Synthesis of α, ω-Dichloro Polyindene and Poly(isobutylene-b-indene-b-isobutylene) Employing Kennedy's Inifer Technique

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Summary
        Kennedy's inifer technique has been modified and used for the preparation of α,ω-dichloro polyindene (PInCl$_2$). This telechelic has subsequently been used as initiator for the cationic isobutylene polymerization in conjunction with AlEt$_2$-Cl coinitiator. The resulting materials have been characterized by fractionation and GPC investigations.

Introduction
        The recently invented inifer method (KENNEDY and SMITH 1980) has been employed very successfully for the preparation of chlorine-telechelic polyisobutylenes. Using highly selective organic reactions a whole class of terminally difunctional and three arm star functional polyisobutylenes has been derived by KENNEDY and workers. From these telechelics novel isobutylene containing block copolymers could be synthesized. By the conventional inifer technique, however, no monomers other than isobutylene could be polymerized successfully to telechelics with quantitative terminal functionality. In this paper we demonstrate that the inifer technique can be modified and thus extended to other monomers such as indene.
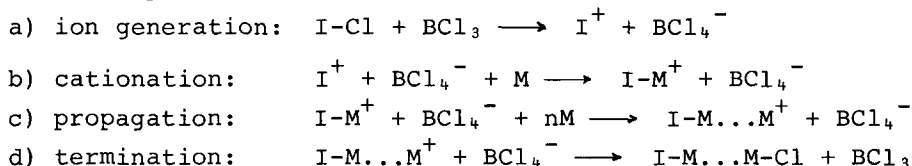
Experimental
        Materials: p-Dicumyl dichloride (DCC) was prepared following a synthesis developed in KENNEDY's laboratory: dimethyl terephthalate was first converted into 1,4 Bis(2-hydroxy isopropenyl)benzene by a Grignard reaction and subsequently the OH-groups were exchanged by Cl-groups with HCl in CH$_2$Cl$_2$. Isobutylene was dried over Na/K alloy and condensed in baked out storage vessels. Commercial indene (99%) was purified by the usual methods and distilled twice under dry argon atmosphere from CaH$_2$ and immediately used for polymerizations. CH$_2$Cl$_2$ (p.A.) was purified by conventional methods and distilled twice each from P$_2$O$_5$ and CaH$_2$ under dry argon atmosphere. After this procedure the water content of solvent and monomers was below the detection limit of the Karl-Fischer-titration (<1 mM). BCl$_3$ (Merck) was used without further purification. AlEt$_2$Cl was used as a 10% solution in pure heptane.
        Polymerizations: All polymerizations and block copolymerizations were carried out under a dry argon atmosphere in specially designed baked out glass reactors. The reactor was charged with solvent, monomer and initiator (DCC for preparation of telechelics and PInCl$_2$ for blocking experiments). The

mixtures were stirred at the desired temperature using a Dry
Ice/methanol bath. The polymerizations were then started by
direct introduction of the coinitiator solutions (BCl$_3$ in CH$_2$-
Cl$_2$ and AlEt$_2$Cl in heptane). After one minute for telechelic
preparation and 30 minutes for blocking experiments, respec-
tively, the reactions were terminated by the addition of a few
ml of methanol. The resulting materials were precipitated in-
to methanol and reprecipitated twice from benzene/methanol
(1:5). Fractionation of block copolymers was carried out by
precipitation of benzene solutions of the materials into pen-
tane and ethyl methyl ketone (MEK). The products were char-
acterized by double detection GPC, VPO and ^{1}H-NMR.

