Lewis Acid on Polymeric Carriers as Initiators in Carbenium Ion Polymerizations: Polystyrene–Aluminum Chloride

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Synopsis

The scope and limitations of aluminum chloride bound to polystyrene matrix as an initiator in carbenium ion polymerizations have been studied and compared with the performance of free aluminum chloride in homogeneous solutions. Under comparable conditions, the resin-bound aluminum chloride is less efficient than free aluminum chloride; however, the molecular weights of polymers obtained from both classes of initiators are essentially similar.

INTRODUCTION

Attachment of a homogeneous catalyst to an insoluble polymeric carrier has the potential of conferring on such catalysts certain special advantages not available to simple homogeneous catalysts. Increased attention has been given in recent years to this aspect of catalysis and a number of organic chemical transformations have been subjected to supported homogeneous catalysts.[1]

However, very few reports on the applicability of a polymerization initiator attached to an insoluble polymeric carrier have appeared in the literature. Brief mention has been made on the use of ion exchange resins,[2] a phenyl (dipyridyl)–nickel chloride complex supported on polystyrene,[3] and oxidized powdered isotactic polypropylene[4] for vinyl polymerizations. In contrast, the use of inorganic carriers as supports for polymerization catalysts has attracted considerably greater attention and forms the basis for commercial production of linear polyethylene and polypropylene.[5]

Recently, brief reports on the applicability of polystyrene-bound aluminum chloride to organic synthesis have appeared in the literature.[6] Aluminum chloride is a catalyst of commercial importance in the polymerization of cationically polymerizable olefins such as isobutylene and β-pinene. However, its use in polymerization is beset with certain problems. It is a highly reactive material which makes the handling of catalyst difficult and is excessively active in polymerization resulting in high heat buildup and requiring efficient and expensive heat removal techniques. Further, the criteria of uniform activity and a constant physical state, so advantageous both in laboratory synthesis and industrial processes, are not met by aluminum chloride.

It was felt that supporting aluminum chloride on a polymeric carrier could offer some advantages in the use of this initiator. In this paper we report the scope and limitations of polystyrene–aluminum chloride in ionic polymerizations.

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EXPERIMENTAL

Materials

All solvents and monomers used in this study were rigorously dried, purified by standard procedures, and freshly distilled under nitrogen prior to use. They were stored at $-20°C$ in serum rubber-capped bottles. All transfers of liquids were either effected through nitrogen-flushed hypodermic syringes or within a dry box under a positive pressure of high-purity nitrogen. Aluminum chloride was repeatedly sublimed in vacuo until the product did not yield any residue upon further volatilization. Analysis by titrimetry according to reported procedures gave satisfactory results.[7] Transfers of solid aluminum chloride were effected through a solid addition tube under nitrogen.[8]

Preparation of Crosslinked Polystyrene Resins

Polystyrenes crosslinked with variable degrees of divinylbenzene were prepared by methods described in the literature with or without the inclusion of a solvent.[9] In the former case toluene was employed, and the ratio of total monomer to solvent (F_m) was 0.5. All polymers were routinely extracted to remove variable amounts of soluble polymers prior to use. The crosslinked resins were characterized by their toluene regain according to the method of Pepper.[10]

Preparation of Polystyrene–Aluminum Chloride Resins

Aluminum chloride, either as a neat powder or in solution, was added to a slurry of the resin, swollen in an appropriate solvent (15–20 ml solvent/g resin). The reaction mixture turned deep red in less than 1 min. The mixture was agitated for 3 hr at 25°C. The excess aluminum chloride was destroyed by addition of alcohol at which time the red color was partially discharged. The resin was thoroughly rinsed with additional amounts of alcohol acetone and dried in vacuo at 50°C for 24 hr.

Aluminum and Chlorine Analysis of the Resins

Total aluminum contained in the resin was estimated by gravimetric techniques using standard procedures.[11] The chlorine content was determined using a hydrolysis reaction of aluminum chloride by methanolic sodium hydroxide in the presence of a solvent capable of swelling the resin, such as benzene. Accordingly, 0.5 g dried resin was suspended in 20 ml benzene and 8 ml $0.15N$ methanolic sodium hydroxide and refluxed for 5 hr. From the amount of sodium hydroxide consumed, the percent chlorine in the sample was estimated.

