Characterization of Molecular Structure of Emulsion Acrylic Microgels: Exploring the Impact of Molar Mass on Coating Properties of Self-Crosslinkable Latexes

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ABSTRACT: Self-crosslinkable latexes of core−shell microgel particles were synthesized by the emulsion polymerization of acrylic monomers. The molar mass of copolymers forming the shell layer was gradually reduced by isooctyl 3-mercaptopropionate included in the synthesis of the shell layers. The molar mass distribution of latex particles was determined using size exclusion chromatography and asymmetric flow field flow fractionation, respectively, both separation methods being coupled with a multi-angle light scattering detector. The results confirmed theoretical predictions and described empirically the effects of molar mass of the shell layer copolymer on decreasing the minimum film-forming temperature and influencing the end-use properties of coatings.

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Introduction

Aqueous acrylic copolymer dispersions synthesized by emulsion polymerization are frequently used as binder components in water-borne coating compositions. These polymers are naturally branched or even crosslinked inside each particle and form branched structures or even microgels during the synthesis [1,2,3] as a consequence of the coupling of propagating branches generated through chain transfer to a polymer [4,5,6,7,8,9]. The branching degree increases with the content of acrylate monomer in the reaction mixture, as acrylates, in contrast to methacrylates, are highly prone to chain transfer. The final coating is then formed by the coalescence of individual particles into a film. In order to obtain a macroscopically strong film, the polymer chains must inter-diffuse at the interfaces between the particles [10,11]. This is, of course, not a problem for linear polymers of low glass transition temperature (T_g) but the coalescence of lightly crosslinked microgels results in interfaces that remain weaker than the particles and a lightly crosslinked network is not continuous, which typically leads to worse final coating properties [12]. A simple way to control the crosslinking or branching during the emulsion polymerization of acrylic monomers is to use a chain transfer agent (CTA) during the polymerization. This strategy is widely used in emulsion polymers to control the level of crosslinking in each particle [2,13,14]. Hence, the desired film properties like hardness or minimum film forming temperature can be tuned by varying the molar mass of emulsion copolymers.

Currently, the self-crosslinkable acrylic latexes based on diacetone acrylamide (DAAM) and adipic acid dihydrazide (ADH) crosslinking system have been studied

extensively [15,16,17,18,19,20]. The reaction between the carbonyl functionalities of DAAM and hydrazine groups of ADH proceeds rapidly at ambient temperature and is favored by the loss of water and the simultaneous decrease in pH arising from the evaporation of ammonia or amines during the film forming process [21]. The network formation mechanism based on the keto-hydrazide crosslinking reaction is depicted schematically in Fig. 1. By introducing the self-crosslinkable chemistry in emulsion polymers, the physical and chemical integrity of latex films is enhanced, while the film formation process may be complicated [22]. In order to possess increased final coating properties, a balance between chemical crosslinking and polymer chain mobility resulting in sufficient inter-diffusion and entanglement of polymer chains during the particle coalescence stage has to be maintained [23,24,25].

As the precise control of latex copolymer particles structure from the point of view of the molar mass distribution may be particularly important in the case of self-crosslinkable latexes, there is a strong need in the characterization and control of the molecular architecture of these polymers. The combination of size exclusion chromatography (SEC) with a multi-angle light scattering (MALS) detector has been numerously shown as a powerful technique for the determination of molar mass distribution of various synthetic and natural polymers. However, SEC may fail in case of polymer samples containing ultra-high molar mass fractions or branched macromolecules that can be degraded by shearing forces in SEC columns or elute abnormally due to anchoring of branched chains in the pores of column packing [26,27]; and also carboxylic groups typically added to stabilize aqueous dispersion of final latex particles may contribute to enthalpic interactions between macromolecules and column packing. Asymmetric flow field flow fractionation (A4F) can be used as an alternative separation technique with several advantages over traditionally used SEC. The main differences of A4F compared to SEC are the lack of stationary phase and

significantly reduced operating pressure (typically around 10 bar). The lack of stationary phase completely eliminates the anchoring of the branched macromolecules as in the A4F channel filled solely by the carrier there is nothing the branches could penetrate to and anchor. As a matter of fact, it was A4F that helped explain the reason for the abnormal SEC behavior of branched macromolecules [26]. In addition, the enthalpic interactions are strongly reduced as the surface of the semipermeable membrane is several orders of magnitude smaller than that of packed SEC column [27,28]. Actually, polymers interacting with SEC column packing, ultra-high molar mass polymers and branched polymers belong to key application areas of A4F.

Since the self-crosslinkable latexes based on keto-hydrazide crosslinking can get cured rapidly at room temperature and do not need additional crosslinker to be added before use, they have attracted a tremendous amount of research activity [29,30]. Kan et al. [31] studied the effects of different preparation methods of the p(styrene-butyl acrylate-acrylic acid-DAAM) latexes and the DAAM amount used in the emulsion polymerization on the morphologies of the latex particles. Li et al. [32] investigated the influence of DAAM monomer dosage and the ratio of DAAM to ADH on properties of self-crosslinkable polyacrylate latexes. They also evaluated the effect of different glass transition temperatures of core and shell finding that latexes with a high T_g core and a low T_g shell can coalescence better than the representatives with a low T_g core and a high T_g shell. However, no investigations on the dependence of molar mass on film-forming and fundamental coating properties of self-crosslinkable latexes were performed. This lack of information has motivated this present work.

The goal of the current study was to demonstrate and compare the molar mass determination of structured emulsion microgels by means of SEC-MALS and A4F-MALS analytical systems. The object of our interest focused on latexes based on DAAM and ADH crosslinking system. As these latexes are usually composed of

core−shell particles with DAAM repeat units incorporated into the polymer backbone of the shell layer, the molar mass of the shell layer was systematically varied by a chain transfer agent and its effect on end-use coating properties was explored in particular.

