



Facile synthesis of tunable alkali soluble latexes



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ABSTRACT

Highly hydrophobic and highly hydrophilic (meth)acrylic monomers were copolymerized in heterophase system via a miniemulsion analogous polymerization technique. The versatility of the approach was demonstrated by the direct synthesis of hydrophobically modified alkali soluble emulsions (HASE) without the use of otherwise commonly required specialty monomers. It was demonstrated that copolymer composition drift during the course of the free radical heterophase polymerization can be effectively regulated by the initial monomer ratios. This feature was employed to achieve (1) a more even distribution of acid functionalities throughout the growing polymer chains and the corresponding latex particles, (2) improved dissolution behavior upon deprotonation of the acid groups and (3) the possibility to tailor rheological properties at elevated pH values. Highly soluble HASE systems with surprisingly low contents of ionogenic groups and strong thickening effect were synthesized, which can provide beneficial characteristics in the coatings and adhesive sector.

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1. Introduction

Despite its enormous industrial relevance, traditional oil-in-water (o/w) free-radical emulsion polymerization does not allow the direct incorporation of highly hydrophobic monomers, due to its diffusion driven latex growth mechanism which requires significant monomer solubility in the aqueous phase. On the contrary miniemulsion polymerization works best with components of negligible water solubility, which is a consequence of the so-called nanoreactor concept based on suppressed interparticle diffusion. The fact that in both cases certain restrictions apply in terms of monomer choice gives rise to the question, whether the respective limitations can be overcome by modifying the existing techniques.

To investigate the feasibility of applying the miniemulsion polymerization technique beyond its classical borders, which is restricted to the application of hydrophobic monomers and the suppressed diffusion, we have chosen the synthesis of hydrophobically modified alkali soluble emulsions (HASE). HASE polymers require drastically divergent hydrophobicities along the polymer backbone. They represent a widely investigated special class of highly acid-functionalized polymers, which are stable

suspensions at lower pH and become polyelectrolytes upon deprotonation of the acid groups at higher pH values. The deprotonation is accompanied by a drastic viscosity increase due to formation of negative charges on polymer backbones and corresponding swelling or dissolution of the latex particles. HASE systems have been investigated intensively and are widely used as rheology modifiers in multiple applications, such as water-borne paints, coatings, detergents and other fields [1–3].

In general, the overall rheological behavior of HASE systems is highly complex and strongly depends on various parameters like polyelectrolyte type and composition, molecular weight, concentration, pH, ionic strength, etc. The hydrophobic modification leads to the formation of hydrophobic associates which act as physical crosslinks and hence drastically alter the rheological and mechanical behavior, which also explains the superior performance characteristics of HASE compared to their non-modified analog [4,5]. Even though this work mostly focuses on the feasibility of extending the miniemulsion polymerization approach to a more versatile technique which allows the copolymerization of significant fractions of highly water soluble monomers, special interest will be given to the neutralization behavior of obtained HASE systems. These observations can be considered as an indirect measure of the composition of synthesized polymers and latex particles and reflect the monomer distribution along the polymer chains [6,7].

Typically HASE systems are synthesized by conventional emulsion polymerization. They mostly represent random copolymers of

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ethyl acrylate (EA), methacrylic acid (MAA) [1,8,9] and a small amount of a hydrophobic modifier. EA provides a good balance between glass transition temperature and hydrophobicity [10], the MAA content usually is close to 50 mole-%. The hydrophobic modifier, often referred as macromonomer, typically represents a partially water soluble monomer with an amphiphilic structure, in which a strongly hydrophobic moiety (e.g. a long alkyl chain) is separated from the polymerizable double bond via a hydrophilic polyethylene glycol (PEG) spacer chain [1,11]. Owing to their structure, these specialty monomers also can act as copolymerizable surfactants.

The described HASE systems suffer from certain drawbacks, e.g. the macromonomers are comparably high cost specialty chemicals and the variation of viscoelastic properties is limited to a relatively narrow range. Furthermore, the use of EA is highly unfavorable for industrial applications because of its low odor threshold. Several works have been published searching for the solution for this latter issue. Verbrugge et al. have tested various monomers, such as styrene, methyl methacrylate (MMA), butyl acrylate (BA), 2-ethyl hexyl acrylate (2-EHA) and their mixtures with various ratios in emulsions polymerization together with MAA and evaluated the dissolution and viscosity behavior of the obtained alkali soluble latexes [12]. More recently the synthesis of ASE and HASE systems, employing BA, MMA, 2-EHA and the mixtures thereof as substituents for EA have been investigated by Moraes et al. [10] Emulsion and miniemulsion polymerization techniques were employed in these investigations. However, the miniemulsion approach was found to be unsuccessful in these particular experiments, which was explained by the strong copolymer composition drift during the polymerization.

It should be noted that various synthetic procedures towards hydrophobically modified polyelectrolytes or other types of water soluble thickening polymers are known, e.g. solution polymerization in organic solvent, polymer analogous reactions or micellar copolymerization. However, these alternative approaches also suffer from various drawbacks like the necessity of using the volatile organic solvents (VOC), low control, tedious synthetic procedures or large amounts of required surfactants [3,13–15].

