

Initiation Methods

Criticism of Hypotheses by Gandini and Cheradame Regarding the Initiation of Carbocationic Polymerization

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Abstract

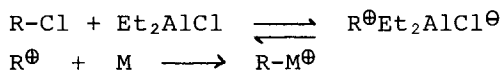
In the framework of their review of carbocationic initiation of olefin polymerization Gandini and Cheradame have hypothesized that carbocationic blocking and grafting of alkenes in the presence of Friedel-Crafts acids may also proceed by an "onto" mechanism and not by a "from" process suggested by Kennedy et al. A wide battery of facts and recently generated information substantiate the blocking and grafting from mechanisms and refute Gandini and Cheradame's onto hypothesis.

Introduction

The exact mechanism of initiation of carbocationic polymerization is of great interest not only from a purely esoteric-theoretical point of view but also for practical reasons. Thus insight into the detailed mechanism of this process enables and guides the polymer chemist to design and to incorporate into macromolecules useful head groups, be these small functional groups leading to macromers, or large molecules leading to block and graft copolymers.

Gandini and Cheradame, G & C, recently reviewed in great detail the field of initiation of carbocationic olefin polymerizations(1) and criticized Kennedy's initiation mechanism which provided essential guidance among other things to the efficient synthesis of block and graft copolymers, and other head-functionalized polymers.

According to Kennedy the polymerization of olefins can be readily initiated by labile halogen containing organic compounds RX, where R = tertiary, benzylic, allylic and X = Cl or Br, be these small or polymeric molecules, in conjunction with alkylaluminum compounds carrying two or three alkyl substituents, e.g., Et₂AlCl, Et₃Al, Me₃Al (for a comprehensive summary, see ref. 2). Initiation is visualized to involve ion generation immediately followed by cationation, for example



where M = cationically polymerizable monomer. When RX is a suitable polymeric halide, block or graft copolymers can be obtained; specifically block copolymers will arise when X is a halide at the end of a chain, and grafts when X's are

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randomly distributed along a chain. The large number of mechanistic studies that have been carried out relative to this mechanism have recently been summarized (2).

G & C question this "blocking from" or "grafting from" mechanism and argue without experimental evidence "that grafting onto the polymer occurs rather than from it" (pages 174 and 241 of ref. 1). These authors visualize the formation of block or graft copolymers by the growing polymer cations attacking (alkylating) unsaturations and/or aromatic rings in preformed polymers. It is the purpose of this article to refute this hypothesis. First we examine the evidence presented by G & C, and then we present proof that proves the correctness of the grafting from mechanism.

Gandini and Cheradame's Arguments in Favor of a Grafting-Onto Mechanism

G & C cite two references (refs. 613 and 858 in their review) which indicate grafting onto. (A third reference (615) is to an obscure "private communication" without any specific data and therefore cannot be taken seriously). According to the first of these references, Sigwalt et al. (3) grafted polyindene onto chlorinated butyl rubber, i.e., a rubber that contains a few percent allylic chlorines and unsaturations, and chlorinated ethylene/propylene copolymer, i.e., a saturated rubber that contained a few percent of most likely tertiary chlorines. Careful reading of this reference reveals that these grafting experiments have invariably been carried to 100% conversions! Under these conditions grafting from will occur (at low monomer conversions) which is then followed at high conversions by a mixed grafting from/grafting onto phase: when the monomer supply diminishes and grafting from decelerates, the growing polyindene cations will start to alkylate (grafting onto) freshly formed polyindene branches. At high monomer conversions grafting onto must sooner-or-later arise because in the virtual absence of monomer the most nucleophilic sites in the system will be unsaturations in the preformed polymer backbone or aromatic rings in the freshly formed polyindene, poly(α -methylstyrene) branches. Thus these experiments carried to \sim 100% conversions cannot give information as to the grafting from mechanism. Kennedy et al.'s grafting from and blocking from experiments have been purposefully carried out at low monomer conversions and often yielded 100% grafting efficiencies (G_{eff}) (2).

In the second reference cited by G & C (4) copolymers of isobutylene/p-chloromethylstyrene were prepared ($t\text{BuCl}/\text{TiCl}_4$ or $t\text{BuCl}/\text{Et}_2\text{AlCl}$ initiating system at -60°C) and used as backbones in the presence of Et_2AlCl coinitiator to graft styrene, α -methylstyrene and indene, again to very high (80-100%) conversions. The same comments as above hold: While grafting onto can be forced to occur at very high monomer conversions (in this case grafting onto freshly formed polystyrene or other aromatic branches), these experiments have very little diagnostic value to prove the absence of grafting from. Meaningful data to prove or disprove grafting from can only be

obtained at low monomer conversions, i.e., conditions used in Kennedy et al.'s experiments (2). Evidently G & C failed to appreciate the necessity of this circumstance.

Facts Proving Blocking- or Grafting From and Refuting

the Hypothesis of Blocking- or Grafting Onto

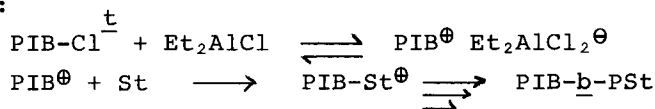
1.) The Effect of Conversion on Grafting Efficiencies. It is an experimental fact that carbocationic grafting of various monomers (isobutylene, styrene) involving a variety of chlorinated backbones (Cl-EPR, PVC, Cl-IIR) yields close to 100% G_{eff} 's at low (5-10%) monomer conversions (2,5). Indeed, according to the theory of grafting from, 100% G_{eff} must occur at infinitesimally low monomer conversions i.e., grafting must originate exclusively at the polymer cation. In contrast, it is very difficult to conceive a grafting onto scenario that would yield high G_{eff} at low monomer conversions. In the references cited by G & C (see above) grafting onto occurs only at high monomer conversions i.e., at low monomer concentrations.