Materials and methods

MATERIALS

Self-crosslinkable latexes investigated in this research work were synthesized of methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), diacetone acrylamide (DAAM), and allyl methacrylate (AMA). All the monomers were purchased from Roehm (Germany). Disponil FES 993 IS (BASF, Czech Republic) was used as a surfactant and ammonium persulfate (Lach-Ner Company, Czech Republic) was utilized as an initiator of the polymerization reaction. Isooctyl 3-mercaptopropionate (Sigma−Aldrich, Czech Republic) served as a chain transfer agent (CTA). Adipic acid dihydrazide (ADH) was utilized as the crosslinker and was purchased from Sigma−Aldrich, Czech Republic. Tetrahydrofuran (THF, Sigma−Aldrich, Czech Republic) was used as the SEC and A4F carrier. All the chemicals were utilized as received without any further purification.

LATEX PREPARATION AND CHARACTERIZATION

Water dispersions of structured microgel particles were synthesized comprising a variable content of acrylic monomers (see Table 1). The core/shell weight ratio of the samples was 2/3, which means a shell thickness of about 26 % of the particle diameter. The nature of acrylic monomers forming core and shell phases was chosen to achieve a calculated T_g (using the Fox equation [33]) of approximately 6−8 °C. A slight cross-linking inside the latex particle core was achieved by a controlled amount of AMA. The level of isooctyl 3-mercaptopropionate CTA included in synthesis of each of the shell

layers was systematically varied. The shell layer included a constant amount of DAAM repeat units to provide ketone carbonyl functionalities for interfacial crosslinking by reaction with ADH added during latex formulation. To improve the colloidal stability of latexes and to ensure the acid catalysis of keto-hydrazide crosslinking reaction, carboxyl functionalities were introduced into the structure of core and shell layers by copolymerization with a constant amount of MAA into all the prepared copolymers.

For comparison and better interpretation of results, water dispersions of copolymers (without core–shell structure) having the identical composition as the shell layer of microgel particles (see Table 1, the composition of monomer feeds is listed in the column shell) were synthesized according to the procedure mentioned above. However, the step of core preparation was avoided. The recipe of emulsion polymerization remained similar as provided in Table 2, only a difference in avoiding the monomer emulsion forming core was obeyed. Similarly, the latex of copolymers having the identical composition as the core phase of microgel particles was synthesized, avoiding the step of shell preparation.

The latexes were produced in a 700 ml glass reactor by the semi-continuous non-seeded emulsion polymerization under nitrogen atmosphere at 85 °C. This procedure ensured relatively homogeneous latex particles of statistical copolymers. The reactor charge was put into the reactor and heated to the polymerization temperature. Then the monomer emulsion was fed into the stirred reactor at feeding rate about 2 ml/min in two steps (1. core preparation, 2. shell preparation). After that, during 2 h of hold period the polymerization was completed. The recipe of emulsion polymerization is shown in Table 2. The latex was cooled to room temperature and filtered to remove any coagulum. The pH was adjusted to 8.5 with ammonia solution. To produce self-crosslinkable latexes of structured microgel particles, a 10 wt.% aqueous solution of

ADH in the amount corresponding to the molar ratio ADH:DAAM =1:2, was added to the aqueous core−shell microgel dispersion with agitation.

The average particle sizes of structured microgels in the water phase were obtained from dynamic light scattering experiments performed using a Coulter N4 Plus instrument (Coulter, Corp., UK). All DLS measurements were conducted at 25 °C. The concentration of the measured microgel dispersion was approximately 0.05 wt.% of solids. The minimum film forming temperature (MFFT) was measured using the MFFT-60 instrument (Rhopoint Instruments, UK) according to ISO 2115. The MFFT is defined as the minimum temperature at which a film cast from the polymer dispersion becomes continuous and clear.

MOLAR MASS DETERMINATION

The average molar masses and molar mass distribution curves of pure core and shell copolymers and core−shell microgels were determined using A4F-MALS. An instrumental setup consisted of an A4F system Eclipse 3+ (Wyatt Technology Corporation), a HELEOS MALS photometer and an Optilab rEX refractive index (RI) detector (both Wyatt Technology Corporation). The review of theoretical principles as well as the details of the A4F instrumentation can be for example found in the recent reference [28]. Both MALS and RI detectors operated at 658 nm. The instrumental set-up was completed with a Waters 2487 dual wavelength Absorbance detector that was set to the operating wavelength of 254 nm. A long channel with a wide 350 mm spacer and a regenerated cellulose 5 kDa membrane was used for the A4F separation using linear cross flow gradient from 3 mL/min to 0.1 mL/min within 15 min, followed by 30 min isocratic step at 0.1 mL/min and 10 min at zero mL/min. Elution and focusing steps (2 min each) preceded the injection + focusing step (3 min) that was followed by additional 10 min focusing. That means the elution started at 17 min.

In addition to A4F-MALS, the average molar masses and molar mass distribution curves of shell copolymers were also determined using SEC-MALS. An instrumental setup consisted of a set of two PL gel Mixed-B 300 mm x 7.5 mm columns (Agilent, USA), an Agilent 1100 Series HPLC pump and the same detectors as used for A4F. Tetrahydrofuran (THF) was used as the mobile phase for both SEC and A4F experiments at SEC flow rate and A4F detector flow rate of 1 mL/min. Samples of latexes without ADH were injected as solutions in THF in the volume of 100 μL and the concentration of about 0.2 % w/v. All prepared solutions were filtered with 0.45 μm filter before the injection into SEC columns or A4F channel. The data acquisition and processing were carried out by ASTRA 6 software (Wyatt Technology Corporation). The MALS data were processed using Berry light scattering formalism. The dn/dc of copolymers was calculated based on the dn/dc values of parent homopolymers and the weight fractions of monomers in a given copolymer. The calculation of molar mass was performed assuming chemical homogeneity of the prepared copolymers. Although this assumption may not be completely fulfilled it must be taken in order to get molar mass from the MALS detector.

