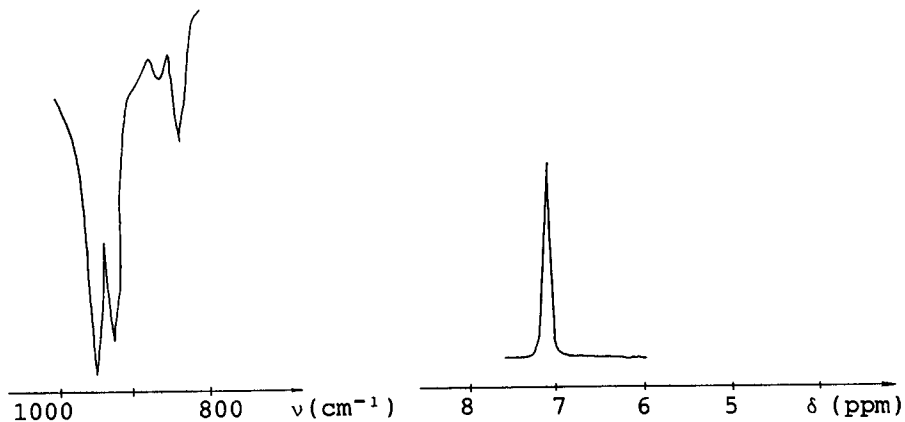

Figure 8. ^{1}H NMR and IR spectra of indane-free telechelic PIB prepared by the pDiCuOMe· $TiCl_4/IB/(CH_3Cl/n-C_6H_{14}$ 40/60 v/v)/-80°C system. ($[pDiCuOMe]_O = 1.6x10^{-3}$ mole; $[TiCl_4]_O = 2.5x10^{-2}$ mole; $V_O = 250$ mL; IB = 6.8 mL)

C) The $-CH_2(CH_3)_2Cl$ End Group

The end groups of PIBs obtained by the pDiCuOMe· TiCl₄ initiating system at -80°C and quenched by CH_3OH have been analyzed by ¹H NMR spectroscopy and were found to be $-CH_2(CH_3)_2Cl$, i.e., identical to those found previously in similar systems (1,6,10). To facilitate quantitative analysis the t-chlorine end groups were converted to isopropenyl termini $-CH_2\overline{C}(CH_3)=CH_2$ by the well established method (14). The ¹H NMR spectrum of the final product, the overall formula of which is shown in the introduction (Ia) was identical to that published earlier (6).

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