

**New Telechelic Polymers and Sequential Copolymers  
by Polyfunctional Initiator-Transfer Agents (Inifers)  
10. Three-Arm Star Telechelic Polyisobutylenes Carrying Chlorine,  
Olefin or Primary Alcohol Endgroups**

**Joseph P. Kennedy, Louis R. Ross, Jeffrey E. Lackey and Oskar Nuyken\***

Institute of Polymer Science, University of Akron, Akron, Ohio 44325, USA

Summary

Three-arm star telechelic liquid polyisobutylenes carrying exactly three  $-C(CH_3)_2Cl$  endgroups have been synthesized and characterized. Subsequently the tertiary chlorine endgroups have been quantitatively converted to terminal olefins and these in turn to primary alcohols. These terminally trifunctional oligomers are most valuable intermediates for the preparation of networks.

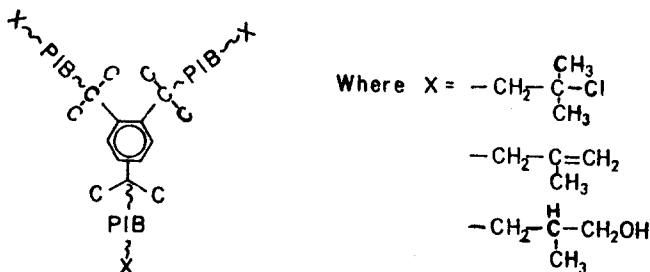
Introduction

The synthesis and characterization of linear telechelic ( $\alpha, \omega$ -difunctional) polyisobutylenes have recently been described (KENNEDY and SMITH 1980). The synthesis principle involved the use of bifunctional initiator-chain transfer agents, inifers. For example, the use of the p-dicumyl chloride/ $BCl_3$  inifer system led to the preparation of polyisobutylenes carrying exactly two  $-CH_2C(CH_3)_2Cl$  termini with a functionality of 2.0. Dehydrochlorination of these polyisobutylene  $\alpha, \omega$ -dichlorides with a hindered base quantitatively yielded telechelic polyisobutylene  $\alpha, \omega$ -diolefins (KENNEDY et al. 1979) which upon hydroboration quantitatively yielded telechelic polyisobutylene glycols (B. IVAN et al. 1980). The latter have been reacted with isocyanates giving rise to new polyisobutylene-based polyurethanes (KENNEDY et al. to be published; NUYKEN et al. to be published) whose exploration is actively pursued in our laboratories.

In the course of these investigations the thought occurred to us to extend the inifer concept used for the synthesis of linear telechelics (KENNEDY and SMITH 1980) to the preparation of star-shaped (radial) telechelic polymers. Indeed we were able to demonstrate that tri-functional initiator-chain transfer agents, so-called trinifers, are eminently suitable for the synthesis of three-arm telechelic stars and that the polymerization mechanism leading to these terminally trifunctional products is even less prone to undesirable

\* Visiting Scientist, permanent address: Lehrstuhl für Makromolekulare Stoffe, Technische Universität München, D-8046 Garching, W. Germany

side-reactions (ROSS 1981) than the route that leads to linear telechelics. This paper concerns the synthesis and characterization of a new family of three-arm star telechelic polyisobutylenes i.e., radial polyisobutylenes carrying exactly three  $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{Cl}$  termini, and quantitative transformation of these endgroups into triolefins and primary triols:

