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Functional Polymers by Cationic Techniques

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ABSTRACT

Extensive studies on the mechanism of carbocationic polymerization initiation and particularly termination yielded information useful for the synthesis of a variety of new mono- and difunctional (telechelic) polymers. Unraveling aspects of initiation has opened new avenues toward the synthesis of novel cationic graft copolymers. Understanding details of termination has led among other products to cyclopentadiene-ended polyisobutylene and cyclopentadienylated rubbers. The latters crosslink by Diels-Alder addition and produce thermally reversible networks. Combination of controlled initiation and termination yielded telechelic products e. g., α,ω-diene-polyisobutylene. The use of Cl_2/BCl_3 combinations led to the synthesis of α,ω-dichloropolyisobutylenes.

INTRODUCTION

Recent research in this author's laboratory concerned the understanding of mechanism of elementary events occurring in cationic olefin polymerization. Investigations focused on elucidating and subsequently controlling initiation and termination of polymerizations induced by cationogenic initiators in conjunction with Lewis acid coinitiators. It was projected that by controlling these events the synthesis of a variety of new useful functional polymers will become possible.

A thorough and continuous study of ionic polymerizations in general and cationic polymerization in particular leads this author to believe that this field of polymer synthesis is somewhat overlooked by contemporary investigations in favor of the study of anionic polymerizations. One of the reasons for this benign neglect is most likely the fact that the chemistry and kinetics of anionic polymerizations are simpler and better understood than those of the cationic systems. This is particularly true of "living" anionic polymerizations, i. e., of systems devoid of termination and chain transfer, which readily lend themselves for the synthesis of some well defined macromolecules. Conventionally, the mechanism of a carbocationic polymerization is discussed in terms of five elementary events:

Ion generation or "priming":

$$\text{HX or RX} + \text{MeX}_n \longrightarrow \text{H}^{\oplus} \text{ or } \text{R}^{\oplus} + \text{MeX}^{\ominus}_{n+1} \qquad (1)$$

Initiation:

$$\text{H}^{\oplus} \text{ or } \text{R}^{\oplus} + \text{C=C} \longrightarrow \text{H(or R)}\!-\!\text{C}-\text{C}^{\oplus} \qquad (2)$$

Propagation:

$$-\text{C}^{\oplus} + \text{C=C} \longrightarrow -\text{C}-\text{C}-\text{C}^{\oplus} \qquad (3)$$

Chain transfer (to monomer):

$$-\text{C}-\text{C}-\text{C}^{\oplus} + \text{C=C} \longrightarrow -\text{C}-\text{C=C} + \text{C}-\text{C}^{\oplus} \qquad (4)$$

Termination:

$$-\text{C}^{\oplus} \longrightarrow -\text{C} \qquad (5)$$

Steps (1) and (2) usually are not separated and are considered together as the initiation step. Among the numerous chain-transfer possibilities, chain transfer to monomer is most prevalent, however, chain transfer to solvent, polymer, and/or counteranion may also occur.

Very few authors inquired seriously into the nature of termination in carbocationic polymerizations and analyzed the question of why these polymerizations stop.

The quest for living cationic systems is on, and considerable progress toward this goal has recently been made by using heterocyclic monomers, e. g., tetrahydrofuran [1]. Living carbenium ion polymerizations have not yet been found and due to the inherent reactivity (lability) of carbocations, the prospects for discovering such a system are rather dim.

It occurred to us that the synthetic versatility of living systems could be approached, indeed surpassed in certain respects, by developing carbocationic polymerization systems which proceed in the absence of chain transfer and whose initiation and termination steps can be controlled. The mechanism of such a system would involve only three events (ignoring solvation, rapid ion generation, aggregation, etc. effects):

Initiation:

$$R^{\oplus} + C{=}C \longrightarrow R{-}C{-}C^{\oplus} \tag{4}$$

Propagation:

$$-C^{\oplus} + C{=}C \longrightarrow -C{-}C{-}C^{\oplus} \tag{5}$$

Termination:

$$-C^{\oplus} + MeX_{n+1} \longrightarrow -C{-}X + MeX_n^{\ominus} \tag{6}$$

With this in mind we set out to find olefin polymerizations that in addition to propagation involve only well defined and understood initiation and termination events; the absence of any kind of chain transfer was of course of paramount importance. We projected that by controlling (i. e., selecting) appropriate initiating R and terminating X groups a large variety of new functional materials could be produced.

This presentation concerns recent advances in our laboratories toward elucidating the mechanism of initiation and chain breaking (chain transfer plus termination) in carbocationic polymerizations and specific examples of new products the syntheses of which became feasible by exploiting this knowledge. The first part of this paper focuses on research on initiation, the second on termination, and the third on possibilities offered by controlling simultaneously in the same system initiation and termination. Finally, a new initiator system Cl_2/BCl_3 is introduced that was employed in the synthesis of α,ω-dichloropolyisobutylenes, a new class of telechelic polymers.

UNDERSTANDING, CONTROLLING, AND EXPLOITING INITIATION IN CARBOCATIONIC POLYMERIZATION

Research in this area started by the discovery [2] that mixtures of cationically quite reactive olefin monomers and certain alkylaluminum compounds can be stirred in polar or nonpolar solvents without reaction; however, immediate or sometimes even explosively rapid polymerization occurs upon the introduction of cationogens, i. e., Brønsted acids or carbenium ion sources:

$$Et_3Al + CH_2{=}C(CH_3)_2 \xrightarrow[-78]{CH_3Cl} \text{no reaction}$$

$$Et_3Al + CH_3{=}C(CH_3)_2 + HCl \longrightarrow \text{immediate polymerization; high molecular weight product}$$

$$Et_3Al + CH_2{=}C(CH_3)_2 + \underline{t}\text{-}BuCl \longrightarrow \text{immediate polymerization; high molecular weight product}$$

The mechanism of these polymerizations has been largely elucidated and the effect of variables on the rate and molecular weight was discussed [3]. A considerable body of evidence indicates that among the main events leading to the formation of high polymer are rapid ion formation (priming) and cationation (where R = H or *t*-Bu):

$$Et_3Al + RCl \longrightarrow R^{\oplus}\, Et_3AlCl^{\ominus} \tag{7}$$

$$R^{\oplus} + CH_2{=}C(CH_3)_2 \longrightarrow R{-}CH_2{-}C^{\oplus}(CH_3)_2 \tag{8}$$

A number of investigations in this [4] and other laboratories [5-7] concerned the exploration of these reactions using a variety of cationogenic initiators, alkylaluminum coinitiators and monomers.

