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Solubility of ionic oligomers formed during nucleation in emulsion polymerization monitored by isotachopheresis.
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Introduction

Reliable information on the water solubility of charged oligomeric radicals, and through this of the moment of their entry into micelles and polymer particles during emulsion polymerization would provide valuable information about nucleation phenomena. However, at present the analysis of oligomeric radicals in the water phase is not yet possible. On the other hand, knowledge about the termination products of these radicals in the water phase should give sufficient information about the presence of the precursing radicals, that can be used in kinetic studies and to estimate the oligomeric contribution to emulsion stability. If potassium persulfate (PPS) is used as an initiator the termination products will be mono- and disulfates containing one or more monomeric units. By using capillary isotachopheresis (ITP) it recently has become possible to analyse: qualitatively as well as quantitatively the charged oligomeric species formed during the emulsion polymerization of butadiene^{1,2}. In order to understand the isotachopherograms presented here, we give a very brief summary of the method, the details of which have been described elsewhere³.

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 factors. 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 charged water soluble oligomers according to the number of monomeric units and the number of ionic end groups. In an isotachophoretic experiment, the sample is placed in between two electrolytes of different composition in a capillary tube with an internal diameter of .5 or 1.0 mm. The leading electrolyte contains the constituent with the highest effective mobility, i.e. the leading ion (L^-). The terminating electrolyte contains the ion with the lowest effective mobility, i.e. the terminating ion (T^-). If an electric current is applied, the leading ions will migrate and remain in front; the sample ions with the highest effective mobility, for instance A^- , will migrate immediately behind the leading zone. Consequently, a zone with only A^- ions is formed, followed by a mixed zone AB, a zone B which has a lower mobility, and so on to the terminating zone. After some time all components are separated and a train of zones are moving with equal velocity to the anode (Figure 1a). During the course of the migration of the ions through the capillary the counter ions will be replaced by the counter ions of the leading electrolyte and the concentration of the components in the various zones changes till it has reached a value related to the concentration of the leading electrolyte, according to the regulating function of Kohlrausch³. In all day practice when using strong monofunctional electrolytes this means that the concentration of the components in the zones are only negligibly less than the concentration of the leading electrolyte. The various components can be detected, for instance with a conductivity cell, which outputs the resistance of each zone (Figure 1b). The step height is characteristic of the

component. The length of a zone, and therefore the length of the corresponding step, is a measure of the quantity of the component. With model components the zones can be calibrated. There are some drawbacks:

- There is a possibility of mixed zones if two components do not separate under the conditions used;
- Ions slower than the terminator are hidden in the terminator zone;
- Appropriate model compounds for oligomers are mostly very difficult to obtain.

Experimental

A mixture of 100 g distilled water, 2 g methyl methacrylate or styrene, 1.0 g potassium persulfate and 0.1 g potassium carbonate was heated to 62 °C in a stirred reaction vessel. Since polymer particles might affect the isotachopheretic analysis, during the experiment described here experimental conditions were chosen in such a way as to minimize particle formation. This was achieved by using low monomer content as a dispersifier, thus practically avoiding $MISO_4$ formation but still allowing oligomer production. The ITP conditions are described elsewhere². In the case of styrene two model compounds were used: p-styrenesulfonate (PSS) and 2-(p-phenylsulfonate)ethylsulfate (PSES), representing the termination products of a styrene monomer with one and two sulfate groups, respectively. The isotachopherograms of these compounds are shown in Figure 2a and 2b, respectively. In Figure 2b the step marked PSOL is probably a hydrolysis product of PSES. Figure 2c shows an isotachopherogram of the reaction product of the experiment with styrene. The only model compound for methyl methacrylate available at present is the methyl ester of 2(3)-sulfonic propionic acid (MSPE), $O_3SCH_2CH_2(CO)OCH_3$. As a byproduct the 2-sulfonic propionic acid (SPA) is formed, as can be seen in the isotachopherogram (Figure 3a). Figure 3b shows an isotachopherogram of the reaction product of the experiment with methyl methacrylate.

In the isotachopherograms of the model compounds maleic acid (MA) is used as an internal standard.

Discussion

The isotachopherograms clearly show the presence of oligomers. The positions marked with $MISO_4$ and $MISO_4)_2$ are step heights in agreement with the model compounds. The definite assignment of the other steps to oligomers requires the synthesis of additional model compounds, application of electrophoretic laws, and isotachopheresis under different conditions. As expected, the experiment with methyl methacrylate gives a much larger number of oligomers than the experiment with styrene. In the isotachopherogram of the styrene experiment a mixed zone of higher oligomers can be observed (see * in Figure 2c). These problem will be solved by applying different ITP conditions.

Recently, we obtained results strongly suggesting that (mixed) micelle formation of oligomeric species can be observed by ITP. This possibility and other points of interest, i.e. the relation between the oligomers distribution and kinetic parameters as well as the monomer-water interaction, are presently being investigated.

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The important contribution of C.G. Pijls to the experimental work is gratefully acknowledged.

Figure 1a. Schematic view of ITP detection

Figure 1b. Conductivity detector signal

Figure 2a.
Isotachopherogram of
p-styrenesulfonate

Figure 2b.
Isotachopherogram of
2-(p-phenylsulfonate)
ethylsulfate

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Figure 2c.
Isotachopherogram of the
reaction product of styrene
and potassium persulfate

Figure 3a.
Isotachopherogram of the
methyl ester of 2-sulfonic
propionic acid

Figure 3b.
Isotachopherogram of the reaction product of
methyl methacrylate and potassium persulfate