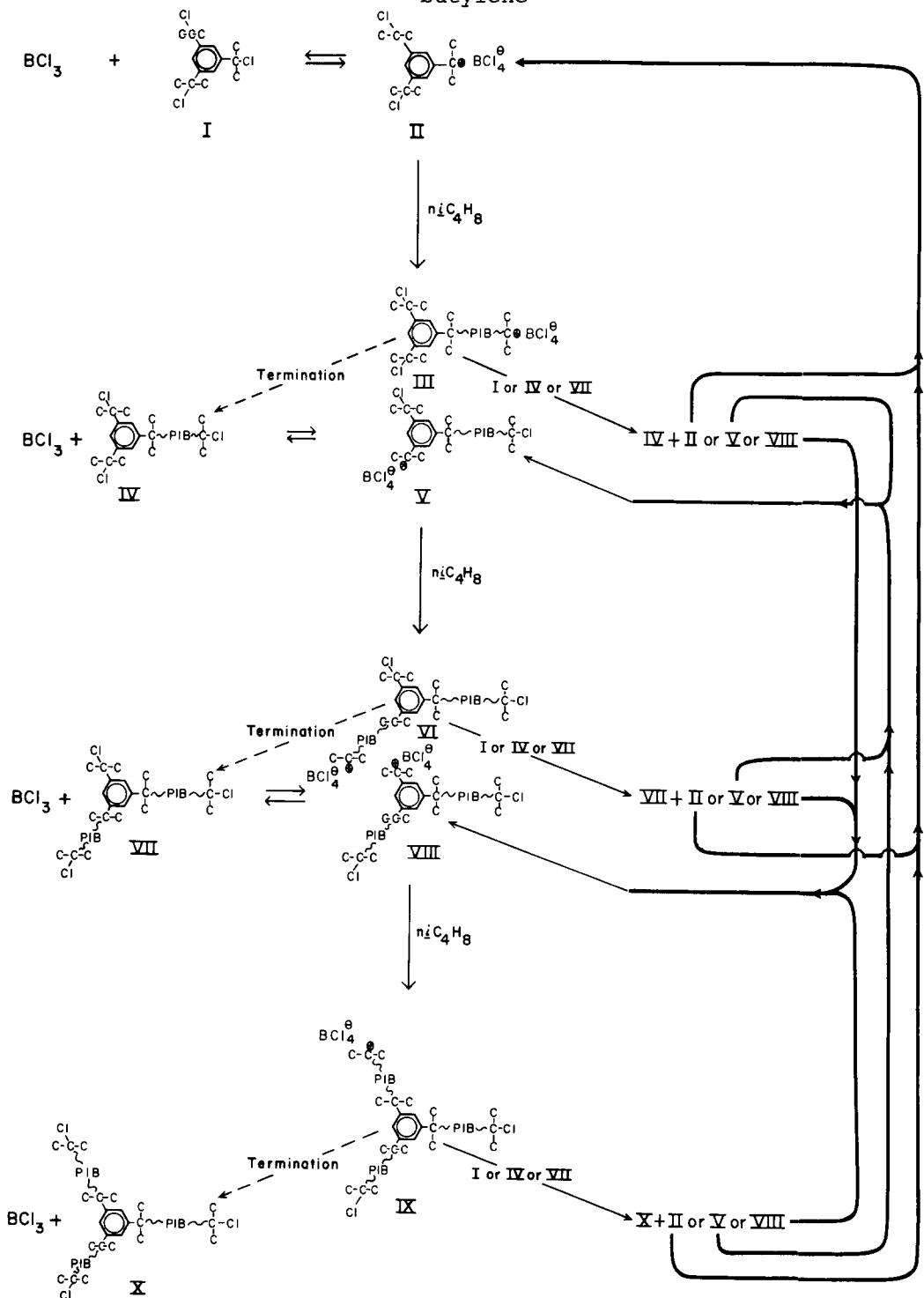


## Results and Discussion

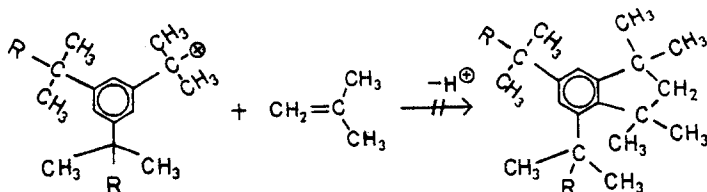
### A. Synthesis of Three-Arm Star Polyisobutylene Trichloride X.