GEL CONTENT AND GLASS TRANSITION TEMPERATURE MEASUREMENTS

For the glass transition temperature (T_g) and the gel content measurements, specimen was prepared by pouring the latexes into a silicone mould. Films were formed by water evaporation at room temperature for a month. The T_g of the dried microgel copolymers was determined by means of differential scanning calorimetry using a Pyris 1 DSC instrument (Perkin-Elmer, USA). The measurements were carried out at the heating rate of 10 °C min^{-1} with N$_2$ atmosphere. The testing temperature range was −80 to 120 °C. The gel content of microgel copolymers was determined according to CSN

EN ISO 6427 using a 24-h extraction with tetrahydrofuran in a Soxhlet extractor. Around 1 g of the sample was dried in a desiccator overnight, and put into the thimble. After the extraction, the thimble was dried in an oven at 75 °C for 6 h, cooled in a desiccator overnight, and the gel content was calculated from the initial and final weights, assuming that the gelled material remained in the thimble.

COATING PREPARATION AND EVALUATION

The coating films with a wet thickness of 120 μm were cast on glass and metallic panels by drawing the self-crosslinkable latexes using a blade applicator. No coalescing solvents were used. After curing at room temperature (23 °C) for 1 month, the resulting films were evaluated for their hardness, impact resistance and chemical resistance. The dry film thickness was determined using a three-point instrument (BYK-Gardner, Germany) in the case of films prepared on glass panel, thickness of specimen on metallic panels was measured by the Sauter TE 1250-0.1 F Digital Coating Gauche (Sauter, Germany). The hardness of test films was measured by the pendulum hardness tester "Persoz" pendulum (BYK-Gardner, Germany) following the CSN EN ISO 1522. The adhesion was determined using the cross-cut tester (Elcometer Instruments, UK) following the CSN ISO 2409. The impact resistance was evaluated according to CSN EN ISO 6272 using the Elcometer 1615 Variable Impact Tester (Elcometer Instruments, UK) and the chemical resistance was determined by methyl ethyl ketone (MEK) rubbing following ASTM D 4752. All experiments were carried out at room temperature (23 ± 1 °C). For evaluating and comparing the stress−strain behaviour and water absorption, specimen was prepared by pouring the latexes into a silicone mould. Films were air-dried at room temperature (23 °C) for a month. The stress−strain studies were done on MTS-4/M universal testing machine (Sintech − MTS System Corporation, USA) according to CSN EN ISO 527-3 at a tension rate of 10 mm/min at 23 °C. The

specimen size used for the tensile tests was $50 \times 5 \times 0.75$ mm^3. Five specimens of each sample were tested and tensile moduli were obtained from the initial linear part of the stress−strain curve. The water absorption by the latex films was measured by immersing samples in distilled water at 23 °C. The water absorption, A is given by $A = 100(w_t - w_0)/w_0$, where w_0 is the sample weight before immersion and w_t is the sample weight after immersion in water during given time. The swollen films were carefully removed from water, and water from the film surface was removed by touching the polymer with a filter paper. For each sample, three specimens of the approximate dimensions $20 \times 20 \times 0.75$ mm^3 were tested and averaged values of the results were collected as a function of time.

Results and discussion

MOLAR MASS DETERMINATION OF SHELL COPOLYMERS

Molar mass distribution curves of pure shell copolymers determined using SEC-MALS and A4F-MALS techniques are presented in Fig. 2 and the number-average, weight-average and z-average molar masses (M_n, M_w, M_z, respectively) of shell copolymers obtained from SEC-MALS and A4F-MALS are shown in Tables 3,4, and in Fig. 3. It can be seen clearly that increasing the CTA content in the composition of monomer feeds resulted in a shift of molar mass distribution curves to lower values and a considerable decrease in the molar mass averages of shell copolymers. As expected, the effect of molar mass reduction was manifested more significantly in the case of the weight-average and z-average molar masses which are strongly affected by the presence of high molar mass fractions. It is evident that a sharp drop in the molar mass occured particularly by using 0.1 and 0.75 wt. % of CTA, whereas at higher contents of CTA (1.5 and 2.5 wt. %) low molar mass copolymers were formed and the effect of molar mass regulation remained similar.

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The comparison of mass recovery values from SEC and A4F separations showed (see Tables 3 and 4) that reducing the molar mass of shell copolymers using 0.75, 1.5 and 2.5 wt.% of CTA resulted in a significant drop in mass recovery in the case of the A4F separation, whereas measurements of these samples by the SEC technique were found to exhibit almost maximal values of the mass recovery. Reduction in the mass recovery in the case of A4F separation indicates the penetration of oligomeric fractions through the semi-permeable membrane. Therefore, the molar mass averages obtained by A4F-MALS for the samples exhibiting low mass recovery (L0.75, L1.5 and L2.5) are overestimated, especially M_n that reflects mainly the fractions with lower molar mass. On the other hand, A4F separation of the shell copolymers L0 (polymerized without CTA) and L0.1 (polymerized with 0.1 wt.% of CTA) exhibited a nearly maximal mass recovery in comparison with the SEC separation of these samples. It can be assumed that the shell copolymers L0 and L0.1 contain a significant amount of ultra-high molar mass fractions of branched or crosslinked macromolecules that are filtered out by SEC columns, thus lowering the value of SEC mass recovery. It can be concluded that SEC not only provides false information about the molar mass distribution, but the high molar mass fractions retained by the SEC columns deteriorate the column performance.

