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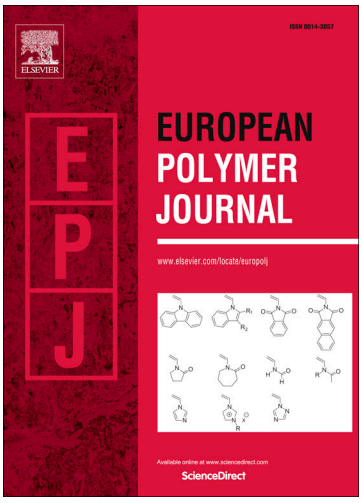

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Abstract

Hydrolysis of water-soluble industrially important mono- and poly(ethylene glycol) methacrylates catalyzed by sulfuric acid and organic monomeric acids (methacrylic and 2-acrylamido-2-methylpropanesulfonic acid) has been studied in aqueous solutions. Chemical stability of the methacrylates in dilute solutions was found to be independent of the length of ethoxylated fragments. Structurization of the studied solutions and the increase in concentration of hydrogen ions in concentrated solutions of the ethoxylated esters were shown to be the reason for the revealed unusual influence of the initial monomer concentration on the hydrolysis rate. The pronounced self-acceleration effect was observed for the methacrylic acid catalyzed reaction with increase in conversion.

Keywords: Poly(ethylene glycol) methacrylates, 2-hydroxyethyl methacrylate, acid-catalyzed hydrolysis, sulfuric acid, 2-acrylamido-2-methylpropanesulfonic acid, methacrylic acid, kinetics, concentration effect, structure of a solution.

1. Introduction

Poly(ethylene glycol) methacrylates (PEGMAs) with various degrees of ethoxylation are currently among the most large-tonnage industrial water-soluble vinyl monomers and are leaders in the growth rates of world production in this group of monomers. The main part of the active substance of modern polycarboxylate superplasticizers consists of PEGMA polymers [1]. PEGMAs exhibit surface active properties as they are amphiphilic monomers due to the presence of the hydrophobic methacrylic fragment and the hydrophilic polyethylene glycol chain [2]. PEGMA-based polymers are also amphiphilic and have unique properties. Copolymers of PEGMAs (with different ethoxylation degrees and terminal hydroxy or methoxy groups) are widely used as superabsorbents [3, 4] and as superplasticizers for concrete compositions [5, 6]. In recent years stimuli sensitive polymers based on PEGMAs were actively studied for use in pharmaceutics [7].

In many cases synthesis, storage, and (co)polymerization of PEGMAs are carried out in aqueous solutions in the presence of acids used as catalysts for the synthesis of PEGMAs, as pH regulators in the course of polymerizations and as comonomers (e.g. acrylic or methacrylic acid [3, 8], 2-acrylamido-2-methylpropanesulfonic acid (AMPSA) [9]). It is well known that acids are effective catalysts for the hydrolysis of esters [10], so one has to take into account the possibility of the hydrolysis of PEGMAs in acidic media. The hydrolysis of PEGMAs will lead to the change in composition of monomer mixtures in the course of the polymer preparation and use.

Mechanism and kinetics of the hydrolysis of esters are well studied [11], however features of the hydrolysis of ethoxylated (meth)acrylates are not described sufficiently in the literature. In one of the few studies the rate constants were determined for the hydrolysis of 2-hydroxyethyl acrylate, hydroxypropyl methacrylate and 2-ethoxyethyl methacrylate in neutral and basic media [12]. The enzymatic hydrolysis of bifunctional ethoxylated methacrylic ester