2.) Carbocationic Grafting Onto Saturated Aliphatic Polymers is Virtually Impossible. Chlorinated ethylene/propylene copolymers and chlorosulfonated polyethylene (containing a relatively small amount of tert.-chlorines) readily give rise to grafts of high G_{eff} 's (up to 90%) under cationic conditions at low to moderate monomer conversions (30%) (2). For example, during the synthesis of EPM-g-PSt alkylation of the saturated polymer by the growing carbocation cannot occur, i.e., grafting onto must be absent (6).

3.) Carbocationic Grafting Onto PVC Impossible. Poly(vinyl chloride) inherently contains very low quantities (~ 0.1 mole%) of labile (allylic, perhaps tertiary) chlorines which in the presence of Et_2AlCl or Et_3Al are excellent grafting sites by a from mechanism. PVC-g-PIB can be readily prepared and good G_{eff} 's can be obtained at moderately low conversions (5). The grafting of PVC by an onto process could not occur under the conditions because a) growing PIB^{\oplus} carbocations would not be able to alkylate PVC and b) the incompatibility between PVC and PIB would prevent physical contact between these polymer segments.

4.) High Efficiency Grafting From Occurs Only with Et_2AlCl , Et_3Al or Me_3Al but not with $AlCl_3$ or $EtAlCl_2$. High efficiency grafting (up to 90%) of chlorine-containing backbones does not occur with $AlCl_3$, $EtAlCl_2$, $MeAlCl_2$, i.e., highly chlorinated aluminum compounds (2,5,6). The coinitiators $EtAlCl_2$ or $AlCl_3$ readily coiniliate the polymerization of isobutylene and styrene in the presence of protic impurities (H_2O) so that grafting onto should occur. In contrast, high G_{eff} 's can readily be obtained with Et_2AlCl , Et_3Al or Me_3Al , i.e., Friedel-Crafts acids that do not coiniliate polymerizations with trace concentration of protic impurities, but require the purposeful addition of small molecule or polymeric initiators RX which give rise to grafting from.

5.) Formation of PIB-b-PSt. Polyisobutylene carrying a tertiary chlorine end group PIB-Cl^{\ominus} in conjunction with Et_2AlCl and styrene readily produces a PIB-b-PSt diblock (7). In view of the very low concentration of terminal tertiary chlorines and aliphatic nature of the PIB chain, it would be very difficult to explain these facts by a blocking onto mechanism. In contrast, a blocking from route readily accounts for the facts (2,7):



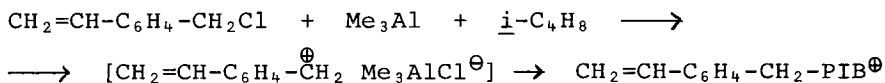
6.) Preferential Grafting of St from Chlorobutyl over Bromobutyl. If a grafting onto mechanism would operate, both halogenated butyl rubbers, chlorobutyl and bromobutyl rubbers, would equally well lead to grafts. This, however, is not the case and chlorobutyl rubber is a far superior graft initiator than bromobutyl (5). The reasons for this unexpected observation have been discussed and are beyond the scope of this paper (8).

7.) Surface Grafting. Various solids, i.e., silicas carrying a very low concentration of the cation precursor $-\text{Si}(\text{CH}_3)_2-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$ (9), PVC (10), and polypropylene fibers carrying tert.-chlorines (11) on or close to the surface of solids have been used to induce the slurry polymerization of isobutylene and styrene in the presence of Et_2AlCl . It is very difficult to conceive grafting onto in these systems, first of all because of the nature of these solids and because of the incompatibility between either of these solids and the growing polycations.

8.) The Synthesis of P α MeSt-b-PIB-b-P α MeSt Triblocks from

Chlorine-Telechelic PIB Only Conceivable by a From Mechanism. tert.-Chlorine telechelic PIB ($\text{Cl}^{\ominus}\text{-PIB-Cl}^{\ominus}$) in conjunction with Et_2AlCl yielded P α MeSt-b-PIB-b-P α MeSt thermoplastic elastomer triblock copolymers (12). It would be virtually impossible to visualize the formation of these linear triblock copolymers by a blocking onto route.

9.) The Synthesis of Polyisobutenylstyrene Macromers Only Conceivable by a From Mechanism. The synthesis of polyisobutenylstyrene PIB-St macromer has recently been described (13). The synthesis involved the initiation of isobutylene polymerization by vinylbenzyl chloride in conjunction of an alkylaluminum coiniciator:



Importantly, the PIB-St macromer contained one styryl head group per molecule. It is inconceivable that such a stoichiometry could be obtained by an onto mechanism.

10.) Direct Spectroscopic Observation of the Blocking and Grafting Sites. Recently poly(indene-g-isobutylene) has been prepared and the structure of these grafts analyzed by ^1H NMR

spectroscopy (14). According to these studies the PIB branches were attached to aliphatic carbons (i.e., benzylic carbons that carried chlorines used for grafting) and not to aromatic carbons in polyindene. Had grafting onto taken place, the growing PIB⁺ cations would have alkylated the aromatic ring. In a similar vein, ring alkylation does not occur during the synthesis of poly(isobutylene-*b*-indene-*b*-isobutylene) and the PIB sequences are exclusively linked to polyindene termini, i.e., blocking from is operative (15).

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