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Synthesis and Some Properties of Functionalized Film-Forming Latexes

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Summary: Semi-continuous emulsion copolymerization was used for preparation different colloid copolymers containig hydroxyl, carboxyl and amide functional groups. Copolymerization of hydroxyethyl methacrylate with styrene and butyl acrylate was investigated. Molecular weight increase in the copolymerization of methacrylamide indicated an extensive branching of macromolecules. Functionalized latexes have been used as binders in water borne paints. In addition to the crosslinking ability the hydrophilic functional monomers positively affect the film formation. The effect of dissociated carboxylic groups on lowering the minimum film forming temperature was much more pronounced if the polymer chains were more polar and softer. Some relationships between the latex flow properties and the film forming ability have been illustrated in this paper.

Introduction

Synthetic latexes, especially acrylic ones have been used for many years as binders in water-borne paints, in various textile technologies as binders for non-woven fabrics, carpet backing or pigment printing, as adhesives including adhesive layers for adhesive tapes, as additives for mortars and concrete etc. Each of the above mentioned examples of applications require very specific properties of the latex in colloidal state and of the polymer itself in dried state as well. These properties, generally, are controlled by the polymer composition, its crosslining, presence of functional groups as well as by type of surfactant and particle morphology. Commercial polymers usually comprise 3 - 5 comonomers, some of them with functional groups. The functional groups serve as *loci* for crosslinking, improve colloid stability, increase polymer polarity, improve adhesion to substrate, enable swellability or solubility of polymer particles in alkaline media. As the synthetic latexes are colloidal dispersions of polymer particles, their colloidal properties

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are superimposed upon those of the polymer. Preparation of a synthetic latex by the emulsion polymerization is a very complex process that is affected by the used monomers, surfactants and initiator selection and also by the polymerization process itself. To synthesize any macromolecule comprising more than one type of structural units means to solve the problem of copolymerization. In general, the copolymerization of two monomers is controlled by their relative reactivities and by the monomer concentrations at the polymerization site[1], i.e. in the immediate neighbourhood of the growing polymer chain radical. In an emulsion copolymerization there is usually a lack of knowledge regarding the exact concentrations of polymerizing monomers in the *loci* of polymerization, i.e. within the latex particles involved in emulsion polymerization, on the particle surface and in the water phase. The latex particles originate either from micelles (in case of hydrophobic monomers and at surfactant concentrations above CMC) as required by the Smith-Ewart theory[2] or by a homogeneous nucleation (in the case of more water-soluble monomers) according theory of Fitch and Tsai.[3] Once generated the monomer concentrations inside the latex particles are determined not only by the total amount of monomers present but also by their distribution between the aqueous phase and the polymer particle. If the polymer chain grows partly in the aqueous phase and partly in the latex particle or at the particle surface, it may develop a broad compositional distribution or even a block copolymer-like structure, especially when a water-insoluble and water-soluble comonomer system is involved. In addition, the particle morphology is often complicated by coagulation processes which occur during particle growth.[4-6] The process is also complicated by the fact that partition coefficients have to be considered not only between water and other monomers but also between water and polymer as it is formed. Semi-batch emulsion polymerization is a suitable procedure for synthesis of emulsion copolymers comprising monomers with different polarity and different polymerization reacitivity.[7,8]

Most of latex applications are based on the film formation phenomenon: upon drying at temperature above the apparent glass transition temperature of the polymer, previously discrete colloid polymer particles form transparent and tough continuous film that may act as binder for pigments, binder for fibers, as adhesive layer etc. This film-formation capability, indeed, is the most important property for latex utilized as binder in paints. Another important property of binders for paints is their flow behaviour that may be strongly affected by different functional groups. Polar groups frequently affect the film formation properties of the latex. Synthesis, flow behaviour at alkaline conditions and film formation of some model functionalized emulsion copolymers are discussed in this paper that is based on parts of several Diploma and PhD. Theses[9-12] processed at the Institute of Polymeric Materials.

Experimental

Monomers: Styrene (S) - technical grade, Kaučuk Kralupy, acrylic acid (AA), ethyl acrylate (EA), butyl acrylate (BA) - technical grade, Eastman CHW Sokolov, 2-hydroxyethyl methacrylate (HEMA), methacrylic acid (MAA), methacrylamide (MAAm), allyl methacrylate (AMA) - technical grade - Röhm Darmstadt, methylene-*bis*-acrylamide (MBA) – Sigma-Aldrich, Disponil AES 60 (sodium salt of alkyl aryl polyoxyethylene sulfate) - Henkel, ammonium persulfate - Air Products, sodium metabisulfite - Lachema Brno.