It is now firmly established that the initiator, RCl in Eq. (7), controls the head group of the polymer. This statement is forcefully demonstrated by graft copolymerization experiments. It has been shown that not only small molecules but macromolecules may also function as cationogens and thus initiate the polymerization of a variety of monomers [Eqs. (9) and (10), where $\bar{P}$ = polymer] [7, 8].

In this context, graft copolymerizations are extensions of fundamental studies directed toward the elucidation of mechanistic details

$$PCl + Et_2AlCl \longrightarrow P^{\oplus}\ Et_2AlCl_2^{\oplus} \qquad (9)$$

$$P^{\oplus}\ Et_2AlCl_2^{\ominus} + C{=}C \longrightarrow P{-}C{-}C^{\oplus}\cdots \longrightarrow \text{graft polymer} \qquad (10)$$

of carbocationic polymerization initiation. A large amount of pertinent information has recently become available [8]. Table 1 is a compilation of graft copolymers prepared by carbocationic techniques to date (entries marked with asterisks in Table 1 fall outside the scope of this presentation). The materials in Table 1 are arranged into two groups, backbones and branches, and within these groups into two subgroups: rubbers and glasses. The backbones are active halogen-containing (allylic, benzylic or tertiary) polymers that can provide macromolecular carbenium ions by reaction with diorganoaluminum halides or triorganoaluminums. These macromolecular initiators in fact produce the "head" group of the graft copolymer. The polymers assembled under branches are obtained by initiating the polymerization of the corresponding monomers by the backbone carbocation. Many of the synthetic possibilities offered by these rubbery/glassy combinations have already been accomplished, and the options of polymer molecular engineering to create new physical-mechanical properties have greatly been augmented by this cationic technique.

UNDERSTANDING, CONTROLLING, AND EXPLOITING TERMINATION IN CARBOCATIONIC POLYMERIZATION

Fundamental studies aimed to unravel the mechanism of alkyl halide + organoaluminum reactions greatly helped in elucidating the mechanism of termination of carbocationic polymerizations. Indeed, the reaction between tertiary BuCl and Me_3Al may be viewed as initiation followed by immediate termination, i. e., a polymerization without propagation

$$t\text{-}BuCl + Me_3Al \longrightarrow t\text{-}Bu^{\oplus} + Me_3AlCl^{\ominus} \qquad (11)$$

$$t\text{-}Bu^{\oplus} + Me_3Al \longrightarrow t\text{-}BuMe + Me_2AlCl \qquad (12)$$

In the presence of a monomer propagation starts to compete with termination and under suitable conditions materials of high molecular weight may be obtained:

TABLE 1. Cationically Prepared Graft Copolymers

	Rubbers	Glasses
Backbones	Poly(ethylene-co-propylene)[a]	Poly(vinyl chloride)
	Poly(ethylene-co-propylene-co-diene)[a]	Chloromethylated polystyrene
	Butyl rubber[a,b]	
	Chlorosulfonated polyethylene	
	Poly(styrene-co-butadiene)[a]	
	Polybutadiene[a]	
	Polychloroprene	
	Poly(p-chloromethylstyrene-co-butadiene)	
Branches	Polyisobutylene	Polystyrene
	Butyl rubber	Poly-α-methylstyrene
	Polychloroprene	Polyindene
	Polytetrahydrofuran*	Poly(indene-co-α-methylstyrene)
		Polyacenaphthylene
		Polydioxolane*
		Poly-1,4-dichloro-2,3-epoxybutane*
		Polyoxetane*

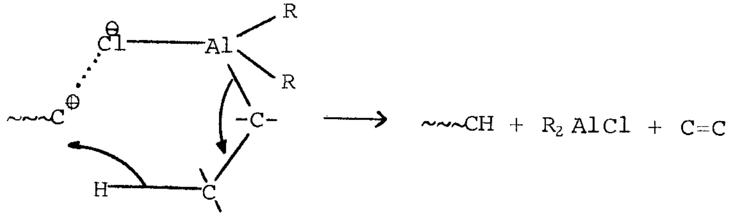
[a] Lightly chlorinated.
[b] Lightly brominated.

$$\text{t-Bu}^{\oplus}\ \text{Me}_3\text{AlCl}^{\ominus} + \text{C}{=}\text{C} \longrightarrow \text{t-Bu}{-}\text{C}{-}\text{C}^{\oplus}\ \text{Me}_3\text{AlCl}^{\ominus} \qquad (13)$$

$$\text{t-Bu}{-}\text{C}{-}\text{C}^{\oplus} + n\text{C}{=}\text{C}\cdots \longrightarrow \text{t-Bu}{\left(\text{C}{-}\text{C}\right)}_n\text{C}{-}\text{C}^{\oplus} \qquad (14)$$

$$\text{t-Bu}{\left(\text{C}{-}\text{C}\right)}_n\text{C}{-}\text{C}^{\oplus}\ \text{Me}_3\text{AlCl}^{\ominus} \longrightarrow \text{t-Bu}{\left(\text{C}{-}\text{C}\right)}_n\text{C}{-}\text{C}{-}\text{Me} + \text{Me}_2\text{AlCl} \qquad (15)$$

Numerous studies have been carried out to explore details of these reactions [4, 9]. Model experiments using nonpolymerizable olefins were particularly useful to substantiate the chemistry of the termination step [3]. Experiments with Me_3Al indicated termination by methylation (see above) while with alkylaluminums containing a hydrogen β-H to aluminum (i. e., triethyl- or triisobutylaluminum) termination involved mainly hydridation [Eq. (16)] [3].