Polymerization Using Polystyrene–Aluminum Chloride

Styrene, α-methylstyrene, and β-pinene were chosen as representative monomers and were subjected to polymerization using polystyrene–aluminum chloride in methylene chloride. The resins used were rigorously dried *in vacuo* prior to use. The polymers were recovered by the procedure recommended by Jordan and Mathieson.[12] The conversions were generally low, but they were

reproducible as shown by at least two successive repetitions of each run. Polymer molecular weights were estimated both by dilute solution viscometry and by using a Hewlett-Packard Model 302B vapor phase osmometer. Similar results were obtained from both measurements.

RESULTS AND DISCUSSION

The nature of our polystyrene–aluminum chloride resin appears in all respects identical to the one previously reported.[6] This is evidenced by the fact that these resins show a characteristic IR band at 1650 cm^{-1}, catalyze the esterification of 1-butanol with propionic acid, and show an aluminum-to-chlorine atomic ratio of 1:3.

The chlorine content in the polymer was determined using a hydrolysis reaction of aluminum chloride with methanolic sodium hydroxide in a solvent capable of swelling the resin. This reaction proved to be a sensitive indicator of the reactivity of the resin-bound aluminum chloride. For example, in a macroporous polystyrene–aluminum chloride resin (7.5% DVB, 16–36 mesh), the chlorine content varied from 0.24% at 0°C to a maximum of 1.57% when the same hydrolysis reaction was performed at 78°C (Table I). A similar variation was also observed with the gel-type resin. This observation is consistent with the fact that the interchain mobility of these crosslinked resins is increased at higher temperatures, leading to its enhanced hydrolytic reactivity. The determinable chlorine content was negligible in the absence of a swelling solvent, confirming the protected nature of this resin-bound aluminum chloride.

The total aluminum content in the polymer was also determined along with the chlorine content. The results are summarized in Table II. For gel-type resins with 1% DVB and macroporous resins with 15% DVB, the experimentally determined % Cl was less than what one would have expected from the total metal content in the polymer, assuming an Al:Cl atomic ratio of 1:3. However, with macroporous resins containing 4% and 7.5% DVB, the % Cl determined was found to be the same as one would have expected and satisfied an Al:Cl atomic ratio of 1:3. These results imply that with gel-type resin and highly crosslinked ma-

TABLE I

Chlorine Analysis of Polystyrene–Aluminum Chloride: Effect of Temperature and Solvent

Resin type[a]	Temperature, °C	% Cl[b]
G[c]	reflux	0.76
G	reflux	0.76
G	25	0.33
G	0	0.21
G[d]	reflux	0.08
G[d]	25	0.04
M	78	1.57
M	25	0.29
M	0	0.24

[a] G = Gel (1% DVB); M = macroporous (7.5% DVB), 16–36 mesh.

[b] 0.5 g resin slurried with 20 ml benzene and 8 ml 0.15N methanolic sodium hydroxide and refluxed for 5 hr; % AlCl$_3$ = % Cl × 3.76.

[c] Refluxed for 10 hr.

[d] Reaction in 100% methanol instead of benzene–methanol mixture.

TABLE II
Chlorine and Aluminum Analysis of Polystyrene–Aluminum Chloride

% DVB	Mesh size (BSS)	% Cl, found[c]	% Al, found[d]	% Cl, expected[e]
Gel-type resin[a]				
1[f]	8–16	0.26	0.34	0.45
1[g]	8–16	0.18	0.26	0.34
1	25–36	0.37	0.59	0.78
1	36–52	0.34	0.49	0.54
1	>72	0.34	0.53	0.70
Macroporous resin[b]				
15	16–36	0.86	0.81	1.06
7.5	16–36	1.57	1.21	1.59
4	16–36	1.60	1.21	1.59

[a] Polystyrene–aluminum chloride was prepared by slurring 2.5 g resin with 0.25 g $AlCl_3$ in 25–30 ml CH_2Cl_2 for 1 hr at 25°C.

[b] Polystyrene–aluminum chloride was prepared by slurrying 2.5 g resin with 0.5 g $AlCl_3$ in 25–30 ml CH_2Cl_2 for 2 hr at 25°C.

[c] % $AlCl_3$ = % Cl × 3.76.

[d] % $AlCl_3$ = % Al × 4.94.