Similar to the synthesis of linear telechelic polyisobutylene dichlorides with the bifunctional inifer ("binifer") p-dicumyl chloride (KENNEDY and SMITH 1980), three-arm star telechelic polyisobutylene trichlorides can be obtained by the use of the symmetrical tricumyl chloride (TCC)/ $\text{BCl}_3$  trinifer system. Scheme I summarizes the reactions leading to three-arm star polyisobutylene trichlorides using this trinifer system. This scheme is conceptually identical to that proposed to account for the formation of linear telechelic polyisobutylene dichlorides (KENNEDY and SMITH 1980), except the earlier scheme has been modified to account for the presence of trinifer TCC in place of the binifer, p-dicumyl chloride. Thus  $\text{BCl}_3$  in conjunction with TCC I yields a tertiary benzylic cation II, which initiates isobutylene polymerization. The propagating tertiary carbenium ion III may be terminated by collapse of the counterion (termination, indicated by the broken line) or by transfer of a tertiary benzylic chloride from I, IV, or VIII (solid line). The product in either case is IV. The two remaining tertiary benzylic chlorines of IV are susceptible to initiation with  $\text{BCl}_3$  or transfer to a propagating tertiary carbocation. These processes continue until all tertiary benzylic chlorines have been converted to tertiary alkyl chlorines incapable of reinitiation with  $\text{BCl}_3$ . The product is the desired three-arm star telechelic polyisobutylene X.

Scheme I. The Trinifer Mechanism Leading to Three-arm Star Telechelic Polyisobutylene



Intramolecular cyclization (indane-skeleton formation) may occur during the synthesis of linear telechelic polyisobutylenes by the binifer technique and synthesis conditions must be carefully controlled to overcome this undesirable side-reaction (CHANG et al. 1980). In contrast, indane-skeleton formation is absent during the synthesis of three-arm star telechelic polyisobutylenes by the trinifer system. A close inspection of the steric course of the initial cumylation step and subsequent first isobutylene propagation step suggests considerable steric hindrance for indane-skeleton formation:



Experimentally we added BCl<sub>3</sub> to stirred TCC/isobutylene charges containing various concentrations of TCC. Representative data are shown in Table I. Initiator (trinifer) efficiency was close to 100% particularly at low [TCC]. Evidently an inverse linear relationship exists between  $\bar{M}_n$  and [TCC]. This effect is similar to that found and quantitatively treated with the binifer system (KENNEDY et al. 1980; FEHÉRVÁRI et al. 1980). Kinetic experimentation is in progress to define the effect of various parameters on the polymerization mechanism.

Table I  
The Syntheses of Three-arm Star  
Telechelic Polyisobutylenes

TCC M x 10 <sup>4</sup>	Conversion %	$\bar{M}_n$ (Osmometry)	Initiator efficiency %
9	36	35,000	94
22	59	27,000	81
50	62	14,000	72

[i-C<sub>4</sub>H<sub>8</sub>] = 1M, [BCl<sub>3</sub>]  $\approx$  10 x [TCC], solvent CH<sub>3</sub>Cl, -70°C, total volume = 300 ml

Characterization of X involved a battery of spectroscopic techniques, i.e., <sup>1</sup>H and <sup>13</sup>C NMR, IR, UV using relatively low molecular weight materials to allow the quantitative determination of constituents, thermal

dehydrochlorination (ROSS 1981) and, perhaps most importantly, the selective oxidation of the central phenyl ring with  $\text{CF}_3\text{COOH}/\text{H}_2\text{O}_2$  followed by  $\bar{M}_n$  determination of surviving polyisobutylene fragments (KENNEDY et al., to be published). Details which conclusively prove that the synthesis of X by the  $\text{TCC}/\text{BCl}_3$  trifer system produces three-arm star polyisobutylene trichlorides will be published separately (ROSS 1981).

