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## Molecular Engineering by Cationic Polymerization Techniques

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### ABSTRACT

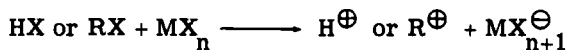
Understanding the mechanism of cationic olefin polymerization has led to the synthesis of various new materials of interesting and unusual physical properties. By elucidating details of initiation, various new graft and bigraft copolymers combining glassy/glassy, glassy/rubbery, and rubbery/rubbery sequences have been obtained. Recent research concerning fundamentals of alkylation and termination was exploited for the preparation of new block copolymers and terminally-functional block copolymers. Initiation by difunctional initiators has led to  $\alpha,\omega$ -difunctional polymers, e. g.,  $\alpha,\omega$ -diphenylpolyisobutylene. Cyclopentadienylation of lightly chlorinated polymers, e. g., chlorobutyl rubber, produced thermally reversible networks.

### INTRODUCTION

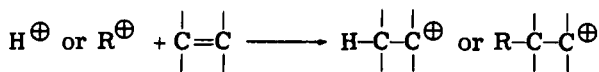
In this lecture I outline new avenues toward the synthesis of new products exhibiting combinations of unusual physical-mechanical properties by understanding mechanistic details of cationic polymerizations. In particular, elucidating the mechanism of initiation and termination led to the synthesis of unique functional polymers, modified polymers, block, graft and bigraft copolymers.

Until about 1970 the mechanism of cationic olefin polymerizations has been discussed in terms of five elementary events:

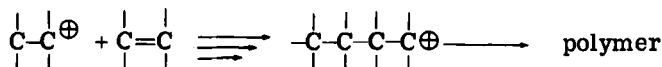
Ion Generation ("Priming"):



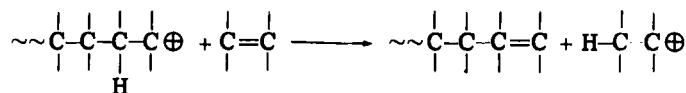
Cationation:



Propagation:



Chain Transfer to Monomer:



Termination:

mechanism unknown

The first two events, ion generation and cationation, were usually not separated but were treated as one step: initiation. Even a cursory examination reveals, however, that the chemistries of ion generation and cationation are distinctly different and should be considered separately. In the first step, an ion, i. e., proton, carbenium ion, halonium ion, is generated which subsequently induces polymerization by cationating olefin.

After the birth of the first propagating carbenium ion, propagation ensues which (in the absence of complications such as isomerization) consists of repetitive olefin alkylation by the growing cation. Polymer chemists usually wish to produce high polymer and consequently endeavor to maximize this step. Molecular weights are determined by the relative rates of propagation and chain transfer to monomer. During chain transfer the monomer, instead of adding to the chain, extracts a proton from the growing carbenium ion and starts a new growing carbocation. In addition to chain transfer to monomer, other kinds of chain transfers are also possible, i. e., chain transfer to solvent, polymer, counteranion; however, these events are

far less important and are more easily controllable than chain transfer to monomer.

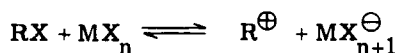
Termination is the irreversible annihilation of propagating ability, and its rate relative to that of propagation determines the yield of polymerization. The chemistry of termination has not been investigated in detail, and except for a few propositions [ 1, 2 ] chemical transformations that accompany termination have remained obscure.

Polymerizations proceeding by this "classical" mechanism produce materials carrying at least two kinds of endgroups, depending on whether the growing chain is terminated by chain transfer or termination. Another undesirable aspect of polymers arising by this mechanism is that the two termini of the macromolecules will be different: the head or  $\alpha$ -group will contain a hydrogen arising by protonation during chain transfer while the tail or  $\omega$ -group will be unsaturated ( $H \sim C=C$ ). Polymers containing a saturated, usually  $CH_3$ , group at the head (arising via protonation of a  $CH_2=$  moiety) are "sterile" for further derivatization. Polymers containing two identical functional endgroups are desirable for further functionalization.

