Inifers

New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator Transfer Agents (Inifers)
44. End-Reactive Three-Arm Star Polyisobutylenes by Continuous Polymerization

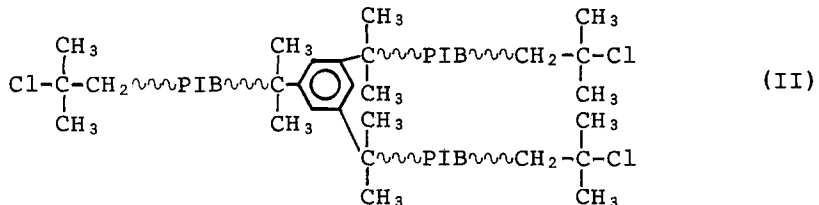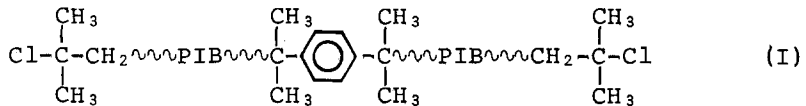**A. Nagy*, R. Faust, and J. P. Kennedy**

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Summary
        Three-arm star polyisobutylenes carrying tert.-chlorine
end groups and a phenyl ring at the center of the star (see
formula II in the Introduction) have been prepared by a contin-
uous polymerization process. Thus into a stirred glass reac-
tor were fed continuously a mixed feed of monomer plus trinifer
(TCC) and a separate feed of BCl_3 coinitiator in methyl chlo-
ride solvent at $-40°C$, and the product plus unreacted ingred-
ients were removed continuously. Stationary conditions were
maintained by keeping the rates of input and output (i.e., vol-
umes) equal and constant. After a short induction phase ($\sim 2-3$
residence times) telechelic polymers of essentially theoretical
number average end functionalities ($\bar{F}_n = 3.0\pm0.1$), close to
theoretical molecular weights ($\bar{M}_n$) and molecular weight distri-
butions were obtained. The polymerization kinetics are dis-
cussed and compared to that of an earlier semicontinuous pro-
cess used for the routine synthesis of telechelic polyisobuty-
lenes.

Introduction
        A semicontinuous polymerization technique has recently
been developed for the synthesis of linear (I) and three-arm
star (II) polyisobutylenes carrying tert.-chloro end groups
and a phenyl ring at the statistical center of the molecule(1):

$$Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2\sim\sim\sim PIB\sim\sim\sim\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\bigcirc-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim\sim\sim PIB\sim\sim\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl \qquad (I)$$

$$Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2\sim\sim\sim PIB\sim\sim\sim\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\bigcirc \begin{cases} -\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim\sim\sim PIB\sim\sim\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl \\ CH_3 \qquad\qquad\qquad CH_3 \\ \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\sim\sim\sim PIB\sim\sim\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl \end{cases} \qquad (II)$$

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In this technique a mixed monomer/inifer (i.e., binifer for the
linear and trinifer for the three-arm star variety) feed is
added at a low constant rate to a stirred charge of BCl_3 coin-
itiator plus solvent. Under stationary conditions well defined
telechelic products with identical end groups, essentially the-
oretical end functionalities, molecular weights, and molecular
weight distributions have been obtained (1). The advantages
of the semicontinuous technique over that of the conventional
technique (i.e., adding BCl_3 coinitiator to monomer/inifer
charges) have been analyzed and demonstrated (1).

This paper describes an improved truly continuous inifer
polymerization process for the preparation of three-arm star
telechelic polyisobutylenes and, specifically, the synthesis of
well-defined three-arm star tert.-chlorine ended polyisobuty-
lenes by this novel continuous technique.

Experimental
The source, purity or purification of isobutylene, BCl_3,
and methyl chloride has been described (1,2). The trinifer,
1,3,5-tri(2-chloro-2-propylbenzene), commonly called tricumyl
chloride (TCC), has been prepared by hydrochlorination of 1,3,5-
triisopropenylbenzene (3) followed by multiple (at least three)
recrystallizations; mp ≃ 69°C. The 1,3,5-triisopropenylbenzene
was prepared by dehydrobromination of 1,3,5-tri(2-bromo-2-pro-
pylbenzene) (4) which in turn was obtained by bromination of
1,3,5-triisopropylbenzene with N-bromo succinimide (5).

Experiments have been carried out in a stainless steel
enclosure under a dry nitrogen atmosphere at −40°C by using a
glass assembly immersed in a thermostatted cooling bath. Fig-
ure 1 shows the scheme of the assembly. Into the reactor (a
250 ml flask equipped with input and exit tubes and stirrer)
were fed by applying a constant nitrogen pressure: 1) a stream
of solution containing isobutylene and trinifer dissolved in
methyl chloride (Reservoir I), and 2) a stream of BCl_3 dissolved
in methyl chloride (Reservoir II). These solutions were

