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Synthesis of sterically stabilized perfluorinated aqueous latices



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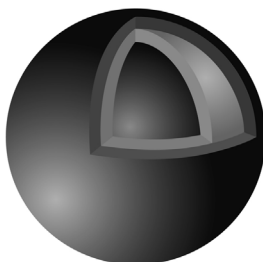
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HIGHLIGHTS

- High fluorinated particles were synthesized by emulsion polymerization.
- Sterical stabilization was attached by atom transfer radical polymerization.
- Two alternative strategies were developed.

GRAPHICAL ABSTRACT



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ABSTRACT

We report on two novel and improved reaction strategies for the synthesis of a recently introduced new colloidal model system [M. Wiemann, R. Schneider, E. Bartsch, *Z. Phys. Chem.* 226 (2012) 761] composed of cores of the highly fluorinated polymer poly(1*H*,1*H*-heptafluorobutyl methacrylate) (PFBMA) and sterically stabilized in water by a poly(ethyleneglycol) (PEG) coating. PFBMA was chosen as its low refractive index allows to prepare highly concentrated dispersions isorefractive in aqueous medium which makes such systems amenable to light scattering studies. In the first approach we use standard emulsion polymerization for synthesis of a PFBMA seed dispersion. The seed particles are then functionalized in a seeded growth polymerization with a thin shell composed of the bromine carrying monomer 2-(2-bromoisobutyryloxy) ethyl methacrylate (BIEM) co-polymerized with FBMA. BIEM is an initiator for atom transfer radical polymerization (ATRP) which is used in the final step to graft the particle surfaces with PEG using the macromonomer poly(ethyleneglycol) methacrylate (PEGMA, DP = 23). In the second approach we combine seed preparation and functionalization into one step with a semi-batch emulsion polymerization, generating a core-shell particle with PFBMA as core and a P(BIEM-co-FBMA) shell, again followed by ATRP to graft PEG onto the particles. Both strategies provide nearly monodisperse particles which are sterically stabilized in water as demonstrated by dynamic light scattering experiments in combination with colloidal stability tests and ¹H-NMR characterization. The merits and disadvantages of these new synthesis strategies for the preparation of model colloids are critically compared.

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1. Introduction

Colloidal dispersions are widely used in industrial applications, e.g. for coatings, adhesives or paints [1]. One of the major objectives for improving dispersion formulations is to lower the costs of

energy and transport. Thus, increasing the solids content by achieving a high volume fraction ϕ of dispersed material is generally attractive as it makes processing more economic (e.g. less water has to be evaporated on drying a latex dispersion in order to generate a polymer coating). On the other hand viscosity increases with increasing solids content and it is well known that on approaching the colloid glass transition at $\phi \sim 0.58$ –0.6 (depending on particle interactions and particle polydispersity) the zero shear viscosity increases dramatically [2]. Thus, to maintain processability and at the same time achieve high solids contents, very often binary mixtures or broad particle size distributions are employed [3,4]. For

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many applications this solution is not feasible or more narrow, monomodal distributions are required. Thus, alternative strategies to obtain highly concentrated dispersions which still easily flow are sought for. One such alternative was suggested recently by Willenbacher et al. [5]. By adding a non-adsorbing free polymer to a colloidal model system (polystyrene microgels in a good solvent) and use of the so-called re-entry effect it could be shown by a combination of dynamic light scattering and rheology experiments that fluid dispersions which are essentially monomodal and have a narrow size distribution can be prepared up to a volume fraction of 0.69. In Ref. [5] it could also be demonstrated that this concept can be transferred from model systems to technical aqueous dispersions. However, there the re-entry effect was significantly weaker allowing preparation of fluid samples only up to $\phi = 0.644$. To better understand the physical origin of the differences between the employed model system and technical dispersions a systematic study of the connection between rheological behavior, dispersion micro structure and particle dynamics in water based dispersion is necessary. Structure and dynamics of colloidal dispersions – to monitor and understand particle nucleation and crystallisation or the processes leading to glassy arrest in dispersions [6–8] – are typically studied by light scattering techniques. These, however, require transparent samples, i.e. the refractive index of the particles should be very close to the refractive index of the dispersion medium to avoid multiple scattering effects which give rise to dispersion turbidity. This isorefractivity condition is, however, difficult to achieve when water is the dispersion medium due to its low refractive index ($n_D^{20} = 1.332$ as compared to 1.48–1.59 for most common polymers). Thus, the technically most interesting dispersion medium is rarely used in the development of colloidal model systems. Exceptions are a small number of studies [9–11] where perfluorinated monomers have been employed as they provide particles which are nearly isorefractive to water ($n_D^{20} = 1.36$ – 1.38 [12]) so that by addition of a suitable cosolvent or some special salt, isorefractivity can be achieved. However, these perfluorinated latexes are typically charge stabilized so that in order to use them as model systems to mimic the hard sphere system screening by addition of salt is required. In addition, the preparation and handling of highly concentrated dispersions with such particles is tricky as charge-stabilized particles are prone to irreversible coagulation [13]. To avoid these difficulties it would be of high interest to prepare truly sterically stabilized particles which are (nearly) isorefractive to water and whose interactions can be tuned from hard-sphere like to a more softer repulsive interaction potential by varying grafting density and length of the stabilizing polymer. For this reason we have recently started to develop such a new colloidal model system using the highly fluorinated monomer 1H,1H-heptafluorobutyl methacrylate (FBMA) with its low refractive index $n_D^{20} = 1.3317$ [12]. As a stabilizing polymer we used poly(ethyleneglycol) which due to its good water solubility has been widely used to stabilize common polymer particles [14–18]. Using the macromonomer poly(ethyleneglycol) methacrylate with an average $M_n = 1100$ g/mol (PEGMA) as comonomer in a batch emulsion polymerization, perfluorinated and sterically stabilized particles by PEG coated particle surfaces have been obtained [19]. In a first study of the glass transition dynamics the glass transition was found to occur at a much too low volume fraction of $\phi_g = 0.262$ [19]. This observation was attributed to the presence of a very large PEG-layer which is swollen with water. When spinning down the dispersion in a centrifuge to prepare a stock dispersion which can be then assigned the volume fraction of random close packing $\phi_{rcp} = 0.64$ – a standard procedure to define the volume fraction scale of hard sphere-like particles [2] – the water is partially squeezed out of the PEG layer and the volume fraction was thus ill-defined leading to an erroneously low value for the glass transition volume fraction. To improve onto this situation we tried