Standard polymerization recipe: Latexes were produced in a 2500 ml glass reactor by a semi-batch non-seeded emulsion polymerization under nitrogen atmosphere at temperature 80 °C. The reactor charge was put into the reactor and heated to the polymerization temperature. Then the monomer emulsion was fed into the stirred reactor within three hours at a feeding rate about 10 ml/min. After that, during 2 hours of hold period the polymerization was completed.

Reactor charge:

water	200 g
Disponil AES 60	2.6 g
sodium metabisulfite	4.0 g

Emulsion feed:

water	580 g
Disponil AES 60	52 g
ammonium persulfate	8 g
monomers	800 g

Series of emulsion copolymers with different functional monomers were prepared.

A: ethyl acrylate/styrene/acrylic acid (EA/S/AA),
B: butyl acrylate/styrene/2-hydroxyethyl methacrylate /acrylic acid (BA/S/HEMA/AA),
C: butyl acrylate/styrene/acrylic acid (BA/S/AA),
D: butyl acrylate/styrene/methacrylamide (BA/S/MAAm).
E: structured latexes with BA/S/AMA core and BA/S/HEMA/MAA/MBA shell

The minimum film forming temperature was measured using the MFT Tester (Synpo a.s. Pardubice). Minimum film forming temperature is defined to be the minimum temperature at which a film cast from dispersion becomes continuous and clear. The MFT Tester consists of a chromium coated copper slab in which a fixed temperature gradient is maintained by heating at one end (about 40 °C) and cooling at the other (about 0 °C). The polymeric emulsion was cast in a strip along this slab by a coating ruler with height of about 150 μm. The point at which the film becomes discontinuous when dry was observed, and this temperature was recorded as MFT. Tests were carried out after a thermal equilibrium has been reached. Drying material was silica activated for 1 hour / 130 °C before every measurement.

Hydrodynamic volume of latex particles was characterized by their intrinsic viscosities $[\eta]$ obtained by linear extrapolation of $\Phi/\ln \eta_r$ to zero volume fraction Φ of the latexes according to the Mooney equation[13]

$$\eta_r = \exp \{[\eta]\Phi/(1-\Phi/\Phi_c)\} \quad , \qquad (1)$$

where Φ_c is the volume fraction of particles at which viscosity reaches an infinite value (the volume fraction at maximum packing). The relative viscosity $\eta_r = \eta/\eta_s$, where η is the viscosity of latexes and η_s is that of the dispersion medium, was measured using an Ostwald capillary viscometer.

Rheological experiments were performed using two types of rheometers:
Viscotester VT 550 Haake (Germany) for steady-shear viscosity measurements,using the NV system in the range 53 – 1000 s^{-1} a cone-plate rheometer ARES (Rheometrics Scientific) for dynamic measurement with diameters 25 and 50 mm and cone angles 0.1 and 0.02 rad. The experiments were performed in region of linear viscoelasticity; the maximum value of the applied strain amplitude was 30 %.

Other analytical and testing methods used for characterization of latexes and polymeric films:

Free monomers and volatile organic compounds - Gas chromatograph - Varian 3700 (Varian Aerograph Inc.), T_g - Differential Scanning Calorimetry DSC (Hewlett-Packard) and Thermomechanical analyzer TMA CX -04 (RMI), molecular weight - GPC (Waters) coupled with MALLS (Wyatt Technology Inc.), particle size - Coulter N4 Plus (Coulter Corp.)

Results and discussion

Copolymerization of 2-hydroxyethyl methacrylate.

