INITIATORS, CATIONIC

1. Introduction

Cationic polymerization may be induced by a variety of physical methods: high energy radiation, direct or indirect ultraviolet (uv) radiation, and electroinitiation; and chemical methods: protic acids, Friedel-Crafts acids, and stable cation salts. The most important initiating system from a scientific as well as a practical point of view is the cation donor (initiator)/Friedel-Crafts acid (coinitiator) system. Friedel-Crafts acids (Lewis acids) are able to complex the relatively nucleophilic conjugate bases of Brønsted acids leading to quite stable counteranions (see FRIEDEL-CRAFTS REACTIONS). This in turn allows prolonged propagation and leads to high molecular weights. Mixtures of Brønsted and Friedel-Crafts acids therefore have found many applications for cationic initiation.

The major industrial products are butyl-type elastomers, polybutenes, and other hydrocarbon resins. Industrial manufacture and uses of these materials have been recently reviewed (1). Butyl rubber, a copolymer of isobutylene with 0.5–2.5% isoprene to make vulcanization possible, is the most important commercial polymer made by cationic polymerization (see BUTYL RUBBER). The polymerization is initiated by water in conjunction with $AlCl_3$ and carried out at low temperature (-90 to -100°C) to prevent chain transfer that limits the molecular weight. Another important commercial application of cationic polymerization is the manufacture of polybutenes, low molecular weight copolymers of isobutylene and a smaller amount of other butenes used in adhesives, sealants, lubricants, viscosity improvers, etc.

2. Initiating Systems

Unless working with superdried systems or in the presence of proton traps, adventitious water is always present as a proton source. Polymerization rates, monomer conversions, and to some extent polymer molecular weights are dependent on the amount of protic impurities; therefore, well-established drying methods should be followed to obtain reproducible results. The importance is not the elimination of the last trace of adventitious water, a heroic task, but to establish a more or less constant level of dryness.

In place of a proton source, ie, a Brønsted acid, a cation source such as an alkyl halide, ester, or ether can be used in conjunction with a Friedel-Crafts acid. Initiation with the ether-based initiating systems in most cases involves the halide derivative that arises upon fast halidation by the Friedel-Crafts acid, MX_n (2).

2.1. Effect of Monomer.

The efficiency of the initiator–coinitiator system depends greatly on the monomer in question. As a general rule the stability (reactivity) of the initiating cation should be close to that of the propagating chain end. This can be demonstrated by the cationogen efficiency (grams of polyisobutylene produced per mol RCl) of the alkyl halide/$(C_2H_5)_2AlCl$ initiating system in the polymerization of isobutylene (3) (Fig. 1). Since initiation involves two subsequent events, ie, ion generation and cationation, species on the two extremes are less active or may be completely inactive, because they form ionic species very slowly and/or in extremely low concentration (primary or secondary alkyl halides), or form ions in high concentration that are, however, too stable to cationate the monomer (triphenyl methyl halides). Similar results have been observed with the alkyl ester/ BCl_3 initiating system (4,5).

2.2. Nature of the Initiating System. The structure of the initiator influences the initiation step by affecting the rate of ionization and cationation. Ionization is faster and cationation is slower for the more stable cation. It is important to note that back strain, ie, the release of steric strain upon ionization, may contribute significantly to the ease of ionization. Due to the absence of back strain, *tert*-butyl chloride and cumyl chloride are inefficient initiators for the polymerization of isobutylene and α-methylstyrene, respectively. In contrast, the corresponding dimeric chlorides [2-chloro-2,4,4-trimethylpentane (6) and 2-chloro-2,4-diphenyl-4-methylpentane (7)] are excellent initiators.

Since part of the initiator together with the Lewis acid forms the complex counteranion, propagation as well as chain transfer and termination may also be affected by the initiator structure. Results using 2,4,4-trimethylpentyl esters of different acids indicate that the activity of the growing species can be modulated by the nature of the protic acid. Esters of trichloroacetic acid [76-03-9], dichloroacetic acid [79-43-6], acetic acid [64-19-7], phenylacetic acid [103-82-2], phenylbutyric acid [1821-12-1], isobutyric acid [79-31-2], pivalic acid [75-98-9], benzoic acid [65-85-0], and cinnamic acids [621-82-9] have been used as initiators for the polymerization of isobutylene (8) and styrene (9). The overall polymerization rates decrease dramatically in the same order as decreasing strength of the corresponding acid. Investigations with mono- and difunctional esters of different acids indicate that with stronger acids not only polymerization rates, but initiation efficiencies are greatly increased (10). According to recent studies (11) the propagation rate constant is independent of the nature of the counteranion, therefore the large effect in the overall polymerization rates are attributed to the large differences in the active center concentration.

