Determination of molar mass of structured acrylic microgels: effect of molar mass on coating properties of self-crosslinking latexes

Jana Machotova [1], Stepan Podzimek [1,2], Hedvika Zgoni [2,1], Jaromir Snuparek [1], Adela Ruckerova [1]

[1] *Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

[2] *SYNPO, Ltd., S. K. Neumanna 1316, 532 07 Pardubice, Czech Republic*

Correspondence to: Jana Machotová; e-mail address: jana.machotova@upce.cz,
tel.: +420 46 603 7194, fax: +420 46 603 7068.

Abstract The film formation process of emulsion polymers may be affected seriously by introducing the self-crosslinking chemistry. 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, which can be tuned significantly by varying the molar mass of emulsion copolymers. The self-crosslinking latexes of core-shell microgel particles were synthesized by the emulsion polymerization of methyl methacrylate and butyl acrylate as main monomers. The particle core was slightly crosslinked using allyl methacrylate, to prevent the copolymers forming the core phase from migration into the shell phase. For inter-particle crosslinking, diacetone acrylamide was copolymerized into the shell layer of latex particles to provide sites for subsequent reaction with adipic acid dihydrazide. The molar mass of copolymers forming the shell layer was systematically reduced by isooctyl 3-mercaptopropionate included in the synthesis of shell layers. The molar mass distribution of latex particles was determined using size exclusion chromatography (SEC) and asymmetric flow field flow fractionation (A4F), respectively, both separation methods being coupled with a multi-angle light scattering (MALS) detector. Whereas SEC-MALS was found to be convenient for the characterization of low molar mass shell copolymers without crosslinked structure, A4F-MALS was proved as a very efficient technique for the characterization of high molar mass copolymers and core-shell microgels. The results described empirically the effects of molar mass of the shell layer copolymer on influencing the end-use properties of coatings.

Keywords Emulsion polymerisation, Core-shell latex, Keto-hydrazide crosslinking, Molar mass distribution, A4F-MALS

Introduction

Currently, the self-crosslinking acrylic latexes based on diacetone acrylamide (DAAM) and adipic acid dihydrazide (ADH) crosslinking system have been studied extensively [1,2,3,4,5,6]. 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 [7]. The network formation mechanism based on the keto-hydrazine crosslinking reaction is shown in Fig. 1. By introducing the self-crosslinking chemistry in emulsion polymers, the physical and chemical integrity of latex films is enhanced, while the film formation process may be complicated [8]. 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 [9,10,11].

Polyacrylate latexes synthesized by emulsion polymerization are naturally branched or even crosslinked inside each particle and form branched structures or even microgels during the synthesis [12,13,14] as a consequence of the coupling of propagating branches generated through chain transfer to a polymer [15,16,17,18,19,20]. Typical problems connected with utilization of these latexes are often related to film-forming properties of originally discrete polymer particles. In order to obtain a high-quality film, the polymer chains must inter-diffuse at the interfaces between the particles [21,22]. 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 [23]. 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 [13,24,25]. Hence, the desired film properties like hardness or minimum film forming temperature can be tuned by varying the molar mass of emulsion copolymers.

As the precise control of latex copolymer particles structure from the point of view of the molar mass and its distribution may be particularly important in the case of self-crosslinking 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 the 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 abnormal SEC elution of branched polymers and strongly reduces the possibility of enthalpic interactions as the surface of the semipermeable membrane is several orders of magnitude smaller than that of packed SEC column [28]. As a matter of fact, polymers interacting with SEC column packing, ultra-high molar mass polymers and branched polymers belong to key application areas of A4F.

Despite the fact that the film formation process of self-crosslinking latexes can be tuned significantly by varying the molar mass of emulsion copolymers, no investigations on the dependence of molar mass on film-forming and fundamental coating properties of these latexes has been performed. In our present work, we concentrated on the comparison of 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.