Results and Discussion
      The mechanism of inifer polymerizations has been exten-
sively described (KENNEDY and SMITH 1980, FEHERVARI et al.
1981, WONDRACZEK et al. 1982) and the following "inifer scheme"
has been postulated:

a) ion generation: $I-Cl + BCl_3 \longrightarrow I^+ + BCl_4^-$

b) cationation: $I^+ + BCl_4^- + M \longrightarrow I-M^+ + BCl_4^-$

c) propagation: $I-M^+ + BCl_4^- + nM \longrightarrow I-M...M^+ + BCl_4^-$

d) termination: $I-M...M^+ + BCl_4^- \longrightarrow I-M...M-Cl + BCl_3$

The "transfer to inifer" occurs by interaction of regenerated
BCl$_3$ with initiator molecules (DCC or Cl-I-M$_n$-Cl) according to
step a).
      Telechelics with perfect functionality can only be ob-
tained when functional termination (d) is by far preferred to
nonfunctional chain limitation, e.g., transfer to monomer.
This is the case when step (d) is fast and irreversible. Com-
plications during preparation of α,ω-dichloro polyisobutylenes
using the inifer method mainly result from intramolecular re-
actions after cationation (b) (CHANG and KENNEDY 1981). When
using monomers other than IB, however, the termination (d) may
be reversible, i.e. reinitation may occur. The resulting ap-
parently longer lifetime of the chain end carbenium ion may
lead to an increase in nonfunctional chain limitations, e.g.
transfer to monomer.
      The thought occurred to us to investigate the change of
conversion, molecular weight and functionality as a function
of the reaction time during indene polymerization. TABLE I
shows the results of these studies.
      Evidently the conversion is almost complete after one
minute whereas the functionality $\bar{F}_n$ decreases with increasing
reaction time. Increasing molecular weights and broadening of
the GPC elution diagrams (see Figure 1) indicate crosslinking
leading to a loss in chlorine functionality. Because of the
absence of monomer, transfer to monomer cannot be the reason.
Carbenium ions formed by reinitation most likely attack aro-
matic rings of the polymer chain, i.e. alkylation may occur
and lead to more stable carbenium ions:

After addition of fresh monomer these carbenium ions may start new chains.

TABLE I. Characteristic Data of Polyindene (PIn) Prepared by KENNEDY's Inifer Method ([In] = 1 M, [DCC] = 26 mM, [BCl] = 50 mM, CH Cl , 195 °K) as a Function of Reaction Time (Samples taken during a representative run)

t/min	Conv. %	Cl% (EA)[a]	$\overline{M}_n$ (VPO)	$\overline{F}_n$
1	ca. 95	1.28	5.000	1.80
3	ca. 100	1.11	n.d.	n.d.
5	100	1.04	n.d.	n.d.
10	100	0.94	n.d.	n.d.
30	100	0.89	5.500	1.30
60	100	0.76	n.d.	n.d.
90	100	0.54	6.800	1.05
120[b]	ca. 50	0.30	n.d.	n.d.

[a]chlorine by elemental analyses

[b]fresh monomer added after 90 min.; conversion of fresh monomer, bimodal distribution

FIGURE 1. GPC-Elution Diagrams of PInCl as a Function of Reaction Time: A = 1 min., B = 30 min., C = 90 min., D = 120 min. Fresh monomer added after 90 min.
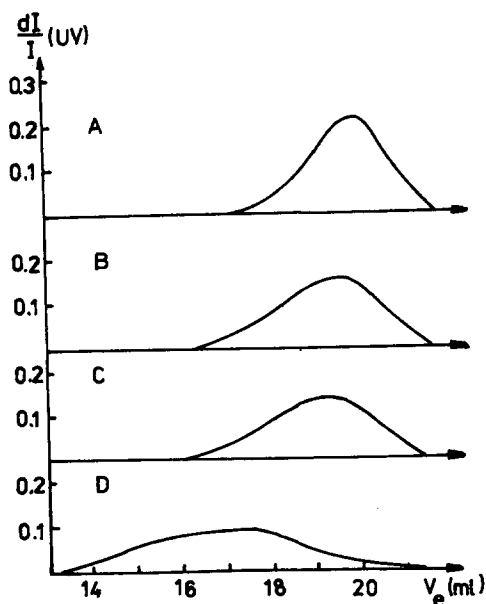
According to these results reinitiation is a very slow process.
This assumption is also supported by the findings of KENNEDY
et al. (1977a) that BCl_3 does not coinitiate cationic polymer-
izations effectively in conjunction with secondary benzylic
chlorides. Furthermore, short reaction times substantially
suppress the undesired reinitiation and polyindenes with close
to theoretical functionality can be obtained.