The activity of an initiating system is also affected by the nature of the Friedel-Crafts (Lewis) acid. This, however, cannot be considered independently of the monomer. While weak Lewis acids such as iodine or zinc halides may be used as coinitiators to polymerize reactive monomers eg, vinyl ethers or *N*-vinyl carbazol, they are ineffective to bring about the polymerization of less reactive monomers, eg, isobutylene or styrene. Recent results (11) show that the propagation rate constant is independent of the nature of the Lewis acid. However, the overall polymerization rates very much depend on the strength of the Lewis acid since it determines the active center concetration. Unfortunetely, a general and quantitative Lewis acidity scale, which relates acidity and polymerization behavior, does not exist. Based on the C=O stretching frequency difference between 9-xanthone and its complex with metal halides, the following acidity scale can be established (12): $BF_3 < AlCl_3 < TiCl_4 < BCl_3 < SbF_5 < SbCl_5 < BBr_3$. The acidity scale, however, may be different when based on other properties of Friedel-Crafts acids, eg, heat of complex formation with amines. Moreover, the Lewis acidity is ambiguous for some Lewis acids, notably aluminum (13), organoaluminum (14), gallium (15), and titanium halides (16) that form dimers and dimeric counteranions under polymerization conditions. The dimeric Lewis acids are much stronger than the monomeric equivalents since the negative charge is dispersed more effectively in the dimeric counteranions. Consequently, even when the dimers are present at very low concentration, inititation and polymerization involves exclusively the dimeric species (the polymerization is second order in Lewis acid). Boron halides are monomeric, and therefore the polymerization is first order in boron halides (17). Moreover the activity of the boron halide -based system is greatly solvent dependent, ie, sufficient activity only occurs in polar solvent. Although among the strongest Friedel-Crafts acids, they form one of the most nucleophilic counteranions. Therefore, in nonpolar solvents where solvation of the counteranion does not promote ion generation, the ionization equilibrium is strongly shifted to the left, and the concentration of cations is extremely small. This results in very low active center concentration, and therefore in negligible polymerization rates.

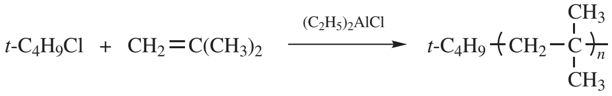
2.3. Solvent Polarity and Temperature.

The dielectric constant and polarizability are of little predictive value for the selection of solvents relative to polymerization rates and behavior. In spite of the similarity of the dielectric constants of CH_2Cl_2, CH_3Cl, and C_2H_5Cl, these solvents yield quite different isobutylene polymerization rates that decrease in the same order. The effect of solvent polarity on the polymerization rate constant is moderate, however, faster ionization and slower termination generally result in higher overall polymerization rates in a more polar solvent.

The effect of temperature is more complex and the overall effect varies for different monomers. Typical cationic polymerizations of alkenes (isobutylene, styrene, etc) proceed with propagation rate constants in excess of 10^8 L $mol^{-1}s^{-1}$ (18). Such fast bimolecular reactions do not have an enthalpic barrier (18) and for these monomers the propagation rate constant is independent of the temperature (11). The overall polymerization rate, however, is very much influenced. For isobutylene, styrene, α-methylstyrene, indene, and some other monomers the polymerization is faster at lower temperature, ie, the activation energy for the polymerization is apparently negative (19), due to faster ionization and slower termination at the lower temperature. In cationic polymerization of vinyl monomers, chain transfer is the most significant chain-breaking process. The activation energy of chain transfer is relatively high; consequently, the molecular weight of the polymer increases with decreasing temperature. Intramolecular alkylation, an undesirable side reaction in the polymerization of styrenic monomers and in the polymerization of isobutylene by the inifer technique, can also be eliminated by lowering the temperature and solvent polarity. However, opposite results were reported for $SnBr_4$ in the polymerization of α-methylstyrene, eg, intramolecular alkylation occurred using toluene but was absent using CH_2Cl_2 (20). Evidently every system has to be examined independently.