In comparison to batch polymerization, relatively homogenous emulsion copolymers can be prepared by so-called semi-continuous or semi-batch processes.[14] In this case, a single reactor is used with the monomer and some of the other ingredients being added continuously over a period of several hours. Despite different values of the monomer reactivity ratios, an equilibrium ratio of the free monomers in the reaction vessel is usually rapidly achieved and the system produces a copolymer whose composition is equal to that of the monomers being fed at any given instant. Thus, over the initial period of the monomer mixture feeding the resulting copolymer is richer in the more reactive comonomer. Thereafter the monomer mixture is gradually enriched by the less reactive component until the monomer ratio in the reactor begins to produce a copolymer composition equal to the monomer ratio in the emulsion feed. Under suitable conditions (i. e. when a sufficiently low feeding rate is employed) the equilibrium ratio is reached soon after starting the polymerization and remains unchanged up to the end of the monomer mixture feeding.[15,16] Semi-continuous emulsion polymerization produces relatively homogeneous copolymers even for styrene acrylic acid copolymerizations with high levels of acrylic acid.[17] The equilibrium state was utilized for determination of reactivity ratios for HEMA/styrene and HEMA/butyl acrylate monomer couples. The experimental results were ploted according to Fineman-Ross method.[18] The effective reactivity ratios for 2-hydoxyethyl methacrylate, styrene and butyl acrylate are summarized in Table 1. These values found for binary mixtures can be used for calculation of terpolymerization of the three monomers.

Table 1. Effective reactivity ratios of butyl acrylate, styrene and HEMA in semi-batch emulsion copolymerization

M_1	M_2	r_1	r_2	Ref.
Styrene	HEMA	0.82	1.95	10
Butyl acrylate	HEMA	0.62	1.88	10
Butyl acrylate	Styrene	0.23	1.10	14

A good agreement with experimental values was obtained with HEMA content in the monomer mixture below 35 wt. %.[10] An example of a steady state free monomers composition in butyl acrylate/styrene/HEMA terpolymerization is shown in Figure 1.

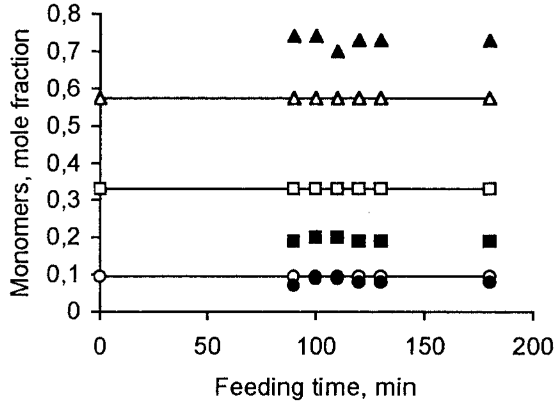

Figure 1. Mole fractions of monomers in the monomer emulsion feed (open points) and the actual mole fractions of monomers in the reaction mixture (full points) in semi-batch emulsion terpolymerization of styrene (△▲), butyl acrylate (□■) and 2-hydroxyethyl methacrylate (○●).

It is evident that mole fractions of free monomers in the reactor reached a constant value. These actual relative concentrations of free monomers differ from those in the monomer feed according to the experimentally determined effective reactivity ratios for BA/S, BA/HEMA and S/HEMA couples.

Effect of methacrylamide comonomer on the particle growth and molecular weight.

As it was already mentioned above, the semi-batch process enables to achieve a relatively homogeneous chemical composition and it is preferred for rigorous process control. Although it is used to prepare various copolymers and many industrial latexes, our understanding of its fundamentals, however, is still unsufficient. Non-seeded or seeded semi-continuous emulsion polymerization with a monomer emulsion feed is used in most cases. Here the particle nucleation and subsequent particle growth are very closely connected with the emulsifier concentration. The reactor charge volume, surfactant concentration and the polymer fraction do change continuously during the monomer emulsion addition. A typical feature of this process is a high immediate conversion of monomers exceeding 90 %. Thus, the free radical polymerization proceeds under so called monomer starved conditions. It was shown in our previous work[17] that the non-seeded process is affected very strongly by initial polymerization conditions. In this process several periods of nucleation of new particle crops are followed by particle flocculation. As it was shown in our previous papers[5,19] the particle number and, consequently, also the specific area and surface tension may exhibit some oscillations during the feeding of monomer emulsion. Development of the mean particle size in the first 30 minutes of the non-seeded emulsion copolymerization of styrene, butyl acrylate and methacrylamide is shown in the Figure 2.