In this work we propose a facile new strategy for the synthesis of hydrophobically modified pH responsive and highly functionalized latexes via a miniemulsion analogous polymerization technique and evaluate the influence of different parameters on the copolymerization character and consequently on the behavior of the obtained HASE systems. This approach simplifies the synthesis and broadens the choice of suitable monomers, including the use of easily available and inexpensive hydrophobic modifiers [16]. These co-monomers with negligible solubility in water can also be considered as polymerizable ultrahydrophobes, which are frequently used in miniemulsion polymerization to suppress Ostwald ripening [16]. Nevertheless, these systems cannot be considered as classical miniemulsions due to the high content of water soluble methacrylic acid. In other words, this method can be considered as an advanced heterophase or modified and extended miniemulsion polymerization technique. Highly divergent monomers with virtually any hydrophobicity can be directly polymerized via this water-based synthetic route.

2. Experimental section

2.1. Materials

Methyl methacrylate (MMA, Merck, >99%), methacrylic acid (MAA, Merck, >99%), butyl acrylate (BA, Acros Organics, 99%), lauryl methacrylate (LMA, Aldrich, 96%), hexadecyl methacrylate (HDMA, ABCR, 98%), tetradecyl acrylate (TDA, ABCR, 95%) hexadecane (HD,

Merck, >99%), hexadecanoic acid (Merck, >98%), hexadecyl alcohol (Sigma, 99%), 1-dodecanthiol (Alfa Aesar, 98%), potassium persulfate (KPS, Merck, >99%), 2,2'-azobis(2-methylbutyronitrile) (V-59, Wako, Japan), sodium dodecyl sulfate (SDS, BASF), sodium hydroxide (NaOH, Karl Roth GmbH, >99%) were used as received.

2.2. Latex preparation

Highly acid-functionalized polymers were prepared by the miniemulsion polymerization techniques similarly to that reported elsewhere [17]. In the standard procedure 72 mg of surfactant (SDS) was dissolved in 22 ml of water (except where the influence of surfactant concentration was investigated), while 100 mg of Initiator (KPS) was dissolved in 2 ml of water. (For oil soluble initiators, only the surfactant was dissolved in 24 ml water, while the initiator was premixed with monomers). 6 g of monomer mixture (composed of three main monomers, ultrahydrophobe (2–4 wt%) and optional 0.048 g (0.8 wt%) chain transfer agent (CTA, 1-dodecanethiol), except for the samples where the dependence of latex stability on the surfactant concentration was investigated) was added to the surfactant solution and pre-emulsified by stirring at 1000 rpm for 10 min (see Table 1 for latex compositions). The miniemulsion was prepared by ultrasonification of the pre-emulsion at 90% amplitude for 120 s (Branson sonifier W450 Digital, 1/2" tip) in an ice bath to prevent overheating. Then the miniemulsion was placed in a round bottom flask and bubbled with nitrogen to get rid of dissolved oxygen under magnetic stirring. The temperature was increased to 70 °C and the initiator solution was added. Samples were stirred at this temperature for 2 h. Full conversion was monitored with solid content analyzer. pH values of the system were ≈ 3 throughout the whole polymerization process.

The chain transfer agent was employed to decrease the molecular weight and to adjust the rheological properties of the systems at higher pH. Low molecular weights lead to lower viscosity and ease of handling. A more detailed investigation of the rheology properties will be described elsewhere.

2.3. Potentiometric titration

The neutralization behavior of the synthesized latexes was investigated by the following typical procedure. 1 ml of latex (solid content 20%) was diluted to 50 ml with distilled water. 0.1 M NaOH solution was added to the latex at constant rate of 0.1 ml/min with constant stirring using a magnetic bar. The pH change was monitored and the data was automatically logged at regular time

Table 1
Composition and basic characteristics of synthesized latexes.

Sample ID	MMA [wt%]	BA [wt%]	MAA [wt%]	Particle diameter [nm] (Pd)	Tg ^a [°C]
L-1	30	30	40	122 (0.070)	60
L-2	35	25	40	121 (0.063)	71
L-3	40	20	40	163 (0.065)	84
L-4	45	15	40	180 (0.122)	96
L-5	50	10	40	210 (0.141)	111
L-6	35	35	30	102 (0.045)	45
L-7	40	30	30	99 (0.031)	56
L-8	45	25	30	109 (0.045)	67
L-9	50	20	30	133 (0.045)	79
L-10	55	15	30	147 (0.055)	92
L-11	60	10	30	167 (0.029)	106
L-12	50	30	20	100 (0.046)	52
L-13	60	20	20	105 (0.049)	75
L-14	70	10	20	143 (0.021)	101

^a 2 wt% TDA was used as copolymerizable ultrahydrophobe in relation to total main monomers combined (MMA/BA/MAA = 100% = main monomers).

^a Glass transition temperatures were calculated using Fox equation.

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