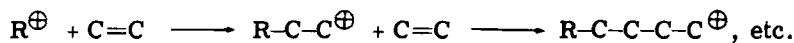
It would be very difficult if not impossible to tailor-make useful polymer molecules by the conventional mechanisms outlined above, i. e., with mechanisms that include chain transfer to monomer and termination of undetermined nature.

According to this analysis, molecular engineering of polymers is possible only with systems that are devoid of chain transfer and in which chemical transformations accompanying termination are understood and controllable. Indeed, the preparative synthetic capability of cationic polymerization would be immensely improved with systems operating by the following three-step mechanism:

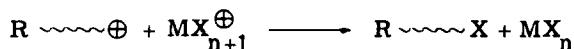
Ion Generation (Priming):



Cationation and Propagation:



Termination:



The polymer  $R \sim \sim \sim X$  arising by the above three-step mechanism can be viewed to consist of three structural units: R = head group,

~~~~ = the main body of the polymer and X = tail group. The three individual steps, ion generation, propagation, and termination, control the chemistry and consequently the nature of these three structural units of the polymer, respectively.

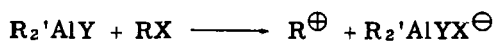
The important difference between the former, conventional, mechanism and the above idealized mechanism is that the latter is devoid of chain transfer and that termination is well defined.

Recent research in our laboratories has uncovered several systems that approach the mechanistic simplicity of the latter idealized system and thus have been used in the preparation of a large number of useful functional polymer molecules of well defined structures. Indeed, the finding of systems in which chain transfer is absent and in which details of termination are understood opens unexpected molecular-engineering capabilities by cationic polymerizations.

The subsequent parts of this lecture concern details of initiation and termination research and illustrates avenues in tailor-making polymers by applying knowledge acquired from mechanism studies.

### GRAFT COPOLYMERS BY UNDERSTANDING INITIATION

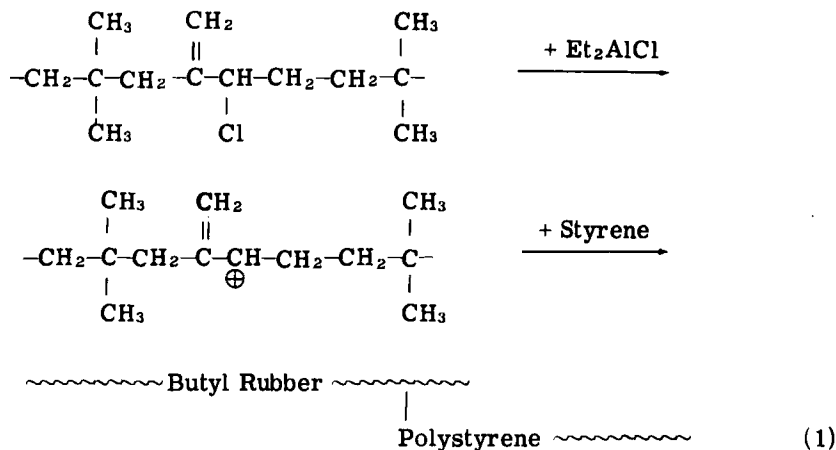
The key to the synthesis of a new family of graft copolymer was the discovery [3] that dialkylaluminum halides and trialkylaluminums coinstantiate the polymerization of olefins and diolefins only in conjunction with small or large organic halides. In general:



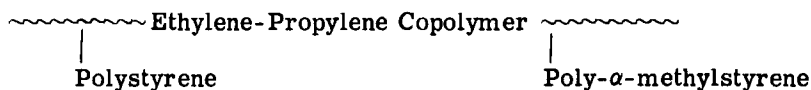
where R = allyl, tert-butyl, benzyl; X = fluorine, chlorine, bromine; R' = methyl, ethyl, isobutyl, phenyl; Y = chlorine, bromine, hydrogen, methyl, ethyl, isobutyl, phenyl. For example, it has been determined that the macromolecular allyl chloride chlorobutyl rubber readily initiates the polymerization of styrene in the presence of Et<sub>2</sub>AlCl [Eq. (1)] and that the graft copolymer is an interesting thermoplastic elastomer [4].