(16)

We view polymer molecules with terminal alkyl groups or hydrogen "sterile," i. e., useless for further derivatization, and searched for methods to introduce versatile functional termini. This work resulted in the synthesis of many interesting new terminally functional e. g., phenyl-ended [10] or vinyl-ended [11], polymers.

A particularly useful research lead involving cyclopentadiene-ended polymers has recently been opened. Impetus for this work was the high chemical reactivity of cyclopentadiene (CPD) function and the ease of analytical detection of CPD groups by UV and NMR spectroscopy.

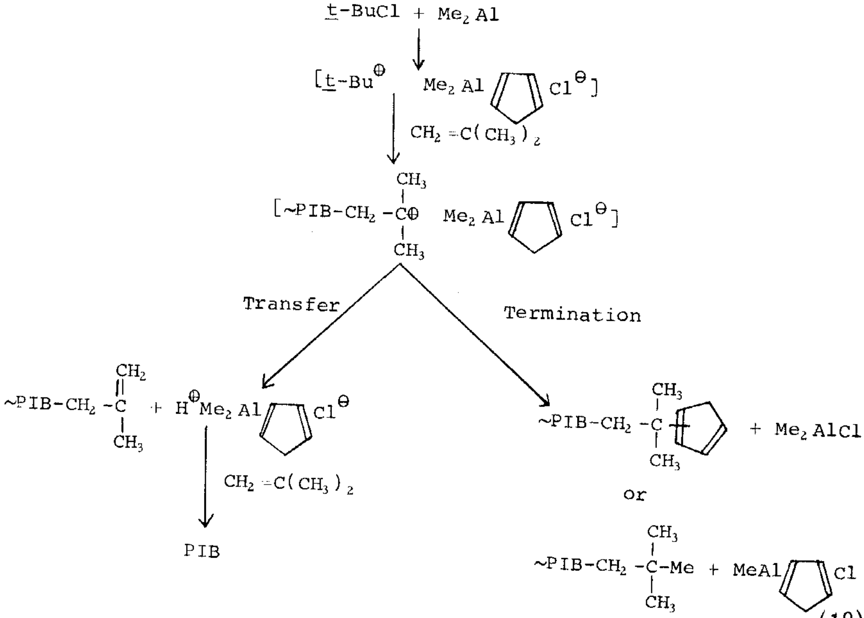
As illustrated by Eqs. (13)-(15), termination of olefin polymerization involves alkylation of the propagating carbocation by the aluminum-containing counteranion and transfer of the organic group originally on the aluminum to the growing chain end. We theorized and subsequently demonstrated that cyclopentadiene-containing aluminum compounds would be sufficiently acidic in the Lewis sense to coinitiate the polymerization of, for example, isobutylene in the presence of t-BuCl, and that termination of this polymerization would occur by transferring the cyclopentadiene bound to aluminum in the counteranion to the propagating isobutylene cation.

Experimentation proceeded along two fronts: (1) model experiments with t-BuCl + Me_2(CPD)Al and (2) isobutylene polymerizations by using the t-BuCl/Me_2(CPD)Al system. As anticipated, model studies carried out in the absence of monomer by using polar solvents at low temperatures [12] indicated the rapid formation of t-BuCPD (and minor quantities of t-BuMe) [Eq. (17)]. The effect of reagent concentration, nature of polar solvent, temperature on the kinetics of the reaction was investigated. According to these studies complete

$$\text{t-BuCl} + \text{Me}_2(\text{CPD})\text{Al} \longrightarrow \text{t-Bu}^{\oplus}\ \text{Me}_2(\text{CPD})\text{AlCl}^{\ominus}$$

$$\longrightarrow \text{t-BuCPD} + \text{Me}_2\text{AlCl} \qquad (17)$$

cyclopentadienylation may be obtained at -55°C by using t-BuCl/Me_2(CPD)Al ratios less than 1.0. These studies provided valuable data in designing reaction conditions for the synthesis of polyisobutylenes with CPD termini. Equation (18) shows the reaction scheme investigated.



(18)

By combining information gathered from model experiments and direct polymerizations, experiments have been run that yielded CPD-terminated polyisobutylenes [12]. In particular, Mayo plots ($1/\overline{M}_n$ versus $1/[M]$) and quantitative endgroup analyses (by UV spectroscopy) indicated the virtual absence of chain transfer and the presence of cyclopentadiene groups in polymerizations conducted at -41°C. Additional proof for CPD endgroups was obtained by applying the well known reaction with maleic anhydride followed by infrared spectroscopy of the anhydride group. Research is continuing with this unique functional polymer.

In addition to experimentation with cyclopentadiene-ended polymers, similar studies in progress in our laboratories involve cyclopentadienylation of active halogen-containing rubbers with a view to preparing novel thermally reversible networks. Thus we theorized that rubbery polymers containing tertiary or allylic chlorines may be cyclopentadienylated by $Me_2(CPD)Al$ and that such cyclopentadienylated products may be reversibly crosslinked by Diels-Alder-retro Diels-Alder reactions.

Experimentally we cyclopentadienylated chlorobutyl rubber (Cl-IIR) and chlorinated poly(ethylene-co-propylene) (Cl-EPM) by stirring these polymers in chlorobenzene solution (2.0-5.0 wt %) at various temperatures, adding $Me_2(CPD)Al$ dissolved in the same solvent, stirring for desired times, quenching the reaction by the addition of a small quantity of methanol, filtering off insoluble aluminum residues, and finally coagulating the product with a 1% 2,6-di-tert-butyl-p-cresol/methanol solution. Subsequently the products were vacuum-dried and stored at -15°C.