[e] Based on aluminum analysis and assuming an Al:Cl atomic ratio of 1:3.

[f] CS_2 was used as solvent in reaction.

[g] Benzene was used as solvent in reaction.

croporous resins, only a fraction of the aluminum chloride contained in the resin is reactive toward the hydrolysis reaction; whereas in the case of macroporous resins with lower degrees of crosslinking, practically all of the aluminum chloride is reactive to hydrolysis. Such a behavior is typical of heterogeneous surfaces where, due to reasons of accessibility, not all active centers are equally reactive.[13]

Effect of Resin Type and Reaction Variables on the Preparation of Polystyrene–Aluminum Chloride

With a view to facilitating the choice of an appropriate polystyrene–aluminum chloride initiator for our study, we undertook a systematic study of the role of resin structure as well as reaction conditions on the preparation of this reagent. Using both gel- and macroporous-type resins and a polymer-to-aluminum chloride ratio of 10:1, we compared the following solvents: ethyl chloride, methylene chloride, carbon disulfide, benzene, and chlorobenzene. It was observed that methylene chloride at 25°C gave the maximum aluminum chloride incorporation. Control experiments with uncrosslinked polystyrene showed that CH_2Cl_2 does not introduce additional crosslinks in the presence of aluminum chloride at 25°C. Use of homogeneous solution did not offer any appreciable advantages over the use of a slurry. Temperatures higher than room temperature or a polymer-to-aluminum chloride ratio greater than 5:1 resulted in variable degrees of chain degradation. With both gel- and macroporous-type resins, the aluminum chloride incorporation by the polymer increased with decreasing degree of crosslinking and increasing polymer size (Tables III and IV).

Our results from the present study are in qualitative agreement with that reported previously in the literature for the preparation of this reagent.[6a]

TABLE III
Preparation of Polystyrene–Aluminum Chloride: Effect of Degree of Crosslinking

Resin type[a]	% DVB	Mesh size (BSS)	% Cl[b]
G	2	8–16	0.86
G	1	8–16	1.05
G	0.5	8–16	1.1
G	0	8–16	0
M	15	16–36	0.86
M	7.5	16–36	1.57
M	4	16–36	1.60

[a] G = Gel; M = macroporous. Polystyrene–aluminum chloride was prepared by slurrying 2.5 g resin with 0.5 g $AlCl_3$ in 25–30 ml CH_2Cl_2 at 25°C for 2 hr.

[b] % $AlCl_3$ = % Cl × 3.76.

TABLE IV
Preparation of Polystyrene–Aluminum Chloride: Effect of Polymer size[a]

Mesh size (BSS)	% Cl[b]
8–16	1.1
16–25	1.05
36–52	0.86
72–100	0.45
100–150	0.37
>200	0.37

[a] Gel-type resin crosslinked with 0.5% DVB; 2.5 g of this resin slurried with 0.5 g $AlCl_3$ in 25–30 ml CH_2Cl_2 for 2 hr at 25°C.

[b] % $AlCl_3$ = % Cl × 3.76.

Polymerization Using Polystyrene–Aluminum Chloride

Styrene, α-methylstyrene, and β-pinene were polymerized using polystyrene–aluminum chloride in methylene chloride. After use, the resins were recovered quantitatively by filteration and subjected to chlorine analysis using the previously standardized hydrolysis reaction. From this one could estimate the aluminum chloride depleted from the resin during polymerization. Some typical results are shown in Table V. It was observed that although the resin used was sufficient to give 1.5 mmol aluminum chloride (assuming that all aluminum chloride on the polymer had equal reactivity), in reality only 0.3–0.6 mmole aluminum chloride were lost from the resin during polymerization. These results are consistent with the reactivity values of these resins estimated at 0°C based on the hydrolysis reaction (Table I). Consequently, we have compared the reactivity of the polystyrene–aluminum chloride with free aluminum chloride using 0.5 mmol anhydrous aluminum chloride in a homogeneous solution in methylene chloride at similar temperatures and monomer concentrations. The results are summarized in Table VI. It is observed that the polymerizations with aluminum chloride in homogeneous solution proceed to give significantly higher conversions compared to the resin-bound analog. Appropriate control experiments established the absence of polymerization in the presence of crosslinked styrene–divinylbenzene copolymer resins containing no aluminum chloride.