A recent book [5] summarizes a large amount of information concerning this subject and describes in detail the synthesis of many graft copolymers by this and similar techniques. The material scientist may combine by this technique a large variety of glassy and rubbery polymer sequences to backbones and branches and may be able to create new graft copolymers of unusual physical-mechanical properties (cf. Table 1).

By an extension of this technique [6-8], bigrafts, i. e., graft copolymers comprising a common backbone to which are attached

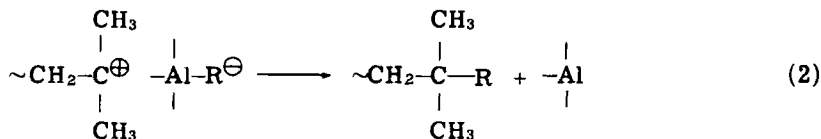


two chemically different branches, can also be prepared [7]; for example:



### BLOCK COPOLYMERS BY UNDERSTANDING TERMINATION

According to the scheme of an ideal cationic polymerization shown above, termination involves the collapse of the growing cation and counteranion to an electrically neutral species. In case of alkyl-aluminum cointiators this ion-pair collapse is tantamount of alkylation, e. g.,  $\sim\text{C}^{\oplus} \text{Me}_3\text{AlCl}^{\ominus} \rightarrow \sim\text{CMe} + \text{Me}_2\text{AlCl}$ . In general, it has been found that by this mechanism various organic groups originally on aluminum can be transferred to polyolefins, i. e., polyisobutylenes, as terminal groups [Eq. (2)],



where R = methyl, ethyl, phenyl, vinyl, cyclopentadienyl [9-12]. In this manner by use of various organoaluminum cointiators engroup

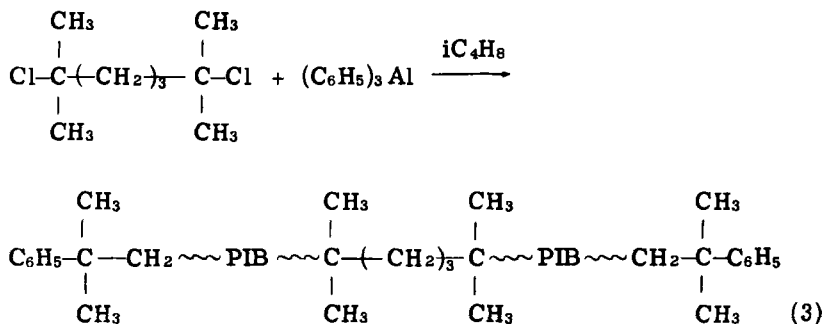
TABLE 1. Polymer Sequences Demonstrated to Yield Graft Copolymers by Cationic Techniques

| Backbones                       |                                                           | Branches                                 |                               |
|---------------------------------|-----------------------------------------------------------|------------------------------------------|-------------------------------|
| Glassy sequences                | Rubbery Sequences                                         | Glassy sequences                         | Rubbery sequences             |
| Poly(vinyl chloride)            | Poly(ethylene-co-propylene) <sup>a</sup>                  | Polystyrene                              | Polyisobutylene               |
| Polystyrene (chloro-methylated) | Poly(ethylene-co-propylene-co-1,4-hexadiene) <sup>a</sup> | Poly- $\alpha$ -methylstyrene            | Poly(isobutylene-co-isoprene) |
|                                 | Poly(isobutylene-co-isoprene) <sup>a,b</sup>              | Polyindene                               | Polychloroprene               |
|                                 | Polyethylene (chlorosulfonated)                           | Poly(indene-co- $\alpha$ -methylstyrene) | Polytetrahydrofuran           |