Significantly, soluble polymers became insoluble after drying for ~72 hr at 23°C; however, they could be solubilized by the addition of maleic anhydride to the swollen systems. For example, a swollen cyclopentadienylated chlorobutyl sample in hot (215°C) hexachlorobutadiene solvent rapidly dissolved upon the introduction of a small quantity of maleic anhydride. Table 2 shows representative data obtained.

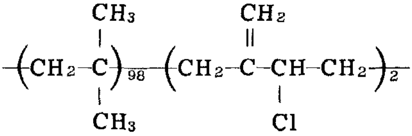
The CPD content was also determined by reaction with maleic anhydride and subsequent infrared spectroscopy. Results obtained by UV analysis and those by IR of the maleic anhydride adducts were undistinguishable.

Evidently, gelation after drying these cyclopentadienylated chlorobutyl samples is not due to permanent crosslinking but to Diels-Alder addition of pendant CPD groups. The addition of maleic anhydride to swollen gels produces the maleic anhydride adduct which prevents further Diels-Alder dimerization of pendant CPD-groups and leads to rapid dissolution of the network. Figure 1 illustrates the reactions that explain these observations.

Cyclopentadienylated poly(ethylene-co-propylene) (CPD-EPM) samples were heated to determine if they would undergo crosslinking via Diels-Alder addition of the CPD pendant groups. The samples of CPD-EPM and Cl-EPM (control) were compression-molded at 150°C for 30 min and 30,000 psi, removed from the rectangular mold, and their shapes and elastic properties noted. Subsequently the samples were cut into small pieces, replaced in the mold, and heated to 170°C to effect cracking of dicyclopentadiene units. After the second "curing" cycle the samples were again removed from the mold, inspected, and the cycle was repeated a third time (170°C).

After the first heating cycle, inspection of the samples indicated

TABLE 2. Cyclopentadienylation of Chlorobutyl with $Me_2(CPD)Al^a$



$$-\left(CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right)_{98}-\left(CH_2-\overset{CH_2}{\overset{\|}{C}}-\underset{Cl}{CH}-CH_2\right)_2-$$

Experimental conditions		
Chlorobenzene (ml)	250	100
Polymer (g)	5.0	2.38
$Me_2(CPD)Al$ (g)	0.35	0.096
Cl/Al ratio	0.55	0.92
Temperature (°C)	-23.0	+24.0
Time (min)	60	20
Results		
Solubility immediately after reaction	Sol.	Sol.
Solubility after drying	Insol.	Insol.
CPD content (wt %) by UV analysis	1.1	-
Chlorine sites substituted by CPD (%)	55	-

[a] Chlorine content of initial polymer, 1.1 wt %; $\overline{M}_n = 200{,}000$.

that the cyclopentadienylated polymer behaved as a crosslinked elastomer. The CPD-EPM sample assumed the shape of the mold cavity and exhibited a smooth surface. Manual stretching to an elongation of ~ 100% showed that the CPD-EPM required a greater force to stretch than that required for Cl-EPM, and upon releasing the tension it snapped back; in contrast, the control sample yielded upon stretching and failed. Also, the flashing from the CPD-EPM sample would not dissolve; however, upon treatment with maleic anhydride as described above, it dissolved.

The second "curing" cycle produced the same results. The derivatized polymer assumed the shape of the mold cavity and was continuous and smooth. Its elastic properties appeared to be the same as after the first cycle. In the third "curing" cycle the derivatized polymer did not flow in the mold and the pieces did not coalesce.

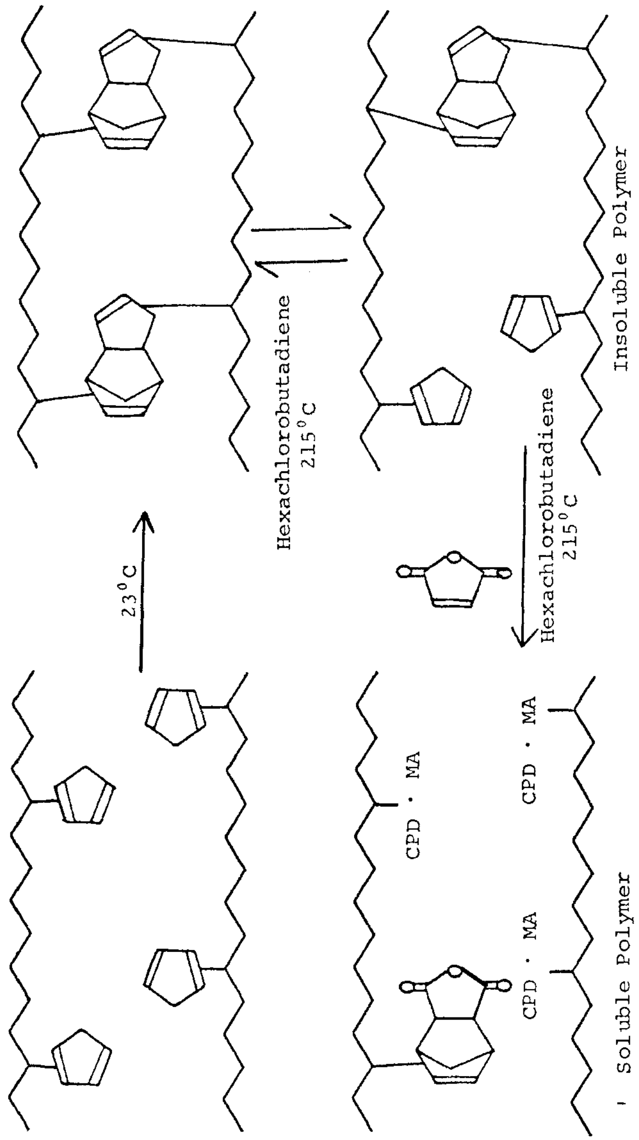


FIG. 1. Scheme for gelation by Diels-Alder condensation and solubilization by maleic anhydride trapping of CPD groups.