As alkyl acrylates are prone to the chain transfer to polymer, the ultra-high molar mass structures were apparently formed during the emulsion copolymerization of BA as a result of inter-molecular chain transfer to polymer [34]. On the other hand, the chain transfer to short polymer chains does not result in complete crosslinking, therefore no structures having extremely high molar mass ($\sim 10^8$ g/mol) were formed in the case of samples polymerized in the presence of higher amounts of CTA. In addition, macromolecules of very high molar mass are prone to shear degradation in SEC columns. Hence, the higher moments of molar mass (M_w, M_z) obtained from SEC-MALS for the shell copolymers L0 and L0.1, are underestimated, whereas the results of

SEC-MALS analysis for low molar mass shell copolymers L0.75, L1.5 and L2.5 can be considered correct. It can be concluded that the molar mass of shell copolymer samples L0 and L0.1 is determined more precisely using A4F-MALS, while the molar masses of low molar mass shell copolymers L0.75, L1.5 and L2.5 are measured more correctly by SEC-MALS.

A4F ANALYSIS OF CORE–SHELL MICROGELS

It has been shown that SEC fails in case of polymer samples containing large branched macromolecules that elute abnormally or ultra-high molar mass fractions that can be degraded by shearing forces in SEC columns. As described in the previous section, SEC is unable to provide true molar mass distribution of the shell copolymers L0 and L0.1 containing high molar mass fractions. For this reason, the investigated ultra-high molar mass microgel structures were analyzed only by means of A4F-MALS as the separation in this technique is not affected by stationary phase. The results of A4F-MALS for core−shell microgels L0 − L2.5 are presented in Fig. 4 and Table 5. For the sake of simplification, only the values of M_w are given in Table 5. Strictly taken, the term molar mass in this case refers to the entire crosslinked particles consisting numerous individual macromolecules covalently bonded by tetra-functional allyl methacrylate and inter-molecular chain transfer. The molar mass versus retention time plots of all microgel samples showed a bimodal molar mass distribution (see Fig. 4) comprising of low molar mass fractions represented by soluble macromolecules of molar mass of $\approx 10^5$ and crosslinked microgel super-molecular structures of molar mass of the order of magnitude of 10^8 g/mol. All samples under investigation showed bimodal molar mass distribution pattern with different ratio of soluble macromolecules and crosslinked microgels. With rising content of CTA in the shell layer of microgel

particles (analogously with decreasing the molar mass of the shell copolymer) the content of low molar mass fractions in microgel samples increased.

In addition to that, the decreasing molar mass of the shell layer resulted in a drop in the values of M_w of core−shell microgels and values of mass recovery. A sharp drop in molar mass occurred particularly by using 0.75 wt.% of CTA. Nevertheless, all the tested microgel samples reached extremely high values of M_w above 10^8 g/mol. Comparison of M_w values of pure core microgels with those of core−shell microgels reveals higher M_w of core−shell microgels. This finding can be explained by the formation of an inter-layer between core and shell phases owing to the interpenetration, entangling and covalent bonding between the two phases. Although the emulsion polymerization was performed at steady-state conditions ensuring an almost immediate reaction and conversion of supplied monomers, the covalent attachment of shell macromolecules to crosslinked structure of core may have occurred via pendant allyl groups (of AMA) that are less reactive than vinyl groups and partly remained unreacted at the end of the synthesis of the core phase before the subsequent addition of monomers and formation of the shell layer.

The effect of CTA content in the shell layer of microgels on the z-average root mean square (RMS) radius (radius of gyration, R_z) and the z-average hydrodynamic radius ($R_{h,z}$) of structured microgels was investigated as well. Comparing the extremely high values of M_w of the order of 10^8 g/mol and the relatively low values of RMS radii and taking into account the fact that linear macromolecules having the molar mass of $\approx$ 10^7 g/mol in thermodynamically good solvent exhibit the RMS radius of about 170 nm [35], it can be assumed that all the studied copolymer microgels are highly compact structures, probably the entirely swollen latex particles. The value of $R_z/R_{h,z}$ ratio suggests as well that the investigated latex microgels are crosslinked particles exhibiting

the typical value of $R_z/R_{h,z}$ ratio in the range of $0.8 - 1$, whereas in the case of linear macromolecules the typical value of $R_z/R_{h,z}$ is in the range of $1.8 - 2.1$ [36,37].

MICROGEL PROPERTIES vs. MOLAR MASS OF SHELL LAYER

Glass transition temperatures and gel content values of the pure core copolymer, shell copolymers, core−shell microgels without and with the addition of ADH crosslinker into the aqueous dispersion were studied simultaneously (see Table 6). Latex particles of the pure core microgel exhibited the T_g of 15.9 °C and 98.7 % of gel, which suggests an almost completely crosslinked core of all the studied microgels. Theoretically, the microgels having the core/shell weight ratio of 2/3 should contain nearly 40 % of gel (suggesting that no keto-hydrazide crosslinking reaction takes place). The consistent gel content value of 41.2 % was determined only in the case of microgels L2.5 having the shell layer of the lowest molar mass. In the case of the other microgels, the gel content exceeded the predicted value, which was found to be more pronounced with increasing molar mass of shell layer copolymers. When comparing the results of the gel content for pure shell copolymers and core−shell microgels without ADH, it can be assumed that higher than predicted gel content of microgels L0, L0.1, L0.75 and L1.5 is related to the formation of a covalently bound inter-layer between core and shell phases, as stated above. This phenomenon was confirmed in the case of core−shell microgels crosslinked with ADH as well. Nevertheless, the ADH-crosslinked microgels exhibited increased gel content in comparison with corresponding microgels without ADH-crosslinking as a result of increasing the network density owing to keto-hydrazide crosslinking.