|                                 | Poly(styrene-co-butadiene) <sup>a</sup>                   | Polyacena $\theta$ thylene               | Poly(isobutyl vinyl ether)    |
|                                 | Polybutadiene <sup>a</sup>                                | Polydioxolane                            |                               |
|                                 | Polychloroprene                                           | Polyoxetane                              |                               |
|                                 | Poly(p-chloromethylstyrene-co-butadiene)                  | Poly-1,4-dichloro-2,3-epoxybutane        |                               |
|                                 |                                                           | Poly(propylene oxide)                    |                               |
|                                 |                                                           | Poly(styrene oxide)                      |                               |
|                                 |                                                           | Poly-7-oxabicyclo-[2,2,1]-heptane        |                               |
|                                 |                                                           | Poly- $\epsilon$ -caprolactone           |                               |

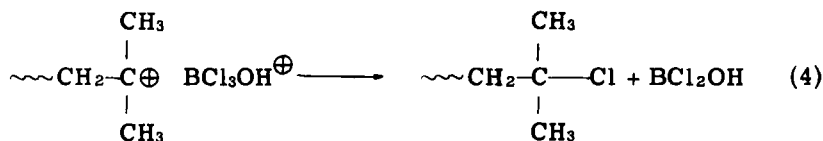
<sup>a</sup>Lightly chlorinated.<sup>b</sup>Lightly brominated.

control became possible. Kinetic, spectroscopic, and chemical evidences indicate the essential absence of chain transfer in these polymerizations.

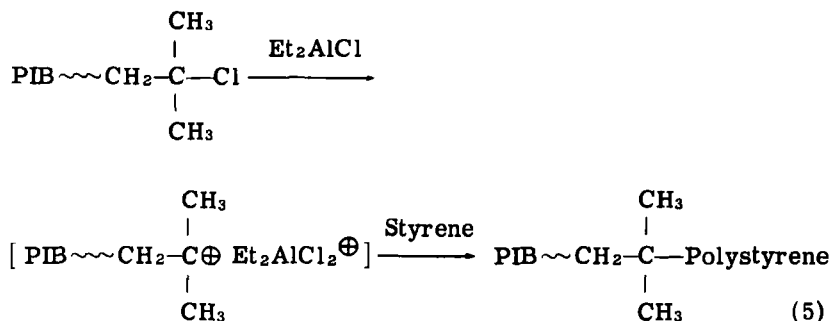
By using bifunctional initiators in combination with suitable organoaluminum coinitiators, valuable bifunctional polymers have been synthesized [ 13].



Recent research has shown [ 14, 15] that termination of isobutylene polymerization induced by the  $\text{H}_2\text{O}/\text{BCl}_3$  initiating system occurs by chlorination [ Eq. (4)].

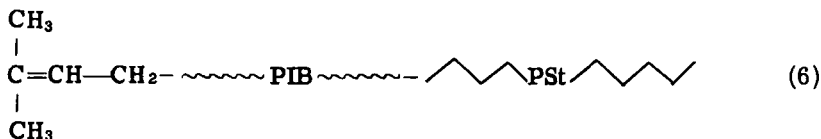


The presence and position of terminal tertiary chlorine has been proven by blocking, for instance [ Eq. (5)], styrene in conjunction with diethylaluminum chloride [ 15].





In the presence of suitable carbenium ion sources such as  $(\text{CH}_3)_3\text{C}=\text{CH}-\text{CH}_2\text{Cl}$ , isobutylene polymerization cointiated by  $\text{BCl}_3$  followed by blocking with  $\text{Et}_2\text{AlCl}$  leads [ Eq. (6) ] to terminally (head) functionalized block copolymers [ 16 ].