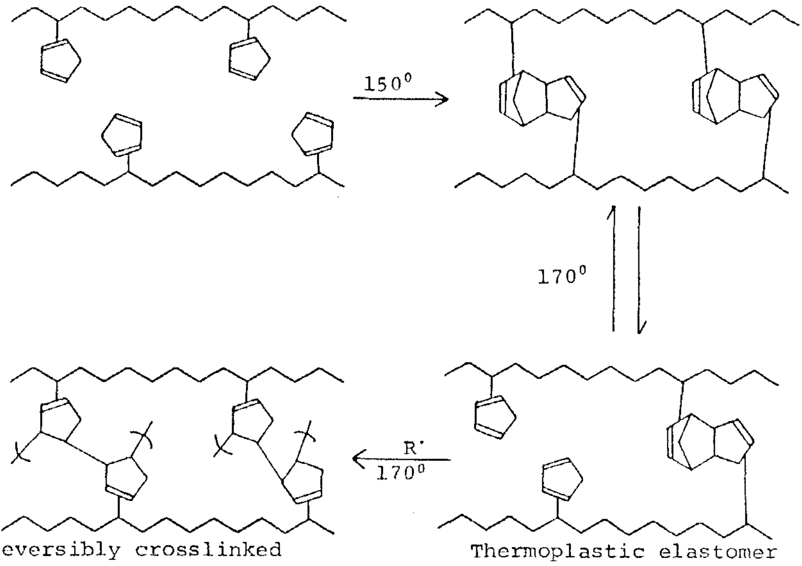


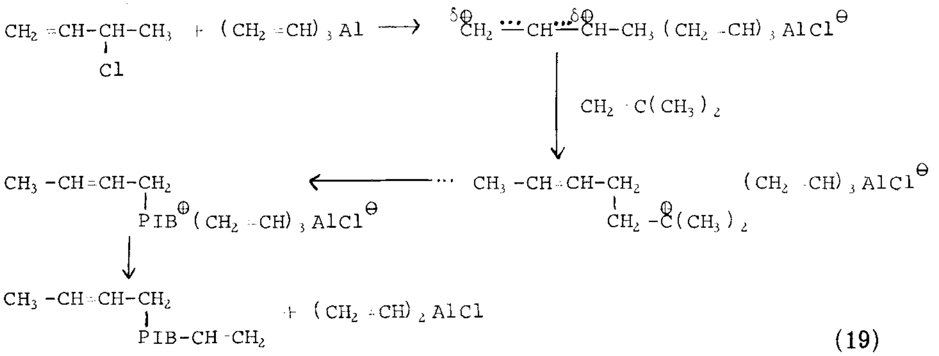
FIG. 2. Scheme for thermally reversible crosslink by Diels-Alder reaction.

These results indicate that the cyclopentadienylated polymer is reversibly crosslinkable by Diels-Alder/retro-Diels-Alder reactions of pendant CPD groups. Failure to undergo flow during the third molding cycle is probably due to formation of permanent crosslinks, most likely caused by radical side reaction of the pendant CPD groups upon repeated heating at relatively high temperatures. The control sample remained soluble through all three cycles. A scheme to account for the results is shown in Fig. 2.

TELECHELIC POLYMERS BY UNDERSTANDING, CONTROLLING, AND EXPLOITING INITIATION AND TERMINATION OF CARBOCATIONIC POLYMERIZATION

After having understood important aspects of chemistries of initiation and termination of a few carbocationic polymerization systems, efforts have been made to combine this information for the preparation of new functional and telechelic polymers. The principle of our approach will be illustrated by an example, the synthesis of α,ω-diene-polyisobutylene.

Some time ago we became interested in exploring the synthesis of telechelic (α,ω-difunctionalized) polyhydrocarbons, in particular the preparation of a polyisobutylene carrying terminal unsaturations. We theorized that α-unsaturation could be obtained by initiating the polymerization using a suitably substituted allylic chloride in the presence of an alkylaluminum. In regard to the introduction of ω-unsaturation we theorized that this objective could be attained by the use of trivinylaluminum. Equation (19) summarizes the blueprint for this project.

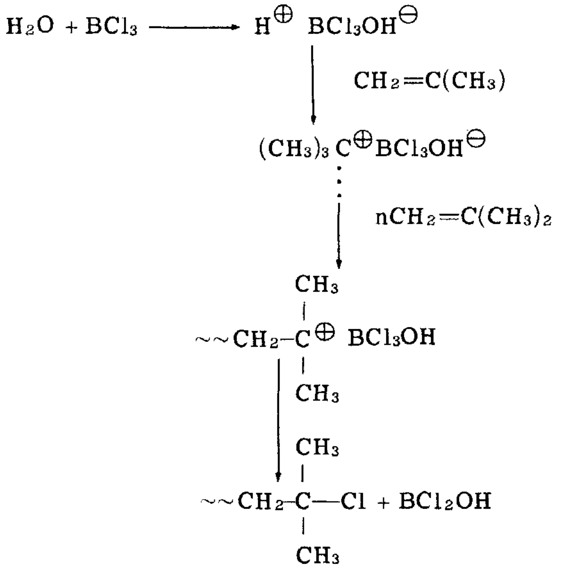


$$\begin{aligned}
&CH_2{=}CH{-}\underset{|}{\underset{Cl}{C}}H{-}CH_3 + (CH_2{=}CH)_3Al \longrightarrow \overset{\delta\oplus}{C}H_2\cdots CH\cdots\overset{\delta\oplus}{C}H{-}CH_3\ (CH_2{=}CH)_3AlCl^{\ominus}\\
&\xrightarrow{CH_2=C(CH_3)_2} CH_3{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{\oplus}{C}(CH_3)_2\ (CH_2{=}CH)_3AlCl^{\ominus}\\
&\longrightarrow CH_3{-}CH{=}CH{-}CH_2{-}PIB^{\oplus}\ (CH_2{=}CH)_3AlCl^{\ominus}\\
&\longrightarrow CH_3{-}CH{=}CH{-}CH_2{-}PIB{-}CH{=}CH_2 + (CH_2{=}CH)_2AlCl
\end{aligned}\qquad(19)$$

