1 Introduction

1.1 Motivation

The field of polymer colloids involves the intersection of the science of polymers and that of colloids. From a selected research topic it has gone to a fast growing one. This is obvious with the rising number of articles and books that have been published in the past several years. Due to the small size and big surface area, colloid dispersions with a narrow particle size distribution found the broad utilization in paints, coatings, textiles, as a calibration standard, as packing materials for high pressure liquid chromatography, etc. Polymer particles with various surface functional groups are extensively used in biomedical field as a carriers for a wide numbers of biological ligands such as DNA fragments, antibody molecules, enzymes, etc.

The emulsion polymerization is a most widely used method to obtain monodisperse polymer dispersions with controlled particle size and morphology. Unfortunately, the usage of classical emulsifiers which are physically attached to the particle surface, brings some disadvantages concerning their desorption from the surface. In the past decades, a lot of research works are aimed to synthesis and utilization of the new class of surfactants-reactive surfactants, which are proposed for better stabilizing properties.

No doubts, a wealth of findings have been constantly contributing to the enhancements of reactive surfactants as well as their use in the process of emulsion polymerization. However, there are always rooms for further optimization or even new explorations. In this regards, the work is narrowed down to the usage of very "exotic" hydroperoxide surface-active initiators. Such substances are indeed sensitive for handling, and therefore not many researches were conducted on them. Nevertheless, these compounds have enormous potentials for assisting emulsion polymerization process. In this context, the hydroperoxide groups could remain on the surface, giving the possibility for further modification. Needless to say, it could also be applicable for human related testings. Hence, promoting even more reasons for this investigation. On the other hand, the findings will provide another valuable legacy, which was never available before for the field of emulsion polymerization. On this basis, this work is undertaken.

1.2 Goals

The principal aim of the current work is to create an alternative way of obtaining amino functionalized microspheres, which can adsorb biomolecules on their surface. The novelty of the method lies in the utilization of newly synthesized hydroperoxide containing inisurfs (molecules which combine initiator functions and surfactant moiety) in emulsion polymerization of styrene. The unique property of using such reactive surfactants is that the hydroperoxide groups remain undecomposed on the surface of obtained nanoparticles and can generate active radicals. This gives the possibility to graft the chains of a second monomer (i.e. amino monomer).

The inisurfs used in the present work are terpolymers based on the hydroperoxide monomer (5-hydroperoxy-5-methyl-1-hexene-3-yne), acrylic acid and styrene. One of the basic works need to be performed in the beginning is the characterization of the raw synthesized terpolymers. Having understood the composition, surface-active properties and decomposition mechanism of the inisurfs' molecules, one could start looking into further investigations. In order to achieve that, the following statements-of-work are assigned:

- Emulsion polymerization of styrene in the presence of inisurfs.
- Modification of obtained particles by 2-aminoethyl methacrylate hydrochloride and N-(3-aminopropyl)methacrylamide hydrochloride.
- Adsorption of human IgG onto the aminated surface.
- Determination of Immunoreactivity by Latex Agglutination Reaction.

It is important to note that the final statement-of-work above is regarding a very practical application. In brief, this work will reveal not only the feasibility of the proposed method but also will provide a vital application of the particles.

1.3 Dissertation Outline

This dissertation is organized in 6 major chapters. In the present chapter, the goals of the current work have been defined. The goals justify the motivation posited earlier to that.
To start off the investigation, an extensive literature review on the subject matter is given in the chapter 2. All the current and past reported findings are carefully studied. Mostly, they are related to the mechanism of the emulsion polymerization process, methods of preparation of functional polymer particles and their potential applications in biomedical field.

The theoretical description of some analytical methods and experimental procedures used in the current work are presented in chapter 3 and 4, respectively.

Chapter 5 is dedicated to the discussion of the main experimental results. The inisurf molecules are analyzed with respect to their composition, structure and surface-active properties. The thermal decomposition of hydroperoxide groups is studied and the activation parameters of the process are calculated. The preparation of polystyrene particles in the presence of inisurfs and influence of different experimental conditions (temperature, inisurf composition and concentration) on the polymerization process is described. The main kinetic parameters (activation energy, polymerization rate constant) and characterization data of obtained dispersions (size, polydispersity, number of particles, amount of surface groups, stability tests) are presented. Then the synthesis of amino modified particles and results of the surface composition analysis (XPS, ^{1}H-NMR, fluorescenometric titration, electrophoretic studies) are included. The final part of chapter 5 is dedicated to the latex-IgG interaction studies. In the end the results of the model immunoassay are presented.

Finally, the conclusions of this work and the possible further investigations/applications are given in chapter 6. The references are compiled in the last part of this dissertation.

2 Theoretical Background

2.1 Introduction

The preparative techniques and systems of microspheres with diameter from 0.1 to above 100 μm have been well established. Polymeric microspheres are produced by either of the two available methods. First starts from monomers and the second from preformed polymers. Most of researches are concerned with the preparation of microspheres via polymerization process, because various microspheres with required functionalities can be obtained economically at high concentration. The preparative methods by a polymerization process include various heterogeneous and homogeneous polymerization such as emulsion polymerization, suspension polymerization, dispersion polymerization, and their modifications. Figure 2.1.1 shows the characteristic particle sizes formed by different types of polymerization.

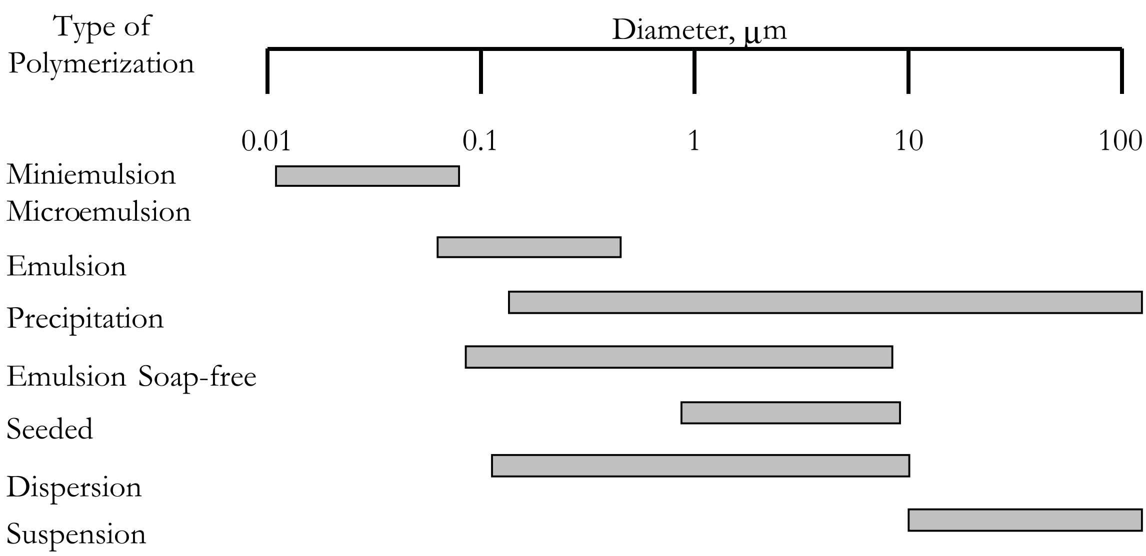

Figure 2.1.1. Size of microspheres prepared by different polymerization methods.

Emulsion polymerization is the most typical and well-known polymerization method for preparing uniform polymeric particles. Almost 7% of the world polymer production is produced as a polymer dispersions [Dis99].