The effect of molar mass of shell layer copolymers on glass transition temperature of structured microgels was investigated as well. It was found that the T_g of shell copolymers was affected significantly by their molar mass, which is consistent with the

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theoretical prediction based on free-volume theory: decreasing the molar mass of a polymer leads to enhancement of the number of polymer chain ends present in the system which exhibit greater free volume. Analogously, the T_g of microgels decreased with reducing the molar mass of shell copolymers. The exception is represented by microgels L0.1 that exhibited higher T_g than microgels L0 (comprising the highest molar mass shell copolymers). A possible explanation for this fact is an increased extent of interpenetration between core and shell phases due to enhanced mobility of less molar mass chains of copolymer L0.1. In this way, physical entanglements could have been formed and subsequently might have been fixed covalently into the microgel structure by the proceeding polymerization. Hence, the segmental mobility of the core−shell polymer structure was decreased causing the elevation of microgel glass transition temperature. T_g values of microgels after crosslinking with ADH were increased in contrast to microgels without ADH-crosslinking, which reveals clearly again that the keto-hydrazide crosslinking reaction occurred during the film-formation of all the studied self-crosslinkable latexes leading to intra- or inter-particle crosslinking.

COATING PROPERTIES vs. MOLAR MASS OF SHELL LAYER

Our system of interest was focused on self-crosslinkable latexes based on DAAM and ADH crosslinking system. As these latexes were usually composed of core−shell particles with DAAM repeat units incorporated into the polymer backbone of the shell layer, the effect of the shell layer on end-use coating properties was explored in particular. For this reason the coating properties of water dispersions of pure shell or core copolymers weren´t the subject of present study. Nevertheless, in contrast to latexes of pure shell copolymers, the latex comprising pure core microgel particles is not supposed to form transparent high-quality films, as the crosslinked structure hinders

the inter-diffusion of polymer chains and particle deformation at the stage of particle coalescence.

Latexes with varying levels of chain transfer agent in shell layer compositions were synthesized by the emulsion polymerization with negligible amount of coagulum (0.1 − 0.8 %) and were stable for over 12 months. Their composition, particle size and MFFT value are listed in Table 1. For proving the core−shell morphology, the latex comprising microgel particles of pure core structure with the diameter of 84 nm was synthesized. The diameter of latex core−shell microgel particles was between 114 − 119 nm, which is in a good accordance with the calculated dimension of shell thickness about 26 % of the particle diameter. The results showed further that the latex particle size was not affected by the amount of the added CTA, analogously by the molar mass of shell-layer copolymer. Nevertheless, the MFFT values were shown to be influenced significantly by the content of CTA in the shell layer of latex particles (more precisely by the molar mass of the shell copolymer). As expected, decreasing the molar mass of shell copolymers resulted in a drop in MFFT values. This phenomenon can be explained by higher mobility and plasticization effect of low molar mass copolymer molecules leading to enhanced coalescence at lower temperatures.

The effect of molar mass of copolymers forming the shell layer of structured acrylic microgels on final coating properties of self-crosslinkable latexes is presented in Table 7. Based on results described in the previous sections, the the molar masses of the shell copolymers L0 and L0.1 were determined using the A4F-MALS analytical system, while the molar masses of other shell copolymers with reduced molar mass were obtained from the SEC-MALS technique. It should be noted that all self-crosslinkable latexes of core−shell microgels were able to form high-quality transparent films and dry film thickness of the coatings was approximately 40 µm. It was found that the investigated coating properties were influenced significantly by the molar mass of the

shell layer of latex microgel particles. As expected, the pendulum hardness, impact resistance, tensile strength, adhesion and MEK resistance of latex films were deteriorated with lowering the molar mass of shell copolymers, whereas elongation at break increased and water sensitivity of coating films after a short immersion in water decreased. The probable reason of the fall of pendulum hardness lies in the plasticizing effect of low molar mass shell copolymers explained by the enhancement of free volume owing to increasing the number of polymer chains ends. The decrease in MEK resistance, impact resistance, tensile strength and adhesion by cross-cut test may be apparently associated with the drop in number of chain inter-particle entanglements and gel forming chain crosslinks due to shortening the polymer chain length. The enhanced coalescence of latex particles caused by favoured inter-diffusion of low molar mass shell copolymers was manifested by the increase in elongation at break and the results of water absorption (given in Fig. 5). With lowering the molar mass of the shell layer of latex particles, the initial speed of water absorption was reduced, while the total water uptake after a long-term immersion was increased as a consequence of better coalescence of particles. The closed film structure hinders the extraction of emulsifier and other water soluble components by water, which causes a greater water uptake due to osmotic pressure [38].

Conclusions

In the present work, we aimed to demonstrate and compare the molar mass determination of structured emulsion microgels by means of SEC-MALS and A4F-MALS analytical systems. The object of our interest focused on self-crosslinkable latexes based on keto-hydrazide crosslinking system. The structured latex particles consisted of an internally crosslinked core and a shell layer containing DAAM repeat units within the polymer chains. Molar mass of the shell copolymer was gradually

reduced with different amounts of isooctyl 3-mercaptopropionate included in the synthesis of the shell layers. Whereas SEC-MALS was found to be convenient for characterization of low molar mass shell copolymers without crosslinked structure, A4F-MALS was proved as a very efficient technique for characterization of high molar mass shell copolymers and core−shell microgels.

Furthermore, the attention was focused on the optimization possibility of desired coating properties of self-crosslinkable latexes by varying the molar mass of the shell layer of latex microgel particles. The results demonstrated that decreasing the molar mass of shell copolymers resulted in a drop in the minimum film-forming temperature of the latexes, obviously due to plasticization effect of low molar mass copolymer molecules leading to enhanced coalescence at lower temperatures. The deterioration of hardness, tensile strength, adhesion and MEK resistance of latex films caused by substantial lowering the molar mass of shell copolymers was described as well. The fall of mechanical properties was attributed to the increased number of polymer chain ends of low molar mass shell copolymers causing the plasticization and decreased number of entanglements, the decrease in MEK resistance and adhesion may similarly reflect the drop in number of chain entanglements and gel forming chain crosslinks due to shortening the polymer chain length. It was demonstrated further that with decreasing the molar mass of the shell layer of latex particles, the initial speed of water absorption into the latex film was reduced, while the total water uptake after a long-term immersion was increased as a consequence of better coalescence of latex particles, which was caused by favoured mutual inter-particle diffusion of low molar mass shell copolymers.