Figure 1. Assembly used for Continuous Polymerization

SAMPLE
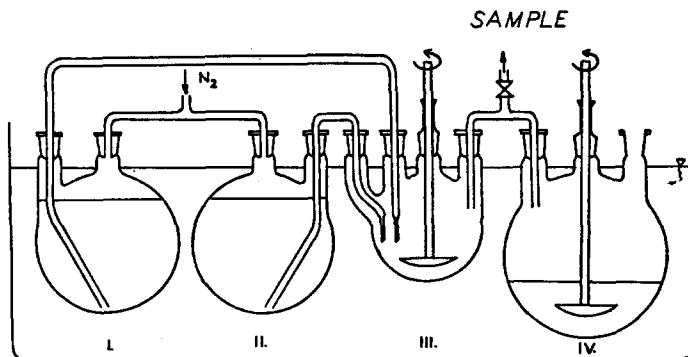
prepared as follows: First the methyl chloride was condensed at -40°C in a calibrated vessel (a generous forecut was discarded) and the required volumes added to Reservoirs I and II. The required amount of trinifer was dissolved in the methyl chloride in Reservoir I and liquefied isobutylene was added. (The isobutylene was condensed in a calibrated measuring cylinder at -40° and a generous forecut was discarded). Finally the required amount of liquid BCl_3 was added to the methyl chloride in Reservoir II. The liquid BCl_3 was obtained by condensing the gas in a culture tube. The input rate was controlled by the nitrogen pressure applied. The exit tips of the isolated Teflon input tubes were equipped with stainlesss steel hypodermic needles to provide a measure of back-pressure and thus to insure a continuous constant flow rate, i.e., to avoid dripping. The product slurry plus unreacted ingredients (i.e., solvent, BCl_3) exited through a Teflon tube into a larger (3) stirred receiver containing some methanol to quench the reaction. The exit tube was equipped with a valve through which samples could be taken to follow the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ profiles during the run.

Details concerning the purification of polymers, structure analyses (by ^{1}H-NMR spectroscopy), and molecular weight determinations (GPC, VPO) have been described (1).

Results and Discussion
Kinetic Considerations

The kinetics of polymerization of isobutylene by the inifer/BCl_3 system has repeatedly been described in terms of the elementary reactions a) ion generation, b) cationation, c) propagation, d) chain transfer to inifer, and e) termination (1, 2,). Kinetic aspects of a semicontinuous process have recently been treated by the use of this scheme also (1). It occurred to us that the kinetics of a continuous inifer polymerization process can be treated similarly to the semicontinuous one, except in the former we have to consider not only the input rates of the ingredients but also the rate of their removal. Figure 2 helps to visualize the overall process,

Figure 2. Scheme of Continuous Polymerization
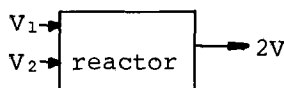
where V_1 = input rate of monomer plus trinifer solution, V_2 = input rate of BCl_3 solution, $2V$ = exit rate of product plus unreacted ingredients. In this system $V_1 = V_2 = V$. Concentration changes during polymerization are described by the following set of differential equations:

$$\frac{d[M]}{dt} = V[M_o] - k_c[I^{\oplus}][M] - k_p[M_n^{\oplus}][M] - 2V[M] \tag{1}$$

$$\frac{d[I]}{dt} = V[I_o] - k_i[I][BCl_3] - k_{tr,I}[M_n^{\oplus}][I] + k_{-i}[I^{\oplus}] - 2V[I] \tag{2}$$

$$\frac{d[M_n^\oplus]}{dt} = k_c[I^\oplus][M] - k_{tr,I}[M_n^\oplus][I] - k_t[M_n^\oplus] - 2V[M_n^\oplus] \tag{3}$$

$$\frac{d[I^\oplus]}{dt} = k_{tr,I}[M_n^\oplus][I] - k_c[I^\oplus][M] + k_i[I][BCl_3] - k_{-i}[I^\oplus] - 2V[I^\oplus] \tag{4}$$

$$\frac{d[M_n]}{dt} = k_{tr,I}[M_n^\oplus][I] + k_t[M_n^\oplus] - 2V[M_n] \tag{5}$$

where I, M and M_n are inifer, monomer and polymer, respectively, $I^\oplus$ and $M_n^\oplus$ are inifer and polymer cations, k_i, k_{-i}, k_c, k_p, $k_{tr,I}$ and k_t are the corresponding rate constants, and the subscript o indicates initial concentrations. Except for the additional last term in eqs 1-5, these expressions are identical to those derived earlier (1). In continuous polymerization systems, under stationary conditions:

the $\dfrac{d[M]}{dt}$, $\dfrac{d[I]}{dt}$, $\dfrac{d[M_n^\oplus]}{dt}$, $\dfrac{d[I^\oplus]}{dt}$, and $\dfrac{d[M_n]}{dt} = 0$ \hfill (6)

i.e., the concentrations of monomer, inifer, cations and polymer are constant.

