



AQUEOUS POLYMERIZATION OF ACRYLAMIDE INITIATED BY REDOX PAIR: CE(IV)—AZO COMPOUNDS WITH METHYLOL FUNCTIONAL GROUPS

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(Received 25 January 1994; accepted in final form 19 July 1994)

Abstract—The polymerization of acrylamide (AAM) initiated by redox pair: the ceric ammonium nitrate[Ce(IV)]-hydroxy containing thermolabile azo compounds (R) has been investigated in aqueous nitric acid at 20°C. It was determined that how the rate of polymerization depends on [AAM], [R] (1 or 2) and [Ce(IV)], respectively. The relationships between degree of polymerization and AAm-, R-, and Ce(IV)-concentrations were also evaluated.

INTRODUCTION

Polymers with azo groups either as part of their side chains or backbone are interesting starting materials for the synthesis of graft or block copolymers [1]. Azo polymers can be prepared from low molar mass azo initiators by means of condensation [1-7], cationic [8] and anionic polymerization [9] processes without any loss of the azo function.

Many reducing agents like alcohols, aldehydes and acids have been used in combination with Ce(IV) for aqueous vinyl polymerization [10-15]. In all these systems, primary initiation species is the radical produced from the substrate by the oxidation with Ce(IV).

Recently, 4,4'-azobis-(4-cyano pentanol) was utilized as a reducing agent with a combination of Ce(IV) in the polymerization of AAm [16]. It was shown, that radical species were efficiently initiating the polymerization of AAM at 30°C. The number of azo groups per polymer chain is controlled by termination mechanism.

Redox reaction of Ce(IV) with HOCH₂-group containing thermo-or photosensitive azo compounds of type 1 or 2 seemed to us a promising way to

synthesize polymeric initiator with azo functions as head and tail groups and for those having azo functions attached to the main chain.

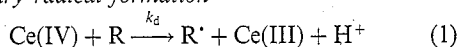
Furthermore, it was of interest to study the polymerization rate as a function of different parameters, such as [1] (or [2]), [monomer] [Ce(IV)] and others and to develop a kinetic scheme of the reaction.

RESULTS AND DISCUSSIONS

Reaction mechanism and rate law

The polymerization can be described by the following fundamental reactions:

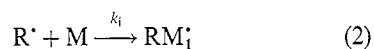
Primary radical formation



where R = 1 or 2

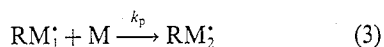
R[·]: the —CH₂OH function of 1 or 2 are converted into —CH₂O[·].

Initiation

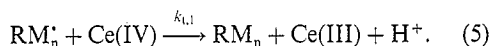


where M = AAm.

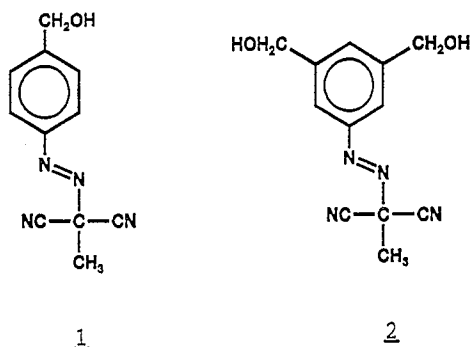
Propagation



Linear termination



Bimolecular termination



Schemes 1 and 2