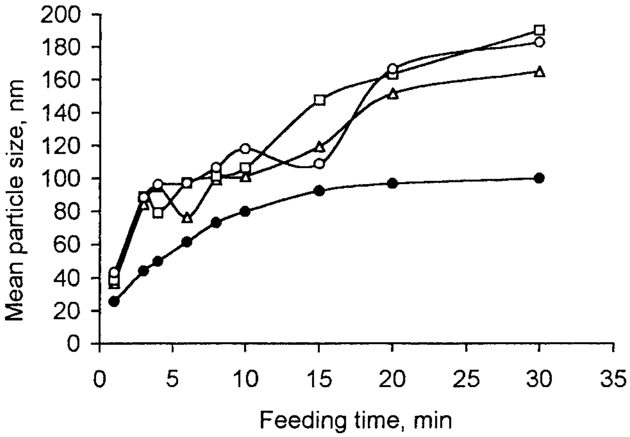

Figure 2. Development of mean particle size during the non-seeded emulsion copolymerization of styrene, butyl acrylate, acrylic acid and methacrylamide. Monomer feed compositions with a constant wt. ratio S/BA = 0.7, acrylic acid 2 wt. %, methacrylamide △ = 0 , □ = 3 , ○ = 5 , ● = 10 wt %. Surfactant R/E = 0/100.

In these experiments the surfactant distribution between the initial reactor charge and the emulsion of monomers was R/E = 0/100. That means that no surfactant was added into the reactor at the start of reaction. Thus, all the surfactant in the system was gradually added together with monomers in an emulsion form. Under such conditions oscillations in the mean particle diameter during the monomer emulsion feeding are typical mainly for hydrophobic monomers and they have been observed also in the case of copolymerization of lower amounts of methacrylamide with styrene and butyl acrylate. Even at a low surfactant concentration at the start of polymerization the polymer particles are readily nucleated. The particles then generate enough surface area causing emulsifier starved system with a very low rate of new particles formation, even with particle coagulation. Since surfactant was continuously added it was possible for the system to return repeatedly to surfactant excess conditions with new particles nucleation. As methacrylamide is a water soluble monomer it increases the extent of homogeneous nucleation in comparison with the micellar one. It is very probable, that this is the reason for monotoneous course in particle growth of copolymers with higher amount of methacrylamide. Similar tendency was found in the HEMA copolymerization. The oscillations in the mean particle diameter vs. feeding time relationships disappeared at HEMA concentrations higher than 20 wt. % in the butyl acrylate/styrene/HEMA copolymerization experimets.[10]

Changes in molecular weight during the emulsion copolymerization of methacrylamide styrene and butyl acrylate was investigated with different methacrylamide contents up to 10 wt. % methacrylamide in the copolymer using GPC-MALLS analysis. It was found that even a low methacrylamide content increases the molecular weight in later stages of the semi-batch process. The M_w vs. monomers feeding time relationships are shown in Figure 3. An increased content of methacrylamide in the reaction mixture has caused a very steep increase of M_w even in the very initial stages of the reaction. The shape of the root mean square radii vs. molecular weight plots[20] and also the mechanical properties of free films cast from the copolymers[11] indicate a presence of branched macromolecules. This indicates that a great extent of radical transfer onto existing polymer chains proceeds in the methacrylamide copolymerization and that this process is enhanced by the methacrylamide content.

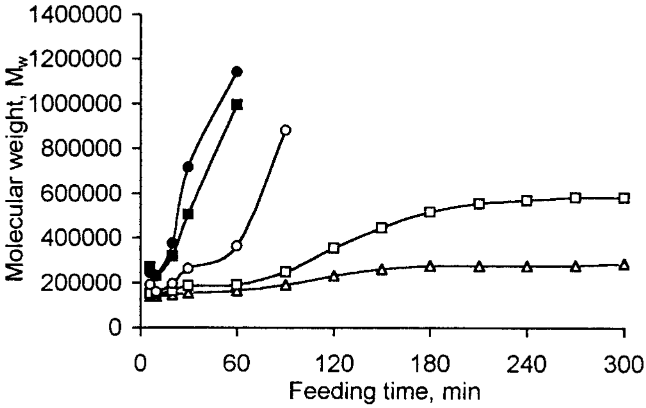

Figure 3. Molecular weight M_w vs. feeding time relationship in butyl acrylate, styrene, acrylic acid and methacrylamide copolymerizations. Monomer feed compositions with a constant wt. ratio S/BA = 0.7, acrylic acid 2 wt. %, methacrylamide △ = 0 , ☐ = 3 , ○ = 5 , ■ = 8, ● = 10 wt %.

Minimum film forming temparature of functionalized latexes.