For the experiments we selected 3-chloro-1-butene initiator. Trivinylaluminum was synthesized from $(CH_2{=}CH)_2Hg$ + Al [13]. Model experimentation in which 3-chloro-1-butene was reacted with trivinylaluminum gave the anticipated vinylated products, 1,4-hexadiene and 3-methyl-1,4-pentadiene [11]. NMR spectroscopy indicated that initiation of isobutylene polymerization occurs preferentially from the primary allylic carbocation. Guided by extensive model and kinetic studies, experimental conditions have been worked out for the synthesis of an α,ω-diene polyisobutylene of $\overline{M}_n$ = 24,000 containing 1.8 ± 0.1 mole C=C/mole PIB [13].

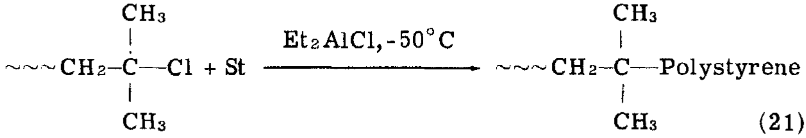
FUNCTIONAL AND TELECHELIC POLYMERS BY BORON TRICHLORIDE-COINITIATED POLYMERIZATION

Recently we discovered that, under carefully chosen conditions, BCl_3 is an efficient coinitiator for the polymerization of isobutylene and other olefins [14]. Among the many initiator/coinitiator systems, combinations of BCl_3 with carbenium ion sources RCl are particularly attractive as they readily provide efficient initiating moieties $R^{\oplus}$ and, importantly, the kinetic chains are devoid of chain transfer. Chain breaking in these systems is exclusively by termination, more precisely by chlorination of the propagating carbocation by the counter anion. The mechanism of isobutylene polymerization with the H_2O/BCl_3 initiator system involves the events shown in Eq. (20).



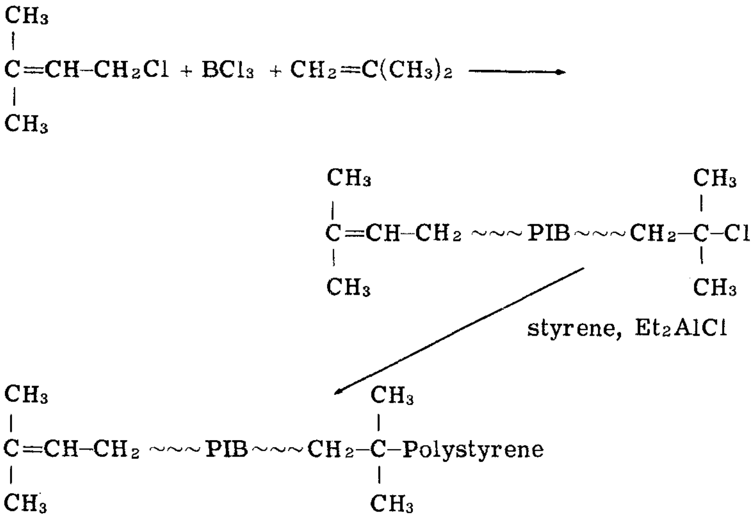
$$H_2O + BCl_3 \longrightarrow H^{\oplus}\ BCl_3OH^{\ominus} \xrightarrow{CH_2=C(CH_3)} (CH_3)_3C^{\oplus}BCl_3OH^{\ominus} \xrightarrow{nCH_2=C(CH_3)_2} \sim\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}}\ BCl_3OH \longrightarrow \sim\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl + BCl_2OH \qquad (20)$$

By this technique it became possible to produce polymers with one single terminal chlorine atom. This has been demonstrated by synthesizing polyisobutylenes carrying a tertiary chlorine terminus [14]. The nature of the chlorine endgroup was proven by utilizing it to initiate in conjunction with Et_2AlCl coinitiator the polymerization of a second olefin, e. g., styrene. In this manner new poly(isobutylene-co-styrene) diblock copolymers have been prepared.



$$\sim\sim\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl + St \xrightarrow{Et_2AlCl,\,-50^{\circ}C} \sim\sim\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\text{Polystyrene} \qquad (21)$$

Very recently we demonstrated the synthesis of diblock copolymers carrying functional head groups. This procedure calls for initiation of isobutylene polymerization with various carbenium ion sources, e. g., 2-methyl-4-chloro-2 butene, cumyl chloride. Equations (22) illustrate the concept.



$$(CH_3)_2C{=}CH{-}CH_2Cl + BCl_3 + CH_2{=}C(CH_3)_2 \longrightarrow (CH_3)_2C{=}CH{-}CH_2\sim\sim\sim PIB\sim\sim\sim CH_2{-}C(CH_3)_2{-}Cl \xrightarrow{\text{styrene, }Et_2AlCl} (CH_3)_2C{=}CH{-}CH_2\sim\sim\sim PIB\sim\sim\sim CH_2{-}C(CH_3)_2{-}\text{Polystyrene} \qquad (22)$$

The mechanism most likely involves the generation of the ion pair $(CH_3)_2{-}{}^{\delta\oplus}C{-}CH{-}{}^{\delta\oplus}CH_2\,BCl_4^{\ominus}$, initiation at the primary allylic carbon, propagation, and termination by chlorination. After removing the unreacted chemicals used in the preparation of the prepolymer, styrene was added and blocking was initiated by introducing Et_2AlCl. Diblocks containing poly-α-methylstyrene as the glassy segment have also been prepared and characterized.

