Synthesis of Taylor-made polymer colloids

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Two series of latexes of poly (methyl methacrylate) PMMA were synthesized in a semi-continuous reactor; two kinds of new emulsifier systems were tested in the synthesis: a mixture of two non-ionic surfactants and an anionic surfactant. The influence of the reactor composition on the average particle size and particle size distribution was determined using methods of scanning electron microscopy and quasi-elastic light scattering.

Keywords: Emulsion; latex particles; scanning electron microscopy.

Dos series de látex de polimetracrilato de metilo PMMA fueron sintetizados en un reactor semicontinuo; en la síntesis se evaluó la capacidad estabilizadora de una mezcla de surfactantes no iónicos y un surfactante aniónico. La dependencia del tamaño de partícula y de la polidispersidad en función de la composición del sistema fue estudiada mediante técnicas de dispersión cuasi-elástica de luz y microscopía electrónica de barrido.

Descriptores: Emulsiones; partículas de látex; microscopía electrónica de barrido.

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1. Introduction

An emulsion or latex consists of polymer particles dispersed in a continuous medium (often water) stabilized by surfactants, which prevent them from flocculating [1]. One of the most important parameters that must be known in polymer dispersions is the particle average size and its distribution, because these physical characteristics affect process variables and application properties of the product [2]. Monodispersed particles with a pre-defined size may be obtained by semi-continuous emulsion polymerization [3]. In this kind of process, the final particle diameter depends mainly on parameters such as temperature, initiator concentration, surfactant nature and concentration [4], etc. Low cost measurements of particle size distribution may be performed quickly by Quasi-Elastic Light Scattering (QELS) techniques. However, a checking by more exact methods, as Scanning Electron Microscope (SEM) [5], is very often required.

In this paper, the synthesis of two series of latex particles based on two new surfactant systems (a non ionic mixture and an anionic phosphate ester) is presented. The average particle size was controlled by means of an adjustment of the “situ” composition. The obtained dispersions were simultaneously characterized by QELS and SEM techniques, and the emulsion stability given by the nonionic and ionic systems was compared.

2. Materials and methods

Methyl methacrylate (National Starch & Chem.) was used as received. The surfactants used to stabilize the latexes were a mixture of the non-ionic surfactants ABEX EP – 120\textsuperscript{≤} and 759 – 31 MA – 80\textsuperscript{≤}, (mix 50/50), and the anionic surfactant was the RHODAFAC RE-610\textsuperscript{≤}, a phosphate ester. All the emulsifiers were kindly given by Rhodia. Ammonium persulfate APS (Aldrich) was employed as initiator. All the reactions were carried out at 70\degree C in a 1 L glass reactor at constant temperature and with a stirring rate of 350 rpm. The system composition is summarized in Table I.

The MMA in “situ” was polymerized for one hour. Once the seed was formed, the pre-emulsion from the feeding tank was introduced into the reactor for an addition period of 4 h. The QELS measurements were made in a Coulter 230 with the software LS32 ver 3.01 and the SEM used was a JEOL 5900 LV.

3. Results and discussion

The first series of latexes were prepared using the non ionic surfactant mixture. SEM images revealed that monodispersed and well defined spherical particles were obtained when the emulsion was stabilized by this mixture of non ionic emulsifiers (Fig. 2). The final average particle size was controlled by simply adjusting the monomer used to prepare the initial seed, as it is shown in Fig. 3; a continuous increment of the average particle size was observed as the monomer content into the reactor decreased. However, when a PMMA seed was not synthesized (monomer content = 0 g) a small particle of 150 nm was found, (isolated point in Fig. 3).

A second series of latex particles were synthesized using the phosphate ester as surfactant. In this case, QELS mea-
TABLE I. Formulation used in the synthesis of latex particles.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Principal reactor (g)</th>
<th>Feeding tank (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant solution (0.5%)</td>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td>Surfactant solution (3.73%)</td>
<td>-</td>
<td>113</td>
</tr>
<tr>
<td>Monomer (MMA)</td>
<td>0, 5, 8, 12, 15 and 18</td>
<td>260, 255, 252, 243, 245 and 242</td>
</tr>
<tr>
<td>APS solution (2%)</td>
<td>7</td>
<td>35</td>
</tr>
<tr>
<td>Distillate water</td>
<td>190</td>
<td>-</td>
</tr>
</tbody>
</table>

measurements showed an irregular behavior of the average particle size with the amount of seed initially formed in the reactor. Indeed, the particle diameter increased with the monomer mass until it reached a maximal diameter of 414 nm and, subsequently, a fall of the colloid size was observed at monomer contents greater than 15 g. When no seed was employed in this synthesis an unstable latex with Dpz = 580 nm was obtained, but it coagulated before the end of the reaction. The SEM characterization revealed a broad size distribution of all these emulsions (see Fig. 4), and the formation of irregular particle agglomerations produced by a poor stabilization of the system. The difference between the non ionic and ionic systems studied here may be due to their different micellar behavior [6]. Indeed, a series of densimetry, conductimetry, and light scattering characterizations were performed in order to determine the micellar behavior of the surfactants employed in this work [7]. The phosphate ester revealed a second CMC (transition from spherical to cylindrical micelles) at very low concentrations. When cylindrical micelles receive the monomer, there is an irregular breakage of the swollen micelles, which generates polymer particles of very different sizes. The mentioned physicochemical study also showed that the non-ionic mixture formed spherical micelles into the same concentration range [8]. Therefore, it is apparent that the studied phosphate ester cannot be employed to synthesize monodisperse latexes. A combination of this phosphated molecule with another surfactant is necessary to prepare high performance coatings [9].
4. Conclusions

Two series of latexes were synthesized, using two new emulsifier systems formed by a mix of non-ionic surfactants and a phosphate ester. QELS and SEM data revealed that a better control of the particle diameter and monodispersity was achieved only when the combination of non ionic surfactants was employed. SEM characterization of latex particles is a useful technique to evaluate the stabilizing ability of surfactants in emulsion polymerization.