Even a relatively small amount of monomer containing carboxylic groups (ca 1% in a copolymer) significantly increase the colloidal stability of the system during emulsion polymerization. Common commercial acrylic latices contain some carboxylic groups in their polymer chains and, as a consequence, on the particle surface. Neutralization of surface carboxylic groups improves the stability of the latex and usually increases its viscosity. A relatively small but very interesting and important group of acrylic latexes involves products with a high number of carboxylic groups in the copolymer. These copolymers are insoluble in water but can be solubilized by treatment with alkali. The molecular weight, type and concentration of comonomers and type of acid groups present influence the solubility and viscosity, as do the alkali or amine used to solubilize the copolymer. It is well known that the flow properties of such materials very sensitively reflect their structures. The ability of a carboxylated emulsion copolymer to swel or dissolve under alkaline conditions depends not only on the content of carboxylic groups but also on the polarity of the rest of polymer chain. An example of ethyl acrylate/styrene/acrylic acid copolymer latexes is given in the Table 2. It is evident, that the copolymer comprising 50 wt. % acrylic acid and 50 wt. % styrene is alkali soluble and a similar behavor exhibited copolymer 25 wt. % acrylic acid, 25 wt. % styrene and 50 wt. % ethyl acrylate or copolymer comprising 10 wt. % acrylic acid and 90 wt. %

Table 2. Appearence of different ethyl acrylate/styrene/acrylic acid copolymer latexes under alkaline conditions (25 wt. % solids).

Latex copolymer composition			Appearence after neutralization
Ethyl acrylate	Styrene	Acrylic acid	
0	75	25	Milky
0	50	50	Clear
25	50	25	Milky
50	25	25	Clear
50	30	20	Hazy
55	30	15	Opaque
90	0	10	Clear

ethyl acrylate. Copolymers with a high content of styrene together with a lower content of acrylic acid behaved as alkali swellable ones and exhibited only milky, hazy or opaque appearence. The extent of particles swelling may be characterized by their hydrodynamic volume i.e. by determination of intrinsic viscosty [η]. Decrease of [η] with increasing styrene content in ethyl acrylate/tyrene/acrylic acid particles is evident from Figure 4.[21]

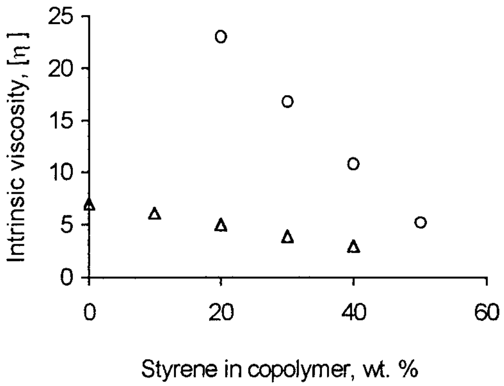

Figure 4. Relationship between the styrene content in ethyl acrylate/styrene/acrylic acid copolymer and the intrinsic viscosity [η] of the resulting latex particles at pH = 9.0. Acrylic acid content in the copolymer 2.0 wt. % (△) and 7.5 wt. % (○).

Swelling of the particle surface under alkaline conditions is important in the process of film formation form polymer dispersions. The alkali swollen latex particles are plasticized by the water phase this increases their viscosity and also enhances the ability of particles to undergo the process of coalescence. Decrease in the minimum film forming temperature MFT and increase in the latex viscosity in relation to degree of neutralization for a typical alkali swellable latex is shown in Figure 5.

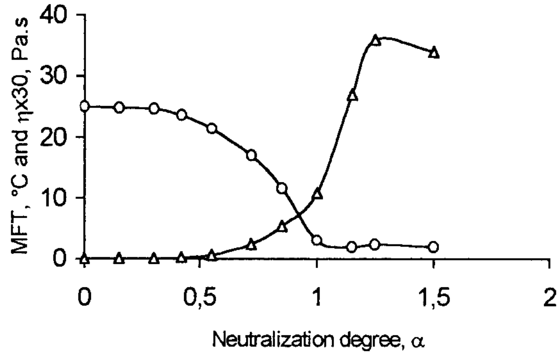

Figure 5. Minimum film forming temperature MFT (O) and viscosity η (△) of copolymer latex ethyl acrylate/styrene/acrylic acid (55/30/15 wt. %), 25% solids.