The number average degree of polymerization is:

$$\overline{DP}_n = \frac{k_p[M_n^\oplus][M] + k_c[I^\oplus][M]}{k_{tr,I}[M_n^\oplus][I] + k_t[M_n^\oplus]} \tag{7}$$

Based on eqs.(1) through (7) after simplification:

$$\overline{DP}_n = \frac{[M_o]}{[I_o] - 2([I] + [M_n^\oplus] + [I^\oplus])} - \frac{2[M]}{[I_o] - 2([I] + [M_n^\oplus] + [I^\oplus])} \tag{8}$$

Under stationary conditions, the values of [M], [I], $[M_n^\oplus]$ and $[I^\oplus]$ are negligible in comparison with those of $[M_o]$ and $[I_o]$. Thus the second term in eq. 8 becomes negligible and the expression $2([I] + [M_n^\oplus] + [I^\oplus])$ in the denominator of the first term of (8) is also negligible; thus eq. 8 simplifies to

$$\overline{DP}_n = \frac{[M_o]}{[I_o]} \text{ feed} \tag{9}$$

Evidently, the number average degree of polymerization of products obtained in continuous polymerizations are identical to those obtained in semicontinuous polymerization systems (1).

Experimental Results

A series of continuous experiments have been carried out and representative results are compiled in Table I. In all experiments the trinifer was TCC, except in the first run where it was the bromo derivative 1,3,5-tri(2-bromo-2-propylbenzene) TCB (tricumyl bromide, for short). The preparation and purification of TCB has been described (5).

After a relatively short induction period (about 2-3 residence times) needed to fill the reactor and to rinse the

reactor of products formed during the nonstationary phase, the stationary phase was reached and the polymer molecular weights remained constant throughout the run. The data in Table I reflect those obtained during the latter stationary phase (after 2-3 residence times whose length depended on the input rate). The $\bar{M}_n$ of the samples were routinely determined by GPC; the variation in the $\bar{M}_n$ data are considered to be within experimental error. In two instances $\bar{M}_n$ was also determined by VPO. The fact that these $\bar{M}_n$ data are close (±10%) to the expected (theoretical) values obtained from eq. 9 and that they are lower than those determined by GPC, enhances their credibility ($\bar{M}_n$ data obtained by VPO are usually lower than those determined by GPC on account of the very high sensitivity of the VPO method toward low molecular weight impurities).

TABLE I. Results of Continuous Polymerizations

Exp. No.	IB	Inifer in feed mole/ℓ	BCl₃	Feed rate ml/min	Time min	$\bar{M}_n$ theor.	exp. GPC	VPO	$\bar{M}_w/\bar{M}_n$	Yield %
2	0.54	1x10⁻²*	0.10	16	60	3400	4200		1.78	∿100
6	0.90	1.3x10⁻²	0.12	25	25		4400		1.64	
					33		4500		1.66	
					39		4700		1.60	
					R	4200	4800		1.62	∿100
7	1.54	2.3x10⁻²	0.20	13	68		3500		1.58	
					74		4600		1.57	
					R	4100	5000	3700	1.57	∿100
8	1.29	2x10⁻²	0.20	18	69**		5000		1.47	
					74		4700		1.57	
					80		4700		1.55	
					R	3900	5100	4300	1.54	∿100
10	0.86	1.16x10⁻²	0.12	16	40		3700		1.49	
					50		4700		1.44	
					55		5000		1.50	
					58		5000		1.53	
					R	4500	5100		1.59	∿100

*Trinifer TCB, R = product in reactor ** = feeding rate was increased to 30ml/min from this point on.

The $\bar{M}_n$ data obtained by GPC was calculated by the use of a calibration curve prepared with well fractionated linear polyisobutylene standards. This calibration curve is not exactly valid for the characterization of three-arm star polymers, however, the error due to this approximation must be small in view of the relatively low molecular weight range (3500-5000) investigated and the agreement between the select GPC and VPO data.

Molecular weight distributions (i.e., $\bar{M}_w/\bar{M}_n$ = 1.5-1.7) were quite close to the expected or theoretical value, $\bar{M}_w/\bar{M}_n$= 1.33 (1) for three-arm star telechelic polyisobutylenes.

Satisfactory agreement between experimental and theoretical $\bar{M}_n$s, and the close to 100% yields (last column, Table I) indicate that the amounts of unreacted monomer and inifer that prevailed in the reactor and left the same were indeed negligible.

As expected, the $\bar{M}_n$ was independent of the feeding rate in the range investigated, i.e., from 13 to 30 ml/min.

The structure of the products has been studied by ^{1}H NMR spectroscopy. To this end the tert.-chloride capped end groups were quantitatively dehydrochlorinated and the isopropylidene-ended three-arm star telechelics analyzed by ^{1}H-NMR spectroscopy. The methodology has been described in detail (1,6). According to these studied the products were free of unreacted and/or "once-fired" end groups, similarly to those obtained by semicontinuous experiments (1).

Conclusions
These studies demonstrate the continuous synthesis of three-arm star tert.-chloro capped polyisobutylenes with well defined symmetrical end groups. Reactor control is readily accomplished and undesirable by-products are absent. After a short nonstationary period [M] and [I] are constant in the reactor and the molecular weight of the product can be readily controlled by the rate of input of monomer and inifer. Yields are ∿100% and molecular weight distributions ($\bar{M}_w/\bar{M}_n$) are close to theoretical.

Acknowledgement

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