Experimental

Materials

Self-crosslinking latexes investigated in this research work were synthesized of methyl methactrylate (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 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 [29]) of approximately 7 °C and 24 °C, respectively. A slight cross-linking inside the latex particle core was introduced 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-hydrazine 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 model 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 polymerisation remained similar as provided in Table 2, only a difference in avoiding the monomer emulsion forming core was obeyed. Similarly, the latex of model 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 polymerisation 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 polymerisation 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 hours of hold period the polymerisation was completed. The recipe of emulsion polymerisation is shown in Table 2. The pH was adjusted to 8.5 with ammonia solution. To produce self-crosslinking 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 the 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 values of molar mass averages and molar mass distribution curves of model core and shell copolymers and core-shell microgels were determined using the 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 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 model shell copolymers were also determined using SEC-MALS. An instrumental setup consisted of a set of two PL gel Mixed-B 300 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.

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-crosslinking latexes using a blade applicator. The film-formation process was performed firstly by warming the films overnight at 35 °C (well above the T_g of the latex particles) to avoid the use of coalescing agents and to reach a high level of conversion of the crosslinking reaction between DAAM functional groups and ADH. The resulting films were left at room temperature for 1 month and then they 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 and the impact resistance was evaluated according to CSN EN ISO 6272 using the Elcometer 1615 Variable Impact Tester (Elcometer Instruments, UK). All experiments were carried out at room temperature (23 ± 1 °C).

For evaluating and comparing the stress-strain behaviour and water absorption, specimen were prepared by pouring the latexes into a silicone mould. Films were warmed at 35 °C overnight and then 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 specimen of each sample were tested and tensile moduli were obtained from the initial linear part of the stress-train 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 70 days. 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 specimen of the approximate dimensions $20 \times 20 \times 0.75$ mm^3 were tested.

Results and discussion

Molar mass determination of shell copolymers

Molar mass distribution curves of model shell copolymers determined using SEC-MALS and A4F-MALS are presented in Fig. 2 and the corresponding values of molar mass averages (M_n, M_w, M_z, respectively) 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 phenomenon of molar mass reduction was manifested more significantly in the case of weight-average and *z*-average molar masses which are strongly affected by the presence of high molar fractions. It is evident that a sharp drop in the molar mass occurred 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.

The comparison of mass recovery values from SEC-MALS and A4F-MALS showed (see Tables 3 and 4) that lowering the molar mass of shell copolymers using various amounts of CTA (samples M0.1 – M2.5) resulted in a significant drop in mass recovery values 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. Fall in the mass recovery values in the case of A4F indicates the undesirable penetration of low molar mass fractions through the semi-permeable membrane. Therefore, the molar mass averages obtained by A4F-MALS for the samples exhibiting low mass recovery are overestimated, especially the number average molar mass that is influenced mainly by number of molecules. On the other hand, the A4F separation of the shell copolymer M0 (polymerized without CTA) exhibited a nearly maximal mass recovery value in comparison with the SEC separation of this sample. It can be assumed that the shell copolymer M0 possessed a significant amount of ultra-high molar mass fractions of branched or crosslinked macromolecules that could be anchored into the pores of SEC column packing, thus lowering the value of SEC mass recovery.

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 [30]. On the other hand, the chain transfer has a minimum effect on the fractions with lower molar mass, therefore no structures having extremely high molar mass (~10^8 g/mol) were formed in the case of samples polymerized in the presence of different amounts of CTA. Hence, the values of molar mass averages obtained from SEC-MALS measurement for the shell copolymer M0, especially the averages M_w and M_z, are supposed to be underestimated, whereas the results of SEC-MALS analysis for low molar mass shell copolymers M0.1 – M2.5 may represent the reality. It can be concluded that the molar mass of shell copolymer samples M0 is determined more precisely using A4F-MALS, while the molar masses of low molar mass shell copolymers M0.1, M0.75, M1.5 and M2.5 are considered to be evaluated correctly by SEC-MALS.

