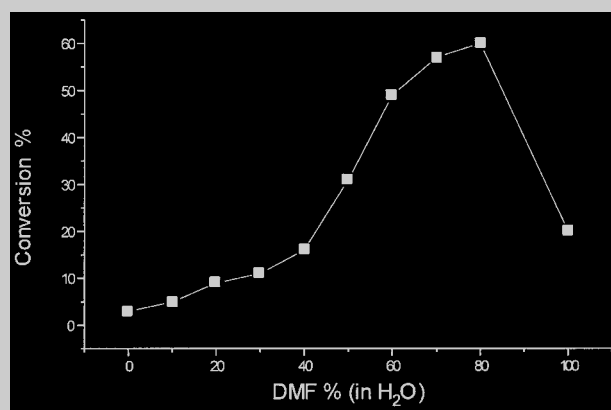


Full Paper: The polymerization of methyl methacrylate (MMA) initiated by Ce^{IV} was conducted in DMF/Water and acetonitrile. The effect of the monomer concentration and the DMF content on the conversion were investigated. The yield of the process, which proceeds under mild conditions in the mixture of DMF and water (80/20) was high. The study was augmented by cyclic voltammetric and spectrophotometric investigation. The resulting polymer was characterized by FTIR spectroscopy, and its M_w was determined viscometrically. A possible mechanism for the polymerization is suggested.

The effect of the the ratio of DMF on the conversion: [MMA] = 0.9 M, $[\text{Ce}^{\text{IV}}] = 5 \cdot 10^{-3}$ M, $[\text{H}_2\text{SO}_4] = 0.6$ M, $T = 25^\circ\text{C}$.



Solvent effect on methyl methacrylate polymerization by cerium^{IV}

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Introduction

The system cerium salt/reducing agent is a well-known and effective initiator for vinyl polymerization.^[1–4] Graft and block copolymers are also prepared with this system.^[5] A free radical is formed when a reducing agent is used in combination with the cerium salt as a consequence of an electron transfer reaction. Chemical polymerization of MMA by a cerium ion-reducing agent were studied in detail previously.^[6–13] In this article we report a chemical polymerization system in the presence of Ce^{IV} in DMF/water mixtures, which produces higher yields of MMA at shorter reaction periods compared with work reported in the literature and reactions in different solvents other than DMF that we have investigated previously.^[14]

Experimental part

Materials

Methyl methacrylate (MMA) was distilled in vacuo before use. Cerium^{IV} sulfate (CS), cerium ammonium nitrate (CAN), sulfuric acid, dimethylformamide (DMF), acetonitrile (ACN) were all Merck reagents and used without further treatment.

Equipment

Spectrophotometric measurements were conducted with a Shimadzu UV-160A UV-Visible Spectrophotometer in a

quartz cell. The UV light source used for the polymerization process was a 300 W mercury lamp. FTIR spectra were obtained on a Mattson 1000 Spectrometer and samples were prepared as KBr pellets. Electrochemical measurements were performed on a Wenking POS 575 Potentiostat equipped with a Kipp and Zonen XY recorder. An Ubbelohde viscometer was used to determine of the polymers' molecular weights using Eq. (1):^[15]

$$[\eta] = 55.9 \cdot 10^{-2} \cdot M^{0.5} \text{ ml/g} \quad (1)$$

in a methanol-toluene mixture (9/5 by volume) at 25°C .

Polymerization procedure

The chemical polymerization was carried out in a three-necked flask equipped with a stirrer and a dropping funnel for the addition of Ce^{IV} solution in a water bath controlled by a thermostat. The Ce^{IV} salt was dissolved in 0.3 M H_2SO_4 . The reaction time was chosen to be 4 h. The Ce^{IV} solution was added using a dropping funnel. Since stirring the mixture during polymerization is known to retard the process,^[14, 16] experiments were conducted under quiescent conditions. PMMA was dissolved in DMF and reprecipitated several times in water. The conversion of MMA was determined by directly weighing the PMMA dried in vacuo. The percentage of conversion was obtained from the ratio between the amount of polymer formed and the initial amount of monomer after the reaction time mentioned above.