3. Controlled Initiation

Initiation by a carbocation source provides control of the head group (controlled initiation) when used in conjunction with a Friedel-Crafts acid, eg, $(C_2H_5)_3Al$, $(CH_3)_3Al$, $(C_2H_5)_2AlCl$, $TiCl_4$, BCl_3 for isobutylene, or I_2 and zinc halides for vinyl ethers, where chain transfer to monomer is absent or negligible, or in the presence of a proton trap to abort chain transfer to monomer (21). That is, initiation from tertiary, allylic, and benzylic halides gives rise to macromolecules carrying tertiary, allylic, and benzylic head groups. Initiation by halogens results in head groups carrying the halogen. Controlled initiation, however, is achieved only when polymer formation from adventitious protic impurities is also absent or negligible.



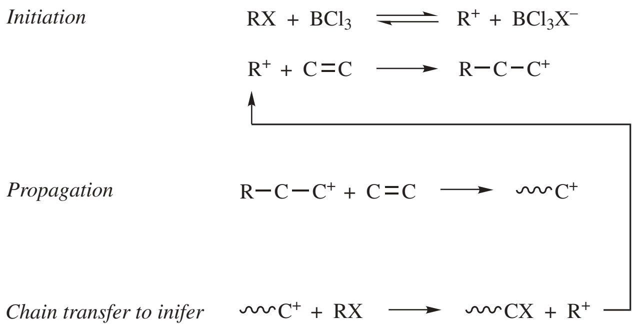
$$t\text{-}C_4H_9Cl + CH_2{=}C(CH_3)_2 \xrightarrow{(C_2H_5)_2AlCl} t\text{-}C_4H_9\left(CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right)_n$$

Polymer formation from protic impurities can be minimized by increasing the concentration of initiator or can be eliminated by the use of proton traps (22), eg, 2,6-di-*tert*-butylpyridine (DTBP) or similar hindered pyridines (eg, 2,6-di-*tert*-butyl-4-methylpyridine), which exhibit extraordinary specificity toward protons owing to their very high basicity coupled with nonnucleophilicity due to steric hindrance (23). Accordingly, they react with HCl, but not with BF_3 or CH_3I. The specificity toward protons has been exploited to obtain high efficiency block and graft copolymer formation by aborting counteranion assisted chain transfer in the polymerization of α-methylstyrene and isobutylene (24,25), and to achieve living homo- and block copolymerization of isobutylene and styrenes (22,26).

When using a cation source in conjunction with a Friedel-Crafts acid the concentration of growing centers is most often difficult to measure and remains unknown. By the use of stable carbocation salts (eg, trityl and tropylium hexachloroantimonate) the uncertainty of the concentration of initiating cations is eliminated. Due to the highly reproducible rates, stable carbocation salts have been used in kinetic studies. Their use, however, is limited to cationically fairly reactive monomers (eg, *N*-vinylcarbazole, *p*-methoxystyrene, alkyl vinyl ethers) since they are too stable, and therefore ineffective initiators of less reactive monomers, such as isobutylene, styrene, and dienes.

3.1. The Inifer Method.

A special case of controlled initiation is the inifer method (27). The word inifer (from *ini*tiator trans *fer* agents) describes compounds that function simultaneously as initiators and as chain-transfer agents. Chain transfer to inifer regenerates R^+. The inifer technique provided the first carbocationic route toward the synthesis of telechelic (α,γ-functional) polyisobutylenes and more recently telechelic poly(*p*-chlorostyrenes) (28). To prepare telechelic products, chain transfer to monomer must be absent, and with BCl_3 as coinitiator this requirement is fulfilled.