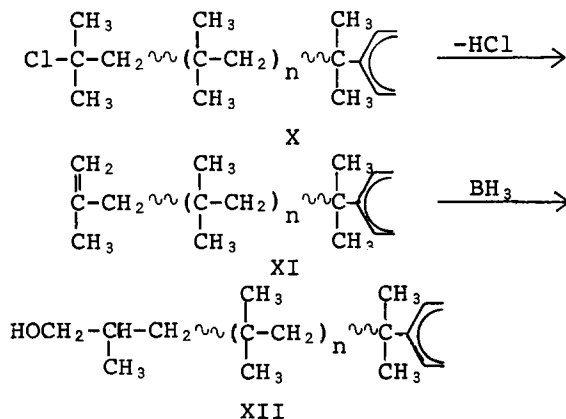
B. Synthesis of Three-Arm Star Polyisobutylene Triolefin XI

The synthesis of XI was carried out by quantitative dehydrochlorination of X with the hindered base *t*-BuOK (see Experimental). Conditions were identical to those used to convert the linear telechelic polyisobutylene dichloride to the exo-diolefin (KENNEDY et al. 1979). Quantitative  $^1\text{H}$  NMR spectroscopy confirmed our expectation that dehydrochlorination of X was complete under the conditions employed and that the product XI was in fact a three-arm star polyisobutylene carrying exactly three  $-\text{CH}_2-\text{C}(\text{CH}_2)=\text{CH}_2$  termini.

C. Synthesis of Three-arm Star Polyisobutylene Triol XII

The conversion of olefins to alcohols by hydroboration followed by alkaline oxidation is a well known quantitative reaction (BROWN 1972). We have used this reaction to convert quantitatively linear telechelic polyisobutylene diolefins to glycols (IVÁN et al. 1980). Similarly, we have obtained XII from XI by hydroboration with  $\text{BH}_3$  in THF and oxidation with  $\text{NaOH}/\text{H}_2\text{O}_2$  (see Experimental).

The following equation helps to visualize these conversions:

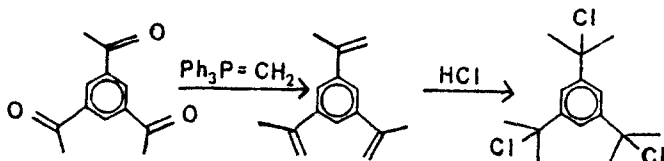


These new terminally functional three-arm star polyisobutylenes open up numerous new avenues toward the synthesis of novel sequential copolymers, radial blocks, networks, etc. of interesting combinations of properties.

### Experimental

#### A. Trinifer (I)

Symmetrical tricumyl chloride (1,3,5-tris[1-chloro-1-methyl-ethyl]benzene, TCC) has been synthesized by conversion of 1,3,5-triacetyl benzene to the olefin via the Wittig reaction and subsequent hydrochlorination:



A 2000 ml 3-neck round bottom flask, equipped with a reflux condenser, stirrer, and  $N_2$ -inlet was charged with 500 ml dry glyme and 0.1 mole (35.72g) methyltriphenylphosphonium bromide, forming a milky suspension. Then 0.11 moles (2.64g) sodium hydride were added and the mixture was stirred for 6 hrs at room temperature. Finally 0.03 moles (6.06g) 1,3,5-triacetyl benzene were added. After 4 hrs refluxing the heat was removed and distilled water was added to destroy the remaining sodium hydride. The contents of the reaction were extracted with diethyl ether and the ether was removed yielding a reddish-brown solid. The 1,3,5-triisopropenyl benzene, an amber oil, was isolated by trituration with n-hexane.  $^1H$ -NMR in  $CCl_4$ ,  $\delta = 7.3$  ppm (3H,s,aromatic);  $\delta = 5.0 - 5.3$  ppm (6H,2s,  $C=CH_2$ );  $\delta = 2.15$  ppm (9H,s, $CH_3$ ).