Extension of these investigations recently yielded α,ω-dichloropolyisobutylenes. The principle for this synthesis was the discovery [15] that elementary chlorine is an efficient cationogen in conjunction with BCl_3 and that Cl_2/BCl_3 combinations readily initiate cationic polymerizations, most likely by the chloronium ion $Cl^{\oplus}/BCl_4^{\ominus}$. It was postualted that isobutylene polymerizations induced by Cl_2/BCl_3 will yield polymer containing chlorine atoms both in the α and ω positions, since initiation and termination involve chlorinations [Eqs. (23)-(25)].

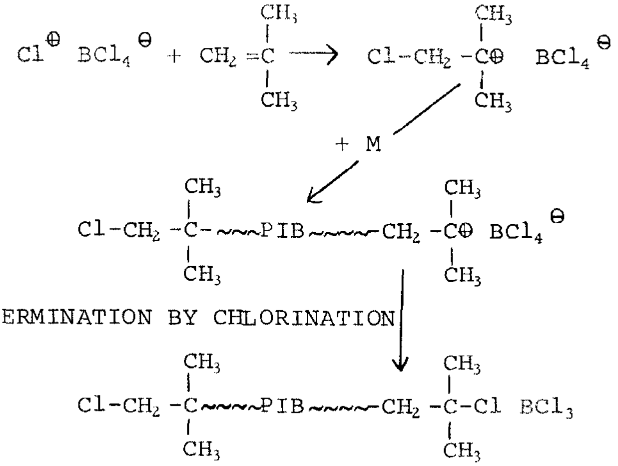
Structural proof for the nature of the terminal chlorines of this telechelic molecule involved derivatizations (blocking reactions) at both termini and NMR spectroscopy using special low molecular weight products to facilitate endgroup characterization.

The identity of the α-tertiary chlorine was determined by blocking

PRIMING(ION GENERATION)

$$Cl_2/BCl_3 \longrightarrow Cl^{\oplus}\ BCl_4^{\ominus} \qquad (23)$$

INITIATION AND PROPAGATION



$$Cl^{\oplus}\ BCl_4^{\ominus} + CH_2{=}C(CH_3)_2 \longrightarrow Cl{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C^{\oplus}}}\ BCl_4^{\ominus}$$

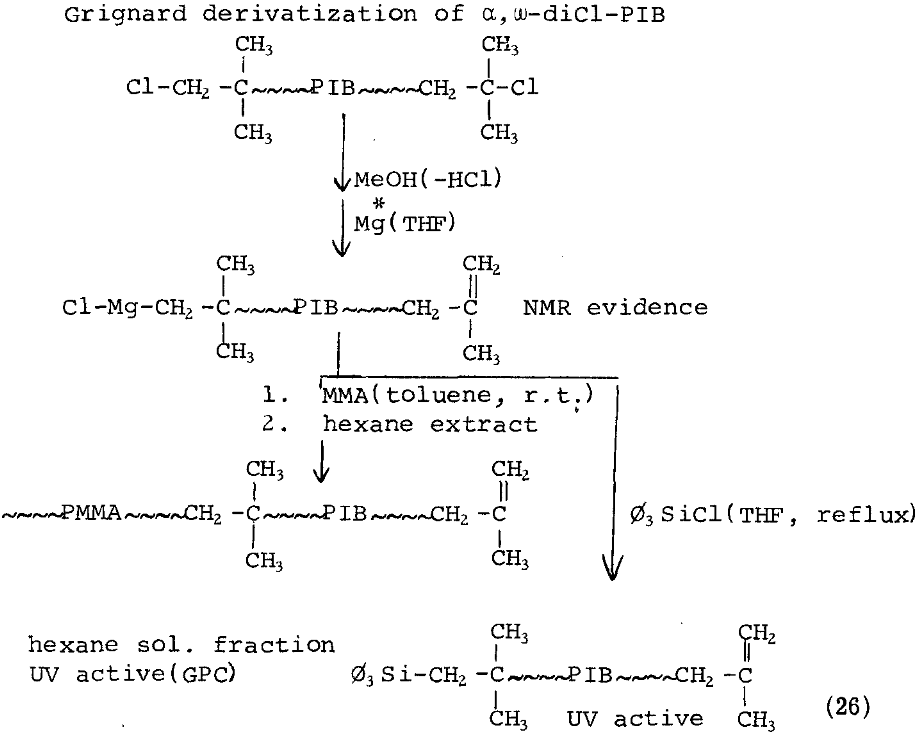
$$Cl{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\sim\sim PIB \sim\sim CH_2{-}\overset{CH_3}{\underset{CH_3}{C^{\oplus}}}\ BCl_4^{\ominus} \qquad (24)$$

$$Cl{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}\sim\sim PIB \sim\sim CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Cl\ \ BCl_3 \qquad (25)$$

styrene and/or α-methylstyrene from the tertiary site by using the cationic blocking technique described above.

The characterization of the head neopentyl type chloride was more difficult on account of its very low reactivity. First the tertiary chlorine was removed by dehydrochlorination upon treatment with methanol. NMR spectroscopy indicated the appearance of terminal unsaturation, $-C(CH_3){=}CH_2$. After numerous trials using a variety of reagents we found that the neopentyl chlorine head group can be transformed with highly reactive magnesium [16] to a Grignard reagent. Subsequently this Grignard compound was used to initiate the polymerization of methyl methacrylate using toluene diluent at room temperature. After removing the unreacted polyisobutylene by extraction with n-hexane, the n-hexane-insoluble fraction indicated the presence of poly(methyl methacrylate) sequences by NMR and UV spectroscopy. The poly(methyl methacrylate-b-isobutylene) prepared in this manner is a new diblock copolymer.