Acknowledgements

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Table 1

Composition and characteristics of self-crosslinkable latexes based on structured microgels

Sample	Composition of monomer feeds (wt.%) MMA/BA/MAA/AMA/DAAM/CTA		Particle size in the water phase (nm)	MFFT (°C)
	Core	*Shell*		
L0	48.5/48.5/1.5/1.5/0/0	47.5/47.5/1.5/0/3.5/0	116	13.3
L0.1	48.5/48.5/1.5/1.5/0/0	47.45/47.45/1.5/0/3.5/0.1	112	12.7
L0.75	48.5/48.5/1.5/1.5/0/0	47.12/47.13/1.5/0/3.5/0.75	108	9.2
L1.5	48.5/48.5/1.5/1.5/0/0	46.75/46.75/1.5/0/3.5/1.5	113	8.1
L2.5	48.5/48.5/1.5/1.5/0/0	46.25/46.25/1.5/0/3.5/2.5	107	5.2

Table 2

Recipe of emulsion polymerization

Reactor charge:	
Water (g)	80
Disponil FES 993 (g)	0.5
Ammonium persulfate (g)	0.4

Monomer emulsion (core):	
Water	50
Disponil FES 993 (g)	5.84
Ammonium persulfate (g)	0.32
Monomers (g)	80

Monomer emulsion (shell):	
Water (g)	90
Disponil FES 993 (g)	8.76
Ammonium persulfate (g)	0.48
Monomers (g)	120

Table 3

Effect of isooctyl 3-mercaptopropionate (CTA) content in shell copolymers on molar mass averages (M_n, M_w, M_z) of shell copolymers determined using SEC-MALS

Sample	CTA content (wt. %)	M_n (10^3g/mol)	M_w (10^3g/mol)	M_z (10^3g/mol)	Mass recovery[*] (%)
L0	0	793	3,300	12,863	83.5
L0.1	0.1	331	604	1,207	86.1
L0.75	0.75	32	57	103	97.6
L1.5	1.5	17	27	44	97.7
L2.5	2.5	12	18	28	99.7

[*] Mass recovery is defined as the ratio of the amount of polymer sample eluted from the SEC column to the amount of polymer sample injected into the column.

Table 4

Effect of isooctyl 3-mercaptopropionate (CTA) content in shell copolymers on molar mass averages (M_n, M_w, M_z) of shell copolymers determined using A4F-MALS

Sample	CTA content (wt. %)	M_n (10^3g/mol)	M_w (10^3g/mol)	M_z (10^3g/mol)	Mass recovery[*] (%)
L0	0	206	7,262	22,465	99.4
L0.1	0.1	125	777	2,302	98.5
L0.75	0.75	40	59	86	85.9
L1.5	1.5	28	31	38	66.7
L2.5	2.5	24	30	36	34.8

[*] Mass recovery is defined as the ratio of the amount of polymer sample eluted from the A4F channel to the amount of polymer sample injected into the channel.

Table 5

Effect of isooctyl 3-mercaptopropionate (CTA) content in shell copolymers on weight average molar mass, z-average radius of gyration and z-average hydrodynamic radius of the pure core microgel (Core) and core-shell microgels L0–L2.5 determined using A4F-MALS

Sample	CTA content (wt. %)	M_w (10^6g/mol)	R_z (nm)	$R_{h,z}$ (nm)	$R_z/R_{h,z}$	Mass recovery (%)
Core	-	166	53	53	1,00	98.7
L0	0	370	68	84	0,81	98.2
L0.1	0.1	358	78	74	1,05	98.8
L0.75	0.75	217	52	69	0.75	92.3
L1.5	1.5	197	52	66	0.79	81.2
L2.5	2.5	180	58	62	0.94	72.4

Table 6

Glass transition temperatures and gel content values of shell copolymers, core–shell microgels without and with crosslinking using ADH as a function of weight average molar mass of shell layer copolymer (determined by means of SEC-MALS)

Sample	Shell copolymer			Microgel without ADH		Microgel after crosslinking with ADH	
	M_w (10^3g/mol)	T_g (°C)	Gel content (%)	T_g (°C)	Gel content (%)	T_g (°C)	Gel content (%)
L0	7,262[*]	16.5	9.1	16.7	87.0	20.9	93.0
L0.1	777[*]	13.5	8.7	19.6	86.3	24.9	90.2
L0.75	57	11.3	0.7	14.7	53.5	18.6	71.5
L1.5	27	7.9	0.6	12.8	49.7	18.1	56.9
L2.5	18	6.5	0.1	9.3	41.2	15.5	50.7

[*] Value obtained from A4F-MALS.

Table 7

Comparison of final properties of coating films cast from self-crosslinkable latexes differing in molar mass of shell copolymers

Sample	M_w of shell copolymer (10^3g/mol)	Pendulum hardness (%)	Impact resistance (mm)	Tensile strength (MPa)	Elongation at break (%)	Adhesion (degree of flaking)	MEK resistance (number of strikes)	a
L0	7,262[*]	39.8	37	20.6 ± 0.7	160 ± 13	0	25	
L0.1	777[*]	39.6	34	18.0 ± 1.7	181 ± 17	0	25	
L0.75	57	35.5	29	13.1 ± 1.8	193 ± 16	0	20	
L1.5	27	31.9	27	8.6 ± 1.1	207 ± 14	1	18	
L2.5	18	27.6	23	5.4 ± 0.6	237 ± 19	2	14	

[*] The value obtained using A4F-MALS.