The extent of the particle hydroplastification depends on the concentration of carboxylic groups an it is effective only at alkaline conditions. The effect of carboxylic groups content in styrene/butyl acrylate copolymer latex on changes in MFT at acidic and alkaline conditions is shown in Fig. 6. The relationships document the increase in MFT with increasing content of acrylic acid due to increased Tg of copolymer. The particlers need higher temperature to undergo the deformation necessary for a film formation *via* coalescence of particles. The sharp drop in MFT of samples with higher content of acrylic acid indicates their effective hydroplasticization under alkaline conditions. As mentioned above, the extent of hydroplasticization depends not only on the content of dissocited carboxylic groups, but also on the composition of polymer chain and its polarity and rigidity. Thus, the hydroplasticization effect does not need to be as high if the composition of butyl acrylate/styrene copolymer chain changes to higher content of styrene. We investigated film formation of structured polymer particles with a soft core based on butyl acrylate/styrene (wt. ratio BA/S = 1.44) slightly crosslinked by allyl methacrylate and with a hard shell comprising 10 wt. % HEMA, different ratios of butyl acrylate and styrene, different concentrations of methacrylic acid and different extent of

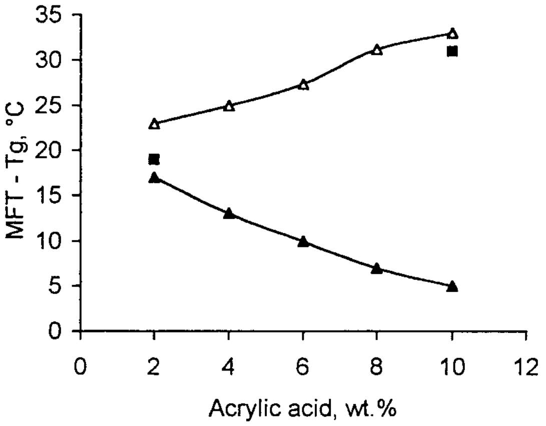

Figure 6. Effect of acrylic acid content in butyl acrylate/styrene/acrylic acid copolymer on T_g (■) and MFT in dependence on pH value. pH = 3 (▲), pH = 7,5 (△), wt. ratio butyl acrylate/styrene = 0.85 remained constant in all copolymers.[9]

the shell crosslinking by methylene-*bis*-acrylamide.[12] It is evident from the Fig. 7 that the minimum film formig temperature of the structured latex particles increased with incresing acrylic acid content as a consequence of increased T_g of the copolymer even at alkaline conditions. The MFT values of neutralized latexes, however, were lower than those of acidic ones. It is also evident that crosslinking of the shell layer with methylene-*bis*-acrylamide was accompanied by the increase of MFT of neutralized samples to values close to those of acidic non-croslinked particles as the crosslinking impedes swelling and, consequently, the hydroplasticization of the particle surface. The effect of dissociated carboxylic groups on lowering the minimum film forming temperature was much more pronounced if the polymer chains were more polar and softer. Comparison of minimum film forming temperatures of structured polymer particles with variable content of styrene in the shells that were crosslinked with 1 % wt. methylene-*bis*-acrylamide is shown in Fig. 8. The effect of softening the shell as well as lowering its hydrophobicity is evident. In the case of a soft shell with decreased content of styrene to only 35 wt. % the MFT drops down with the increasing content of methacrylic acid in the copolymer despite of increasing T_g of the copolymers with higher content of methacrylic acid.

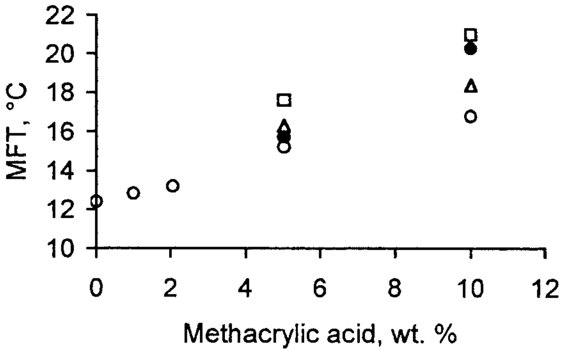

Figure 7. Effect of acrylic acid contentent in the shell layrer of structured core-shell particles on the minimum film forming temperature of neuralized (open points) and acidic (full points) latexes. Shell composition BA/S/HEMA/MAA/MBA : HEMA = 10 wt. % , S = 45 wt. %, MBA (●○) = 0 wt%, (△) = 0.5 wt. %, (□) = 1 wt. %