A4F analysis of core-shell microgels

The well-known fact is that SEC may fail in case of polymer samples containing branched macromolecules or ultra-high molar mass fractions that can be degraded by shearing forces in SEC columns or elute abnormally. As described in the previous section, the impossible utilization of SEC was demonstrated in the case of the shell copolymer M0 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 by means of this technique is not affected by the stationary phase. The results of the A4F-MALS analyses of core-shell microgels M0 – M2.5 are presented in Fig. 4 and Table 5. As the main output of MALS detection is the weight average molar mass, only the values of M_w are given in Table 5. Strictly taken, the term molar mass in this case refers to the entirely crosslinked particles consisting numerous individual macromolecules covalently bonded owing to tetra-functional allyl methacrylate and inter-molecular chain transfer to polymer. 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 ($M \approx 10^5$ g/mol) represented by soluble macromolecules and ultra-high molar mass fractions ($M \approx 10^8$ g/mol) of crosslinked microgel structures. It is evident that all the molar mass distribution curves exhibited a similar character, nevertheless a significant difference between concentrations of low molar mass and ultra-high molar mass fractions appeared. This phenomenon is demonstrated in Table 5 (column Mass fraction) as well. 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.

It was shown further that decreasing the molar mass of the shell layer resulted in a drop in the values of molar mass averages of core-shell microgels and values of A4F mass recovery. It is evident that 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. When comparing the molar mass for model core microgels and core-shell microgels, it can be assumed that the higher molar mass of core-shell microgels is related to 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 (present in AMA crosslinker) that are less reactive than vinyl groups and partly remained unreacted at the end of the synthesis of the core phase.

The effect of CTA content in the shell layer of microgels on *z*-average radius of gyration (R_z) and *z*-average hydrodynamic radius ($R_{h,z}$) of structured microgels was investigated as well. Comparing the extremely high values of M_w in the order of 10^8 g/mol and the relatively low values of R_z and taking into account the fact that a linear macromolecule having the molar mass of about 10^7 g/mol exhibits R_z of about 170 nm in a thermodynamically good solvent [31], it can be assumed that all the studied copolymer microgels are highly compact macromolecules, probably the entire 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 macromulecules the typical value of $R_z/R_{h,z}$ is in the range of 1.8 – 2.1 [32,33].

Film-forming and coating properties vs. molar mass of shell layer

Our system of interest was focused on self-crosslinking 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 model shell or core copolymers weren´t the subject of present study.

Latexes with negligible amount of coagulum (0.1 – 0.8 %) were synthesized by the semi-continous non-seeded emulsion polymerization process with varying levels of chain transfer agent in shell layer compositions and were stable for over 12 months. Their compositions and characteristic properties are listed in Table 1. For proving the core-shell morphology, the latex comprising microgel particles of model core structure with the diameter of 84 nm was synthesized. The diameter of latex core-shell microgel particles was between 107 – 116 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 copolymers. Nevertheless, the MFFT values were shown to be influenced significantly by the content of CTA in the shell layer of latex particles. 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, which is consistent with the 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.

The effect of molar mass of copolymers forming the shell layer of structured acrylic microgels on final coating properties of self-crosslinking latexes is presented in Table 6 and Fig. 5 Based on results described in the previous sections, the the molar mass of the shell copolymer M0 was determined using A4F-MALS, while the molar masses of other shell copolymers with reduced molar mass were analyzed by SEC-MALS. It should be noted that all the self-crosslinking 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 all the investigated coating properties were influenced significantly by the molar mass of the shell layer of latex microgel particles. As expected, the tested mechanical properties of latex films were deteriorated with lowering the molar mass of shell copolymers, whereas strain at break of coating films increased. The probable reason of the fall of mechanical properties 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.

In the case of impact resistance, the low decrease in molar mass of shell copolymers caused enhancement of impact resistance (samples M0.1 and M0.75), probably as a result of plasticization by low molar mass fractions. On the other hand, the additional lowering of molar mass of shell copolymers lead to drop in impact resistance (samples M1.5 and M2.5), which may be attributed to worsening of coating cohesion due to suppressed inter-particle chain entanglement formation. The enhanced coalescence of latex particles caused by favoured inter-diffusion of low molar mass shell copolymers was manifested by the results of water absorption. With lowering the molar mass of the shell layer of latex particles, 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 [34].

Conclusions

The object of our interest focused on self-crosslinking latexes based on keto-hydrazine 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. In the present work, we aimed demonstrate and compare the molar mass determination of the prepared structured emulsion microgels by means of SEC-MALS and A4F-MALS analytical systems. Whereas SEC-MALS was found to be convenient for the characterization of low molar mass shell copolymers without crosslinked structure, A4F-MALS was proved as a very efficient technique for the characterization of high molar mass shell copolymers and core-shell microgels.