The hydrochlorination of 1,3,5-triisopropenyl benzene was carried out using  $CH_2Cl_2$  at  $0^\circ C$  by bubbling dry HCl through the charge for several hours. The  $CH_2Cl_2$  was removed by vacuum and the product was recrystallized from n-hexane yielding 1,3,5-tris-[1-chloro-1-methyl ethyl]benzene (m.p.  $68-69^\circ C$ ) (SEIDEL et al. 1956).  $^1H$  NMR in  $CCl_4$ ,  $\delta = 7.6$ ppm (3H,s,aromatic);  $\delta = 2.0$  ppm (18H,s,methyl).

#### B. Polymerization, Materials and Procedures

Isobutylene and methyl chloride were dried by passing the gases through columns filled with BaO and molecular sieves (4Å). Boron trichloride (Linde Co.) was distilled from lecture bottles. Tetrahydrofuran used in gel permeation chromatography (GPC) analysis was dried over  $CaH_2$  and distilled under  $N_2$ .

All manipulations and polymerizations were carried out in a stainless-steel enclosure under a  $N_2$  atmosphere. Details have been described (KENNEDY et al. 1980).

C. Three-Arm Star Polyisobutylene-Trichloride X

The polymerization was carried out in a 2 l 3-neck round bottom flask equipped with a mechanical stirrer. The reaction vessel was charged with  $CH_3Cl$ , monomer, and TCC and cooled to  $-70^\circ C$ . Polymerization was started by adding a precooled solution of  $BCl_3$ . The reaction became immediately heterogeneous. Thirty minutes after  $BCl_3$  was added prechilled methanol was added to stop the reaction.

D. Three-arm Star Polyisobutylene-Triolefin XI

A 5% (wt.) solution of X in 250 ml dry THF was charged into a three-neck flask equipped with stirrer, condenser, and dropping funnel under a dry nitrogen atmosphere. Then 6.25g t-BuOK (ca. 10 times molar excess of X) dissolved in 25 ml THF were added dropwise over a period of 30 min. After 24 hours of refluxing approximately 200 ml THF was removed. n-Hexane (200 ml) was added, the solution was washed with water and dried. After filtration the solvent was evaporated and the product was dried under vacuum at ambient temperature.  $^1H$  NMR in  $CCl_4$ ,  $\delta = 7.0-7.1$  ppm (3H,s,aromatic);  $\delta = 4.8$  ppm (6H,2s,C=CH<sub>2</sub>).

E. Three-arm Star Polyisobutylene-Triol XII

Hydroboration of XI was carried out in a three-neck flask equipped with stirrer and dropping funnel. A solution of XI in THF (2 wt%) was added into excess  $BH_3 \cdot THF$  dropwise about 30 min under a dry nitrogen atmosphere. After 5 hrs stirring at  $0^\circ C$ , stoichiometric amounts of 3N NaOH and subsequently 30%  $H_2O_2$  were added dropwise maintaining the temperature below  $45^\circ C$ . The mixture was stirred for two hours, then n-hexane was added, stirred for a few more minutes, and the aqueous phase was saturated with potassium carbonate. The organic layer was washed several times with distilled water, separated, and dried with anhydrous magnesium sulfate. After filtration the solvent was evaporated and the product was dried.  $^1H$  NMR in  $CCl_4$ ,  $\delta = 7.0-7.1$  ppm (3H,s,aromatic);  $\delta = 3.0-3.4$  ppm (6H,d,CH<sub>2</sub>OH).

The functionality was determined quantitatively by NMR spectroscopy. The ratio of the area of the peak at 7.0-7.1 to the area of the peaks at 3.0-3.4 was 0.5 indicating a functionality  $F_n = 3$ .

Acknowledgement

Financial help by NSF grant DMR-77-27618, Polymer Program, and the Deutsche Forschungsgemeinschaft (to N.O.) is gratefully acknowledged.

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*Received December 22, 1980*