

Public Disclosure: New Aqueous Carbocationic Polymerization Systems

To date only one initiator system has been disclosed that is capable of producing medium to high molecular (MW) isobutene (IB) based polymers by a cationic mechanism in aqueous media.¹⁻⁴ This approach involved use of chelating perfluoroarylated Lewis acids (PFLAs) as coinitiators in conjunction with adventitious moisture. Recently a number of publications have appeared detailing use of the monodentate PFLA $\{B(C_6F_5)_3\}$ as a coinitiator for polymerization of styrenic monomers and isoprene in the presence and absence of purposefully added initiators.⁵⁻⁷ Initiator systems based on $B(C_6F_5)_3$ are incapable of polymerizing IB and only afford low MW grades of polymers from reactive monomers, slowly.

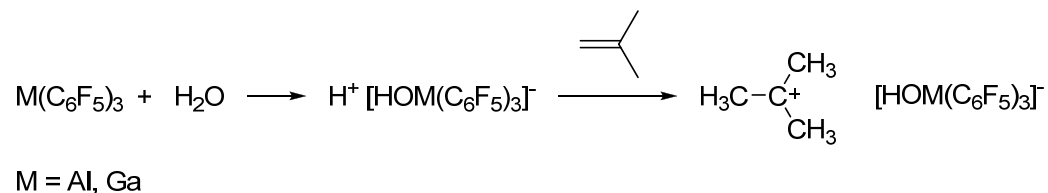
Given the poor progress that has been made in this area of polymer science following his initial invention,¹⁻⁴ Dr. Lewis of Innovative Science Corporation decided to devise yet another system capable of producing medium to high MW IB polymers in aqueous media via a cationic mechanism. This approach makes use of monodentate PFLA coinitiators where the central acidic element is either Al or Ga, in the absence of purposefully added initiators. In contradistinction to $B(C_6F_5)_3$, the Al and Ga counterparts possess a Lewis acid strength sufficient enough to induce polymerization of styrene and IB in aqueous media (Table 1). Initiation is believed to involve protonation of the monomer by a strong hypothetical Brønsted acid derived from the PFLA and adventitious moisture present in the monomer droplet (Scheme 1). MW determinations are underway and based on the qualitative physical properties of the samples obtained would appear to mirror polymers produced from $1,2-C_6F_4[B(C_6F_5)_2]_2$ under otherwise similar reaction conditions. A more detailed disclosure will appear in the peer reviewed journal literature prior to 2012.

Table 1. Aqueous carbocationic polymerization using monodentate Group 13 PFLAs.

Coinitiator ^a (mol)	Monomer (g)	Diluent ^b (mL)	T (°C)	Conv. (%)
$Ga(C_6F_5)_3$ 1.4×10^{-4}	Styrene 1.82	4	0	99
$Ga(C_6F_5)_3$ 1.4×10^{-4}	Isobutene 10.85	13.45	-40	37
$Al(C_6F_5)_3$ 5.2×10^{-5}	Styrene 1.82	4	0	70

^a All coinitiators dissolved in 2 mL toluene.

^b LiCl (23 wt%)/NaCl (1.2 wt%)/H₂O (75.8 wt %).



Scheme 1. Protonic initiation of aqueous polymerization of IB using monodentate PFLAs.

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