[**] Water uptake after a 3-days-long immersion in distilled water at 23 °C.

Figure 1: Scheme showing the crosslinking reaction of ketone carbonyl groups with adipic acid dihydrazide.

Figure 2: Comparison of cumulative molar mass distribution curves of shell copolymers obtained from SEC-MALS (top) and A4F-MALS (bottom). The content of isooctyl 3-mercaptopropionate (CTA) in the copolymer: 0 wt.% (1), 0.1 wt.% (2), 0.75 wt.% (3), 1.5 wt.% (4), 2.5 wt.% (5).

Figure 3: Molar mass averages M_n, M_w, M_z of shell copolymers obtained using SEC-MALS and A4F-MALS as a function of isooctyl 3-mercaptopropionate (CTA) content in the shell copolymer.

Figure 4: Molar mass versus retention time plots overlaid on RI fractograms for the core microgel (1) and core−shell microgels containing different amounts of CTA in the shell copolymer layer: 0 wt. % (2), 0.75 wt. % (3), and 2.5 wt. % (4).

Figure 5: Water absorption of films cast from self-crosslinkable latexes: L0 (1), L0.1 (2), L0.75 (3), L1.5 (4), and L2.5 (5) as a function of duration of immersion in water. Latex films were aged 30 days at 23 °C before testing.
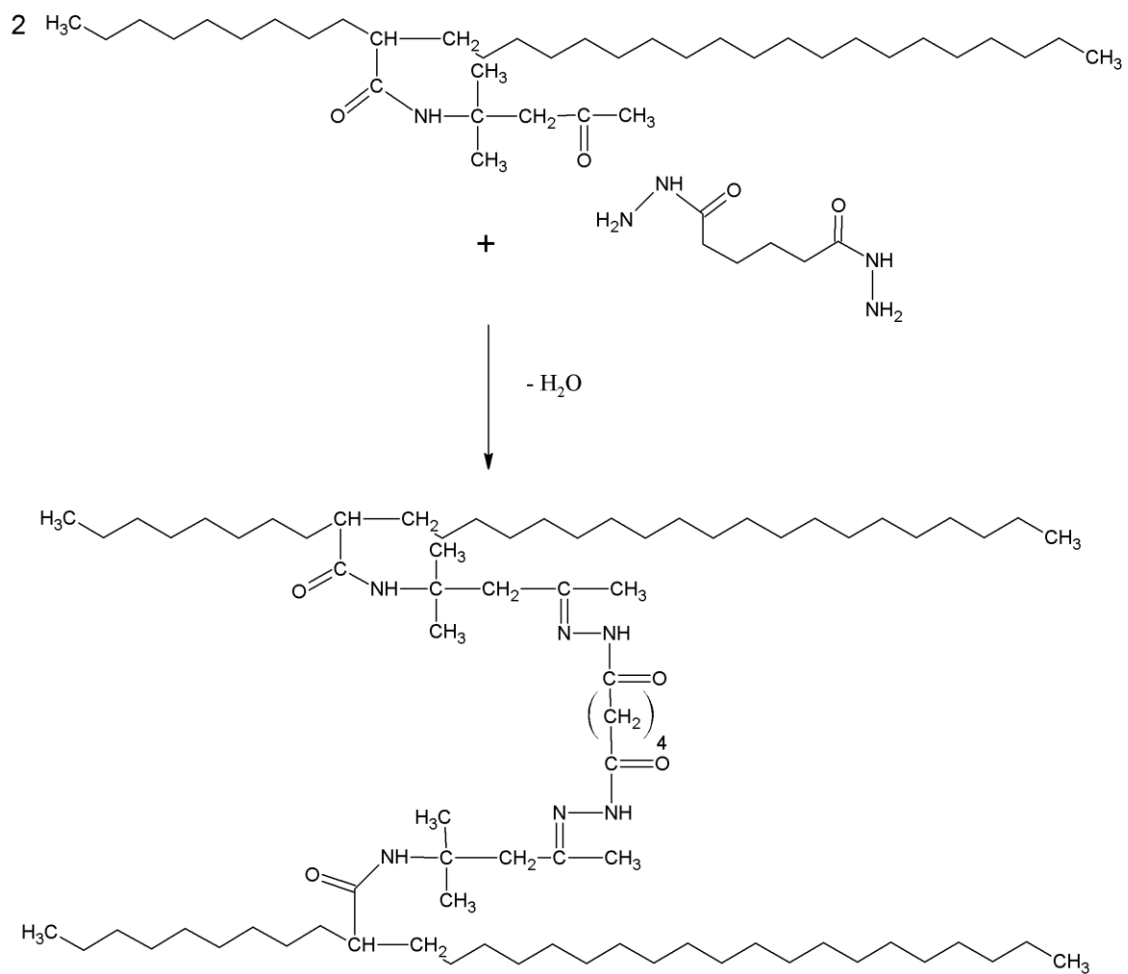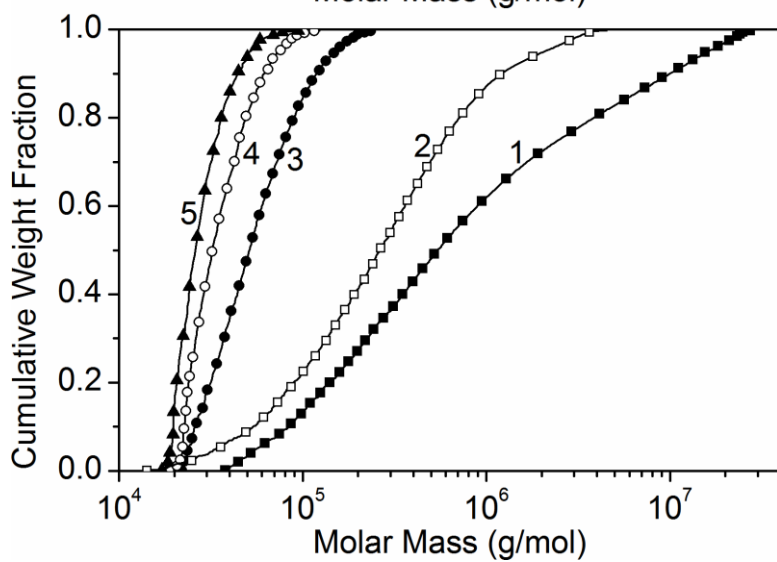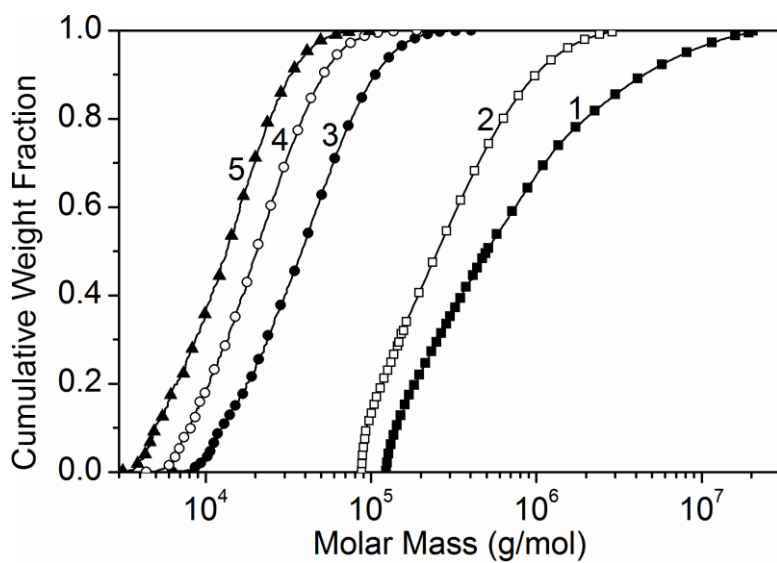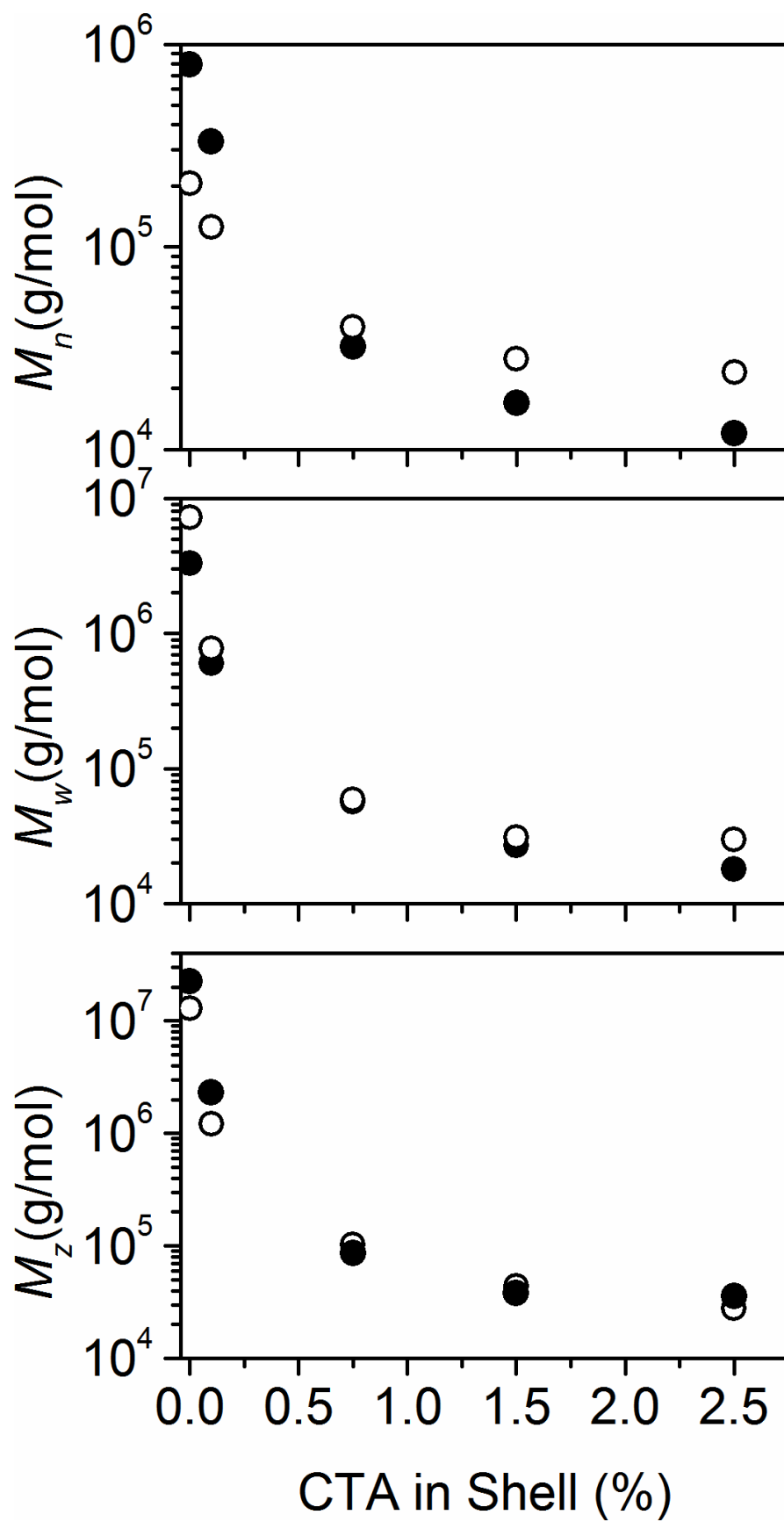
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5