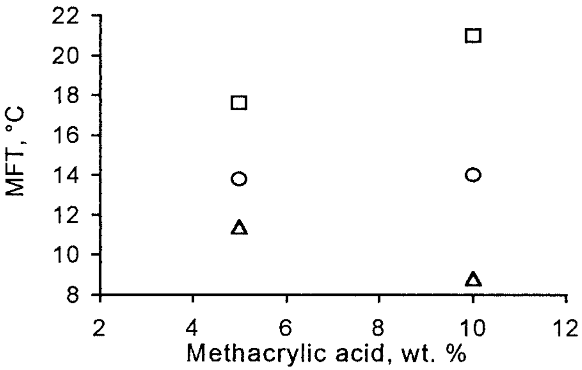

Figure 8. Effect of styrene and acrylic acid content in the BA/S/HEMA/AA/MBA shell layer copolymer on the minimum film forming temperature of structured core shell latexes. Shell composition BA/S/HEMA/MAA/MBA : HEMA = 10 wt. % , MBA = 1 wt. %, Styrene (△) = 35 wt. % , (○) = 40 wt. %, (□) = 45 wt. %

Effect of polar functional groups on the latex viscosity.

The flow behavior of latexes comprising different hydroxyl and amide groups were compared. Capillary viscometry indicated that the dependences of viscosity of different alkalinized latices on their particle concentration considerably differ.[22] It could be assumed that during alkalinization of originally acid latexes, due to electrostatic interactions of ionized carboxylic groups, the effective hydrodynamic volume of latex particles (intrinsic viscosity [η]) increased, which manifested in an increase of the latex viscosity. Similar differences in viscosity found in mere latices appeared also in thickened latex materials where an alkali swellable latex of ethyl acrylate/acrylic acid/methylene-*bis*-acrylamide was used as thickener. Here the strongest thickening effect manifesting both in the highest viscosity - latex particle concentration dependence and in the strongest pseudoplasticity of thickened latex of HEMA containing copolymer was observed. The thickening efficiency of the latex with MAAm comonomer and especially of the latex without hydrophilic groups was lower. It is obvious that the hydrodynamic volume of latex particles and consequently the latex viscosity is considerably influenced by a hydrophilic comonomer used. The hydrodynamic volume of particles plays an important role also if associative thickeners are used as it was demonstrated in series of latexes comprising different amounts of hydroxyethyl methacrylate in the copolymer. [23]

Conclusion

It was shown that the semi-batch emulsion copolymerization is a suitable procedure for preparation copolymers with a relative homogeneous composition. Polar comonomers that are water soluble to a greater extent may influence the particle nucleation and the particle growth mechanisms. Copolymerization of methacrylamide leads to branched macromolecules. Polar comonomers as hydroxyethyl methacrylate or methacryl amide also support the hydroplasticization of latex particles. The most effective in the hydroplasticization process are dissociated carboxylic groups. The extent of hydroplasticization depends not only on the content of dissocited carboxylic groups, but also on the composition of polymer chain i.e. on its polarity and rigidity. The effect of dissociated carboxylic groups on lowering the minimum film forming temperature was much more pronounced if the polymer chains were more polar and softer. As the hydroplasticization is based on the particle surface swelling by water it also is accompanied by an increased latex viscosity. It is also effective if the latex viscosity is controlled by alkali swellable as well as by associative thickeners. In general, the thickening process depends on two main factors: (a) structure and amount of particles present in the thickened systems and (b) their steric and electrostatic interactions. It is obvious that hydrodynamic volume of latex particles is an important factor controlling both viscosity of the mere latexes and their thickening process and that hydrodynamic properties of latexes thickened with an alkali swellable thickener depend predominantly on the total hydrodynamic volume of the latex and the thickener particles and not on any specific interactions of comonomers located on the particle surface. Consequently, latexes of high hydrodynamic particle volume require smaller amount of a thickener to adjust a required rheological properties of the thickened system. In latexes utilized as binders in water borne paints the functional groups serve mainly as *loci* for crosslinking. Besides this, functional groups affect the most important application properties of water borne paint vehicles i.e. the film formation of the binder and the flow behavior of the paint.

Acknowledgment

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