to establish a new synthesis protocol which should provide a thin stabilization layer and allow for independent control of particle size and PEG shell thickness. This was impossible when employing the batch process as there the PEG macromonomer acted as a surfmer, providing particle stability and determining particle size at the same time. For this purpose we devised a core-shell synthesis where a P(FBMA) seed dispersion was prepared by conventional techniques like batch or semi-batch emulsion polymerization. To decouple particle size and the formation of the stabilizing layer we employed atom transfer radical polymerization (ATRP) [20] to graft the PEG macromonomer to the particle surfaces. Thus, the main new step is the introduction of an ATRP-initiator by a seeded-growth copolymerization of a suitable monomer and FBMA onto the seed particles. In the last step the PEG-macromonomer is grafted to the particle surfaces by ATRP. ATRP is a metal-mediated radical polymerization. Fundamental studies were done by Matyjaszewski [20]. Atom transfer radical polymerization is not a new reaction, but its range of application has been widely extended over the last years [21]. This is due to the fact that ATRP on one hand can be used to synthesize linear polymers with a very low polydispersity ($M_w/M_n < 1.1$) [21] and on the other hand it gives access to a controlled molecular architecture. As metal usually $Cu^I Br$ and as ligand 2,2-bipyridine (bipy) are used. Applications of ATRP to self assembled particle formation by copolymerization of poly(ethyleneglycol) methacrylate and pentafluorostyrene have already been shown by Tan et al. [22]. The employment of inorganic silica particles with a shell via ATRP has been demonstrated by Perruchot et al. [23]. Here, we report on the first synthesis and characterization of perfluorinated particles, nearly isorefractive to water and sterically stabilized in aqueous media, by a thin PEG shell applied via ATRP on preformed seed particles.

2. Experimental

2.1. Materials

The monomers 1H,1H-heptafluorobutyl methacrylate, obtained from Alfa Aesar (Germany) (FBMA, Fig. 1) and 2-hydroxyethyl methacrylate (HEMA), obtained from Sigma-Aldrich, were distilled under reduced pressure and stored at $-20^\circ C$ under an argon atmosphere. The macromonomer poly(ethyleneglycol) methacrylate with an average $M_n = 1100$ g/mol (PEGMA, Fig. 1) was used as received. 2-Bromoisobutyrylbromide (BIBB) was obtained from Alfa Aesar and used as received. Sodium dodecyl sulfate (KPS) was obtained from VWR International (England) and purified by recrystallisation from ethanol. The chemicals potassium peroxydisulfate (KPS; Merck), 2,2'-bipyridine (bipy; Merck), $Cu^I Br$ (Aldrich) and chloroform-D1 (99.8%; Alfa Aesar) were used as received. Synthesis of 2-(2-bromoisobutyryloxy) ethyl methacrylate (BIEM, Fig. 1) was performed by using HEMA and BIBB (see below).

2.2. Synthesis

2.2.1. Synthesis of 2-(2-bromoisobutyryloxy) ethyl methacrylate (BIEM)

A mixture of CH_2Cl_2 (100 ml), pyridine (5 ml) and 2-hydroxyethyl methacrylate (7.5 ml, 62.0 mmol, 1.00 equiv.), was cooled to $0^\circ C$. A mixture of 2-bromoisobutyrylbromide (8.0 ml, 64.6 mmol, 1.03 equiv.) in CH_2Cl_2 (20 ml) was added during a time period of 60 min. After the addition was completed, the cooling was removed and the reaction mixture was stirred for another 2 h at room temperature. The white solid precipitate was removed by filtration. The solvent phase was then removed at $40^\circ C$ under reduced pressure. Again a white solid precipitate formed which was removed by filtration. Residual BIEM was extracted from the

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