4. Direct Initiation

The mechanism of initiation in cationic polymerization using Friedel-Crafts acids appeared to be clarified by the discovery that most Friedel-Crafts acids, particularly halides of boron, titanium, and tin, require an additional cation source to initiate polymerization. Evidence has been accumulating, however, that in many systems Friedel-Crafts acids alone are able to initiate cationic polymerization. The polymerization of isobutylene, eg, can be initiated, reportedly even in the absence of an added initiator, by $AlBr_3$ or $AlCl_3$ (29), $TiCl_4$ (30), $AlC_2H_5Cl_2$ (31), and BCl_3 (32). Three fundamentally different theories have been presented to explain the still controversial existence of direct initiation. Halometalation is proposed by Sigwalt and Olah (33). In the presence of excess Friedel-Crafts acid the formed metalloorganic compound may ionize or eliminate HCl, a conventional cationogen. Self-ionization of the Friedel-Crafts acid has been suggested to explain direct initiation (29,30). Allylic self-initiation may also explain results with olefins possessing an allylic hydrogen (34).

All three theories imply that the polymerization system is free of protogenic impurities. Although direct initiation by metal halides has been postulated with the above Friedel-Crafts acids, it was proven only for aluminum halides (29) and more recently for BCl_3 (32). With $TiCl_4$, attempts have been made to observe the corresponding intermediates by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy but without success, which was explained by the known instability of the organotitanium compounds (30). Kinetic investigation of polymerizations by BCl_3 (35) suggests that initiation is by haloboration according to the Sigwalt-Olah theory. Initiation by I_2 in the polymerization of vinyl ethers can be visualized similarly, ie, a 1,2- diiodide is formed first that is subsequently activated by excess I_2 (36).

5. Photoinitiation

Cationic vinyl and ring-opening polymerization can also be initiated by photoinitiation. Diaryliodonium and triarylsulfonium salt photoinitiators, the two most well-known classes of cationic photoinitiators, can initiate the polymerization of virtually all known monomers polymerizable by cationic mechanism.

Ultraviolet-induced photolysis of these initiators results in both heterolytic and homolitic cleavage of the carbon–iodine bond, while the heterolytic pathways dominates for triarylsulfonium salts. The reactive species generated may react with solvents, monomers or impurities to yield protonic acids, which are the true initiators. Onium salt cationic photoinitiators bearing non-nucleophilic anions such as PF_6^-, SbF_6^-, BF_4^-, or AsF_6^- are most useful, since termination by ion-collapse with these anions is slow.

Cationic photoinitiators find applications where a thin film is rapidly crosslinked by exposure to uv light to produce a polymer network. The high rate of cationic crosslinking is ideal for high speed applications such as coatings, printing inks, and adhesives. Excellent reviews on the discovery, development, recent advances, and applications of cationic photoinitiators have been published recently (37–39).

6. Ring-Opening Polymerization

Many initiating systems used in the cationic polymerization of vinyl monomers, eg, protic acids, Lewis acids, and stable organic salts, can also be used to initiate ring-opening polymerization of cyclic monomers such as cyclic ethers, acetals, lactams, lactones, and siloxanes. Initiation with Lewis acids most commonly involves adventitious moisture. In addition to these well-known initiating systems covalent compounds, which are strong alkylating or acylating agents, eg, esters or anhydrides of strong acids, may initiate polymerization. Polymerization of cyclic monomers may involve different types of ionic as well as covalent growing species. Under certain conditions termination processes may be absent. The polymerization of cyclic monomers, however, is almost always complicated by inter- and intramolecular chain transfer to polymer, resulting in cyclic oligomer formation. The extent of cyclic oligomer formation can be minimized in the polymerization of epoxides by the recently discovered activated monomer mechanism (40). The polymerization is carried out in the presence of alcohol at very low monomer concentration by continuous monomer feeding.

Cyclic ether and acetal polymerizations are also important commercially. Polymerization of tetrahydrofuran (THF) is used to produce polyether diol, and polyoxymethylene, an excellent engineering plastic, is obtained by the ring-opening polymerization of trioxane with a small amount of cyclic ether or acetal comonomer to prevent depolymerization (see ACETAL RESINS; POLYETHER ANTIBIOTICS).

7. Living Cationic Polymerization

A variety of initiating systems have been described that allow not only controlled initiation, but also controlled propagation in the polymerization of vinyl monomers. In these living polymerization systems, chain breaking (chain transfer and irreversible termination) is absent. It is apparent that, due to the extremely rapid propagation, if all chain ends were ionized and grew simultaneously, monomer would disappear at such a high rate that the polymerization would be uncontrollable. The key to living carbocationic polymerizations is a rapid, dynamic equilibrium between a very small amount of active and a large pool of dormant species. For a specific monomer, the rate of exchange as well as the position of the equilibrium depend on the nature of the counteranion in addition to temperature and solvent polarity. Therefore, initiator–coinitiator systems that bring about living polymerization under a certain set of experimental conditions are largely determined by monomer reactivity.