### CYCLOPENTADIENYLATION OF MACROMOLECULES

Recent fundamental research into alkylation of alkylhalides by organometal compounds, particularly organoaluminums, produced information valuable for the synthesis of new functional polymers. For example, phenylation with triphenylaluminum [ 13, 17 ] and vinylation with trivinylaluminum [ 11, 18 ] gave unique materials. Recently cyclopentadienylation with dimethylcyclopentadienylaluminum ( $\text{Me}_2\text{CPDAI}$ ) of lightly chlorinated rubbers, e. g., chlorobutyl and EPM, led to thermally reversible networks [ 12 ]. The gist of this development is summarized by Eqs. (7) and (8).

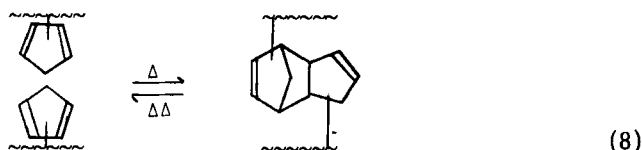
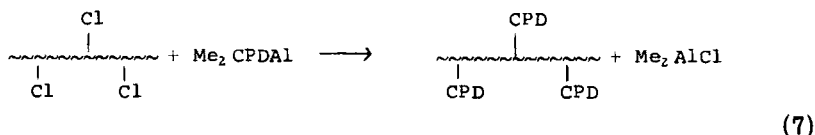


Table 2 shows some experimental details obtained in the course of cyclopentadienylation of chlorobutyl rubber. Chlorobutyl rubber (a product of Exxon Chemical Co.) of  $\overline{M}_n = 200,000$  and with 1.1% by

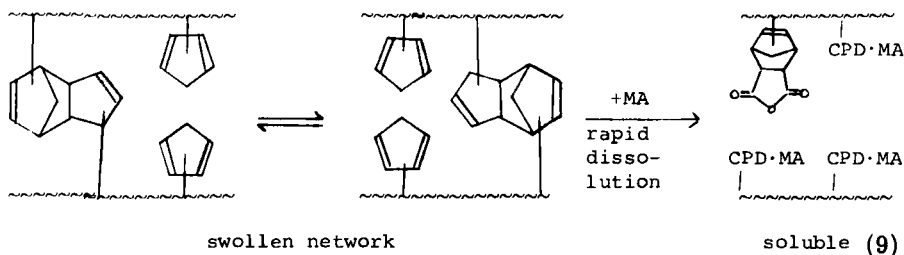
TABLE 2. Cyclopentadienylation of Chlorobutyl Rubber

|                                   | Product 1 | Product 2 |
|-----------------------------------|-----------|-----------|
| <b>Experimental conditions</b>    |           |           |
| Cl/Al                             | 0.55      | 0.02      |
| Temp. (°C)                        | -20       | +24       |
| <b>Characteristics of product</b> |           |           |
| Solubility in 1,2-dichloroethane  |           |           |
| Immediately after reaction        | Sol.      | Sol.      |
| After drying                      | Insol.    | Insol.    |
| CPD content (wt %)                | 1.1       | -         |
| Cl sites substituted (%)          | 55        | -         |

weight of chlorine was used. The Cl/Al ratio indicates the number of chlorine atoms in chlorobutyl per mole of Me<sub>2</sub>CPDAI used.

Significantly, in the reactor and immediately after reaction the rubber was soluble; however, after drying in a vacuum drying oven the product became insoluble in common solvents. Compression molding of the rubber in the absence of additives gave clear, smooth and snappy films which after shredding with scissors could be remolded to again yield clear and snappy test pieces. During the third remolding cycle the materials permanently crosslinked and the test pieces assumed uneven shapes.

The insoluble swollen materials obtained after drying could be readily dissolved by the addition of small amounts of maleic anhydride. For example, in one experiment, cyclopentadienylation chlorobutyl rubber was refluxed in hexachlorobutadiene (212°C), however, the rubber swelled but did not dissolve. Upon the addition of maleic anhydride the material dissolved and a homogeneous solution was obtained. The content of maleic anhydride adducts could be quantitatively determined by infrared spectroscopy. Maleic anhydride (MA)



addition solubilizes the swollen network by reacting with the "open" pendant cyclopentadiene groups and drives the reaction toward the right [ Eq. (9) ].

### ACKNOWLEDGMENT

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