TABLE II shows the results of a number of reproducible
polymerizations of α,ω-dichloro polyindene ($PInCl_2$). These
data clearly prove that the chlorine-telechelic polyindenes
can be synthesized by the inifer technique.

TABLE II. Preparation of $PInCl_2$

| No. | Reaction Conditions | | | | Conv. | $\overline{M}_n$ | $I_{eff.}$ | $\overline{F}_n$ |
	[In]	[DCC]	[BCl$_3$]	T/°K	%	(VPO)	%	(EA)
1	0.7M	20mM	20mM	201	92	7.000	0.48	2.1
2	2.5M	58mM	66mM	201	99	5.000	0.91	2.1

These results intrigued us to carry out blocking experiments
using $PInCl_2$ as initiator and IB as comonomer. The technique
described by KENNEDY et al. (1977b) was slightly modified
(TABLE III). Fractionation experiments showed the absence of
pentane soluble fractions indicating that $PInCl_2$ is completely
consumed. Results of fractionation and GPC investigations,
however, showed that the crude product was chemically inhomo-
geneous (comp. TABLE III and Figure 2).

TABLE III. Results of Blocking Experiments

Reaction Conditions

$PInCl_2$ g	IB g	CH_2Cl_2 ml	T/°K	$AlEt_2Cl$ ml	Conv. IB %	MEK ins.	MEK sol.
1.3	6.3	30	201	0.1	73	90.7	9.3
13	28.0	300	195	0.5	89.6	92.1	7.9

TABLE IV shows characterization data of the block copolymer
prepared from product 1 in TABLE II (which corresponds with
line 1 in TABLE III). The B(UV/RI) are the coefficients of
determination of the correlation between UV and RI responses
of GPC-elution diagrams and allow approximate conclusions on
the homogeneity of the materials. On hand of a linear cali-
bration curve of the intensity ratios of RI and UV detector
responses of indene/isobutylene copolymers (I(UV/RI)) of known
composition, the compositions of the product fractions could
be estimated. These data are in good agreement with those ob-
tained by ^{1}H-NMR analyses.

The main fraction of the crude product obviously consists
of a high molecular weight PIB rich material (pentane-soluble-
and-MEK-insoluble fraction). It is rubbery similar to very
high molecular weight PIB. The minor component is a white
powder. Additional investigations will be carried out to fur-
ther characterize the nature of these products.

FIGURE 2. GPC-Elution Diagrams of the Product Fractions of Blocking Experiments (1) in TABLE III: A = Starting Materials, B = Crude Product, C = MEK Soluble Fraction, D = MEK Insoluble Fraction
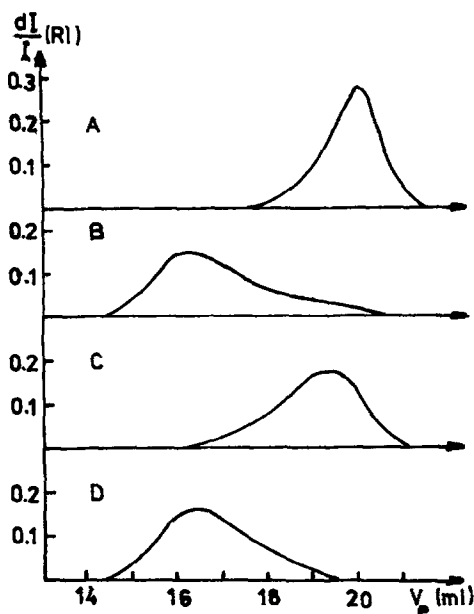

TABLE IV. Characterization of Poly(IB-b-In-b-IB) (Material of Line 1 in TABLE III)

Fraction	I(UV/RI)	B(UV/RI)	$\overline{M}_n$(VPO)	% IB(GPC)	% IB(NMR)
PInCl$_2$ (1)	523/296	0.996	7.000	0	0
crude	133/322	0.740	24.600	78	75
MEK sol.	324/328	0.991	5.300	44	49
MEK ins.	96.5/336	0.989	26.600	85	82

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