The first example of living carbocationic polymerization, the polymerization of isobutyl vinyl ether [109-53-5] with a mixture of hydrogen iodide and iodine (HI/I_2) was discovered in 1984 (41). Since then the scope has been rapidly expanded to different vinyl ethers, propenyl ethers, and other cationically highly reactive monomers, such as *N*-vinylcarbazole [1484-13-5] and *p*-methoxystyrene [637-69-4], and to other initiating systems based on different Lewis acids such as zinc and tin halides, organoaluminum, and organotitanium compounds.

Shortly after the discovery of living cationic polymerization of vinyl ethers, the living cationic homo- and copolymerization of simple olefins was demonstrated (42). The original initiating systems consisted of an organic ester or ether in conjunction with $TiCl_4$ or BCl_3. The living homo- and sequential block copolymerization of isobutylene [115-11-7] and styrene [100-42-5] coinitiated with $TiCl_4$ or BCl_3 has also been achieved using alkyl halide initiators in the presence of proton traps in concentrations comparable to the concentration of protic impurities in the system (17,22,26). In the absence of proton traps, however, induced chain transfer prevents living polymerization with $TiCl_4$. With isobutylene using BCl_3, fast polymerization by the protic impurities occurs masking the much slower living polymerization, and the monomer is essentially consumed by this process unless protic impurities are scavenged. Since the first reports on living cationic polymerization, most cationically polymerizable monomers have been polymerized in living cationic polymerization (43). Key to these successes was the development of new initiating systems where the Lewis acidity (ie, the nucleophilicity of the counteranion) and suitable concentration range of the coinitiator is matched to the reactivity of the monomer (ie, the stability of the polymer cation). With these systems rapid advances have been made toward the synthesis of well-defined materials with controlled architecture, eg, pendant or terminal functional polymers, macromonomers, linear, and nonlinear block copolymers (44).

Since the discovery of living cationic systems, cationic polymerization has progressed to a new stage where the synthesis of designed materials is now possible. The rapid advances in this field will lead to useful new polymeric materials and processes that will greatly increase the economic impact of cationic initiation.

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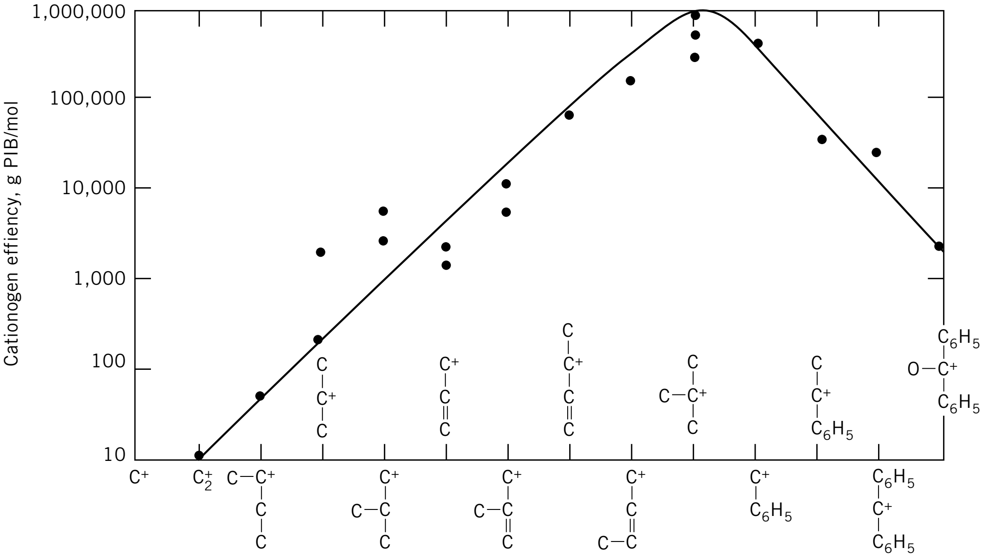

Fig. 1. Polymerization of isobutylene with various initiating ions in conjunction with $(C_2H_5)_2AlCl$ (3). PIB = polyisobutylene.