In addition to experiments with methyl methacrylate the Grignard compound was also reacted with $(C_6H_5)_3SiCl$. After removing the excess $(C_6H_5)_3SiCl$, the derivatized polyisobutylene exhibited strong UV activity indicating the incorporation of phenyl groups. These transformations are illustrated by Eqs. (26).



(26)

TABLE 3. Understanding ⟶ Controlling Initiation (in the Absence of Chain Transfer) Leads to New Products

Initiating cation	+	Monomer	⟶	New product
H⊕ (proton)				H-homopolymer
R⊕ (alkyl or aralkyl group)				R-homopolymer
X⊕ (halonium ion)				X-homopolymer
~~C⊕ (polymer with cation terminus)				A-B block copolymer
~~ (polymer with cations along chain)				branched polymer or graft copolymer or bigraft copolymer

TABLE 4. Understanding ⟶ Controlling Termination (in the Absence of Chain Transfer) Leads to New Products

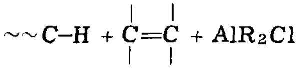
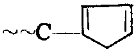
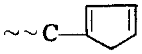
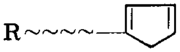
Propagating cation	+	Counteranion	⟶	New product
$\sim\sim C^{\oplus}$		 $HC{-}C{-}AlR_2Cl^{\ominus}$		 $\sim\sim C{-}H + C{=}C + AlR_2Cl$
$\sim\sim C^{\oplus}$		$Me_3AlCl^{\ominus}$		$\sim\sim C{-}Me + Me_2AlCl$
$\sim\sim C^{\oplus}$		$Ph_3AlCl^{\ominus}$		$\sim\sim C{-}Ph + Ph_2AlCl$
$\sim\sim C^{\oplus}$		$(CH_2{=}CH)_3AlCl^{\ominus}$		$\sim\sim C{-}CH{=}CH_2$ $+ (CH_2{=}CH)_2AlCl$
$\sim\sim C^{\oplus}$		 $Me_2AlCl^{\ominus}$		 $+ Me_2AlCl$
$\sim\sim C^{\oplus}$		$BCl_4^{\ominus}$		$\sim\sim C{-}Cl + BCl_3$

TABLE 5. Understanding ⟶ Controlling Initiation and Termination (in the Absence of Chain Transfer) Leads to Combination of New Products

Product of controlled initiation	+	Product of controlled termination	⟶	Product of controlled initiation + termination
H-homopolymer		$\sim\sim C{-}H$		$H\sim\sim\sim\sim H$
R-homopolymer		$\sim\sim C{-}Me$		$R\sim\sim\sim\sim R$
X-homopolymer		$\sim\sim C{-}Ph$		$Cl\sim\sim\sim\sim Cl$
A-B block copolymer		$\sim\sim C{-}CH{=}CH_2$		$R\sim\sim\sim\sim CH{=}CH_2$
Branched polymer				
Graft copolymer		$\sim\sim C{-}Cl$		$Ph\sim\sim\sim\sim Ph$
				A-B-X
				R-A-B
				many other telomers, etc.

SUMMARY

This presentation focused on the understanding of carbocationic polymerization mechanisms and on the subsequent exploitation of this knowledge for the synthesis of new functional, telechelic, graft and block copolymers. Several examples have been discussed and a variety of new possibilities for the preparation of novel polymers have been described. Tables 3 and 4 illustrate new terminally functionalized structures that have been obtained by understanding details of initiation and termination, respectively. A combination of controlled initiation and termination events may lead to new biterminally functionalized (telechelic) polymers as shown in Table 5. Finally, by understanding details of the mechanism of carbocationic polymerizations using Cl_2/BCl_3 combinations new α,ω-dichloropolyisobutylenes have been prepared.

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REFERENCES

[1] S. Penczek and K. Matyjaszewski, J. Polym. Sci. Polym. Symp. Ed., 56, 255 (1976).

[2] J. P. Kennedy, Belg. Pat. 663,319 (April 30, 1965).

[3] J. P. Kennedy and S. Rengachary, Adv. Polym. Sci., 14, 1 (1974).

[4] J. P. Kennedy and J. K. Gillham, Adv. Polym. Sci., 10, 1 (1972).

[5] A. Priola, G. Ferraris, M. Maina, and P. Giusti, Makromol. Chem., 176, 2271 (1975).

[6] A. Priola, S. Cesca, and G. Ferraris, Makromol. Chem., 160, 41 (1972).

[7] P. Sigwalt, A. Polton, and M. Miscovic, J. Polym. Sci. Polym. Symp. Ed., 56, 13 (1976).

[8] J. P. Kennedy, Ed., Cationic Graft Copolymerization, (J. Appl. Polym. Sci., Appl. Polym. Symp., 30) Wiley, New York, 1977.

[9] J. P. Kennedy, N. V. Desai, and S. Sivaram, J. Am. Chem. Soc., 95, 6386 (1973).

[10] L. Y. Chung, Ph. D. Thesis, The University of Akron, 1978.

[11] B. Mandal and J. P. Kennedy, J. Polym. Sci. Polym. Chem. Ed., 16, 833 (1978).

[12] J. P. Kennedy and K. F. Castner, J. Polym. Sci. Polym. Chem., 17, 2055 (1979); U. S. Pat. 4,138,441 (1979).

[13] B. Mandal, J. P. Kennedy, and R. Kiesel, J. Polym. Sci. Polym. Chem. Ed., 16, 821 (1978).

[14] J. P. Kennedy, S. C. Feinberg, and S. Y. Huang, Polym. Preprints, 17(1), 194 (1976).

[15] J. P. Kennedy and F. J.-Y. Chen (University of Akron, 1977) unpublished results.

[16] R. D. Rieke and S. E. Bales, J. Chem. Soc. Chem. Commun., 1973, 879.