CHARACTERIZATION OF IONIC OLIGOMERS FORMED DURING THE EMULSION POLYMERIZATION OF BUTADIENE BY MEANS OF ISOTACHOPHORESIS

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ABSTRACT

The end products of several emulsion polymerizations of butadiene with potassium persulfate as initiator were analyzed by means of isotachophoresis. The results were compared with the analyses of model compounds. The isotachopherograms of the products of surfactant free emulsion polymerizations as well as of polymerization with dresinate 214 as surfactant show oligomers with one or two sulfate end groups and up to 5 monomeric units.

INTRODUCTION

It is generally accepted that in emulsion polymerization with potassium persulfate as initiator, at least some oligomeric radicals are formed in the water phase. Termination of these radicals in the water phase gives oligomers with an amphipatic structure. Qualitative and quantitative characterization of these oligomers should give insight in the propagation and termination reactions in the water phase as well as information about the contribution of the oligomers (radicalic and terminated species) to particle formation. Up to now there are only few references relating to the actual proof of the occurrence of these oligomers [1,2,3], and they are only indicating their presence without any qualitative or quantitative information. Isotachophoresis (ITP) is an excellent method of analyzing ionic components, qualitatively as well as quantitatively. Up
to now several workers have used ITP in applications related to emulsion polymerization. Okubo and Mori [4] measured the decomposition of potassium persulfate with ITP. Ogino, Kakihara and Abe [5] used ITP to determine the CMC’s of sodium alkyl sulfates. Bolesse and Leising [6] showed the possibilities of separating ionic monomers such as acrylic and itaconic acid.

ISOTACHOPHORESIS [7,8]

In ITP discrimination between components is based on differences in electrophoretic mobility which is a function of charge and a parameter involving geometric and interactive components. Within a homologous series with the same ionic group the latter parameter is proportional to molecular weight, so ITP should be a reliable method to separate water soluble oligomers according to number of monomeric units and number of ionic end groups [9,10]. The description and theory of an isotachophoretic experiment is given elsewhere [7,9]. In understanding the isotachopherograms the following typical characteristics are essential. After separation is completed in capillary isotachophoresis all anionic components of the sample are moving behind the leading anion to the anode, while remaining in their own zone (Fig. 1), all cations are replaced by the counter ions of the leading electrolyte. The successive zones are then passing the detector in an order imposed by their

Figure 1. Schematic view of ITP detection