With a view to obtain better initiating efficiencies using polystyrene–aluminum chloride, we have varied a number of reaction parameters, such as solvent (benzene, methylene chloride, and ethyl chloride), monomer concentrations

TABLE V
Polymerization Using Polystyrene–Aluminum Chloride[a]

Resin type	% DVB	M	% Conversion[b]	AlCl$_3$ consumed, mmole	$\overline{M}_n$[c]
β-Pinene, 25°C					
G	0.5	2.0	2	0.7	—[d]
G	1.0	2.0	1	0.7	—
M	4.0	2.0	1	0.8	—[e]
α-Methylstyrene, 0°C					
G	1.0	2.0	4.5	0.3	340
G	0.5	5.0	3	0.4	300
G[f]	0.5	5.0	0	—	—
M	7.5	2.0	2	0.2	430
Styrene, 0°C					
G	1.0	2.0	3.5	0.3	470
G[g]	1.0	1.0	0	1.1	—
M	7.5	2.0	3	0.4	600
M	4.0	0.5	2	0.4	660

[a] Charge = 0.05 mole monomer in CH$_2$Cl$_2$; reaction time = 3 hr. The resin used (16–36 mesh) in the reaction was sufficient to give a maximum of 1.5 mmol aluminum chloride.

[b] Refer to methanol-insoluble portion of the product.

[c] In toluene at 37°C by VPO.

[d] $[\eta]$ = 0.04 in benzene at 30°C.

[e] $[\eta]$ = 0.035 in benzene at 30°C.

[f] Reaction at −20°C for 24 hr.

[g] Reaction at +40°C for 3 hr.

TABLE VI
Polymerization Using Anhydrous Aluminum Chloride[a]

Monomer	M	Temp., °C	% Conversion[b]	$[\eta]$[c]	D.P.
Styrene	1.0	25	78[d]	0.025	7[e]
α-Methylstyrene	1.0	0	26	0.017	2.5[f]
β-Pinene	2.0	25	73	0.04	—

[a] Charge = 0.05 mole monomer in CH$_2$Cl$_2$ containing 0.5 mmole anhydrous aluminum chloride; reaction time = 3 hr.

[b] Refer to methanol-insoluble polymers.

[c] Determined in benzene at 30°C.

[d] Conversions drops to 40% at 40°C.

[e] Using the relationship $[\eta]$ = 0.0115 + 1.8 × 10^{-5} M.[12]

[f] Using the relationship $[\eta]$ = 0.0115 + 1.93 × 10^{-5} M.[14a]

(0.5–5.0M), monomer-to-initiator ratios (200:1, 100:1, 33:1), reaction time (3–45 hr), and the effect of added coinitiators such as water, t-butyl chloride, etc., but with little success. Both the gel and macroporous resins gave similar results.

The molecular weights of polymers obtained using resin-bound aluminum chloride were essentially similar to those obtained from homogeneous reactions (Table V) and are in agreement with the literature values.[12,14]

Any discussion on the exact nature of these resins and their likely mode of reaction must at this time remain purely speculative (see, however, reference 6c, last paragraph). It is most likely that the aluminum chloride is held in the resin by a combination of weak π-bonding forces to the aromatic ring as well as by physical entrapment in the crosslinked polymer matrix. The limiting con-

versions observed with this resin catalyst system are indicative of a situation where monomers must diffuse into a swollen polymer matrix to reach the bound catalyst site, such diffusion becoming a rate-limiting effect. Although we recognized that increasing the temperature may be one way of overcoming this problem, we were precluded from trying this approach in view of the well-known inverse relationship between molecular weight and temperature in case of carbenium ion polymerizations.

CONCLUSIONS

The efficiency of the resin-bound aluminum chloride toward polymerization is inferior to that of aluminum chloride in homogeneous solutions. The other resin-bound polymerization initiators described in the literature also suffer from a similar drawback.[2-4] Although dramatic changes in polymer molecular weights and their distribution have been observed previously when using polymeric initiator systems,[4] we have found that the molecular weights of polymers produced in our study with both free and resin-bound aluminum chloride are essentially similar.

Studies currently in progress indicate that a number of other Lewis acids such as aluminum bromide, boron trifluoride, and alkylaluminum compounds can also be supported on polystyrene resin carriers. Efforts are under way to ascertain the utility of these resin-bound initiator system to ionic polymerizations.

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