In addition to that, the attention was focused on the optimization possibility of desired coating properties of self-crosslinking latexes by varying the molar mass of the shell layer of latex microgel particles. The results demonstrated that reducing the molar mass of shell copolymers resulted in improved latex film-formation at decreased temperatures, obviously due to plasticization effect of low molar mass copolymer molecules leading to enhanced coalescence at lower temperatures. The deterioration of hardness and stress-strain properties 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. The decrease in impact resistance may reflect the drop in the number of inter-particle chain entanglements 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 water sensitivity after a long-term immersion was increased as a consequence of better coalescence of latex particles, which was caused by favoured mutual inter-diffusion of low molar mass shell copolymers.

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

Fig. 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).

Fig. 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.

Fig. 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).

Fig. 5 Dependence of coating properties: tensile strength (1), pendulum hardness (2), impact resistance (3), elongation at break (4), and (5) water absorption after 70-days-long immersion at 23 °C on weight average molar mass of shell copolymers. Properties expressed in rel. % are related to corresponding properties of the coating films cast from the self-crosslinking latex M0 (0 wt.% amount of CTA in the shell copolymer).

Fig. 1

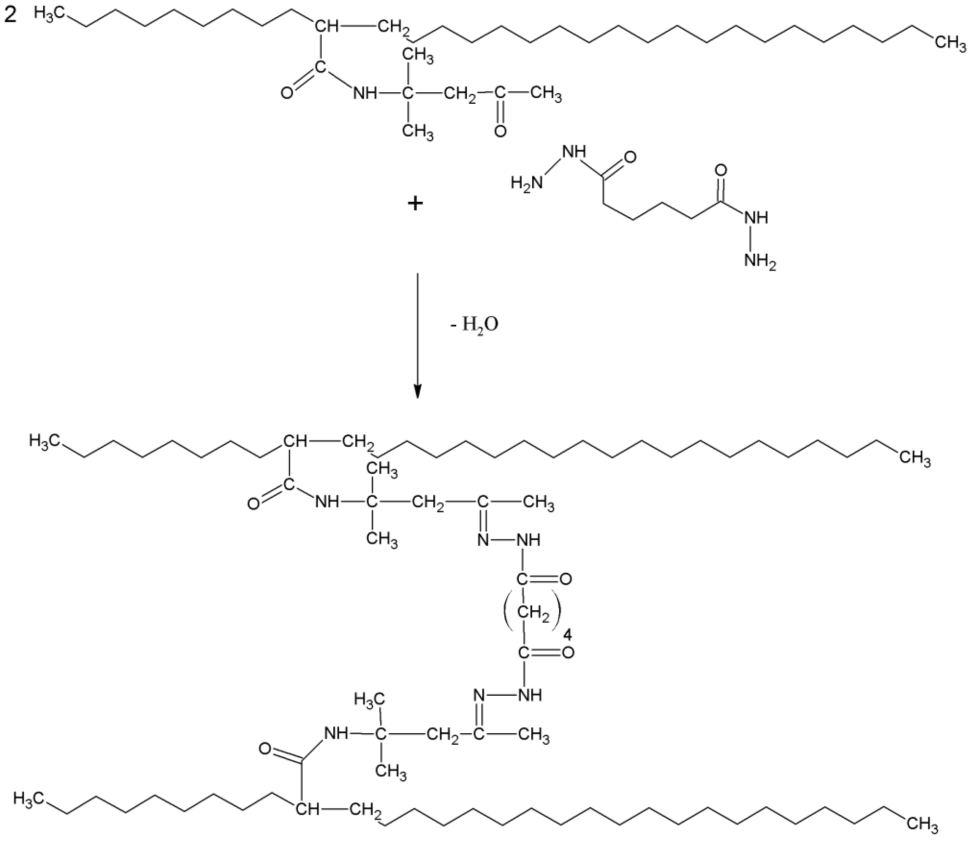

Fig. 2

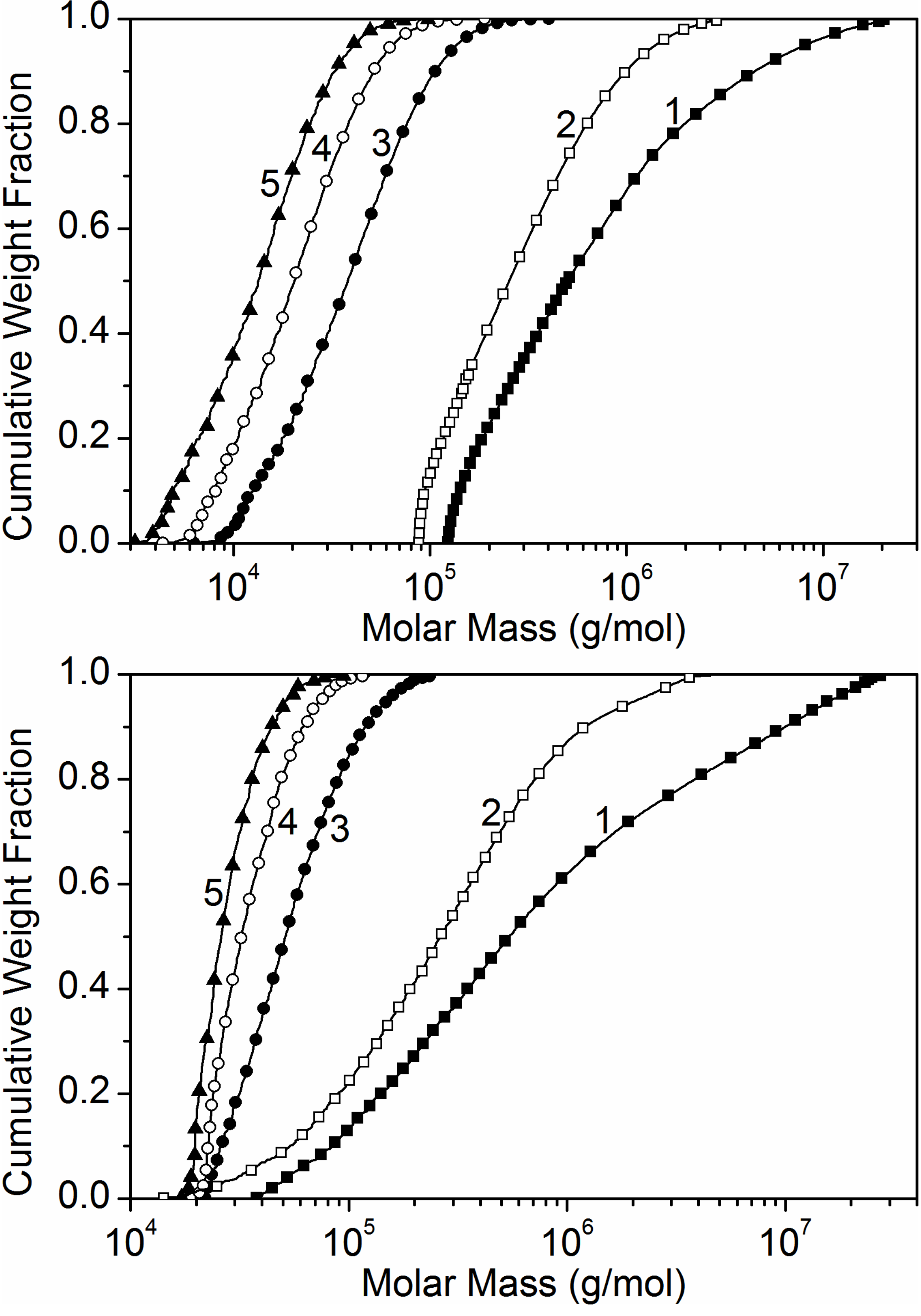
Cumulative Weight Fraction
0.0
0.2
0.4
0.6
0.8
1.0
5
4
3
2
1
10^4
10^5
10^6
10^7
Molar Mass (g/mol)
Cumulative Weight Fraction
0.0
0.2
0.4
0.6
0.8
1.0
5
4
3
2
1
10^4
10^5
10^6
10^7
Molar Mass (g/mol)

Fig. 3

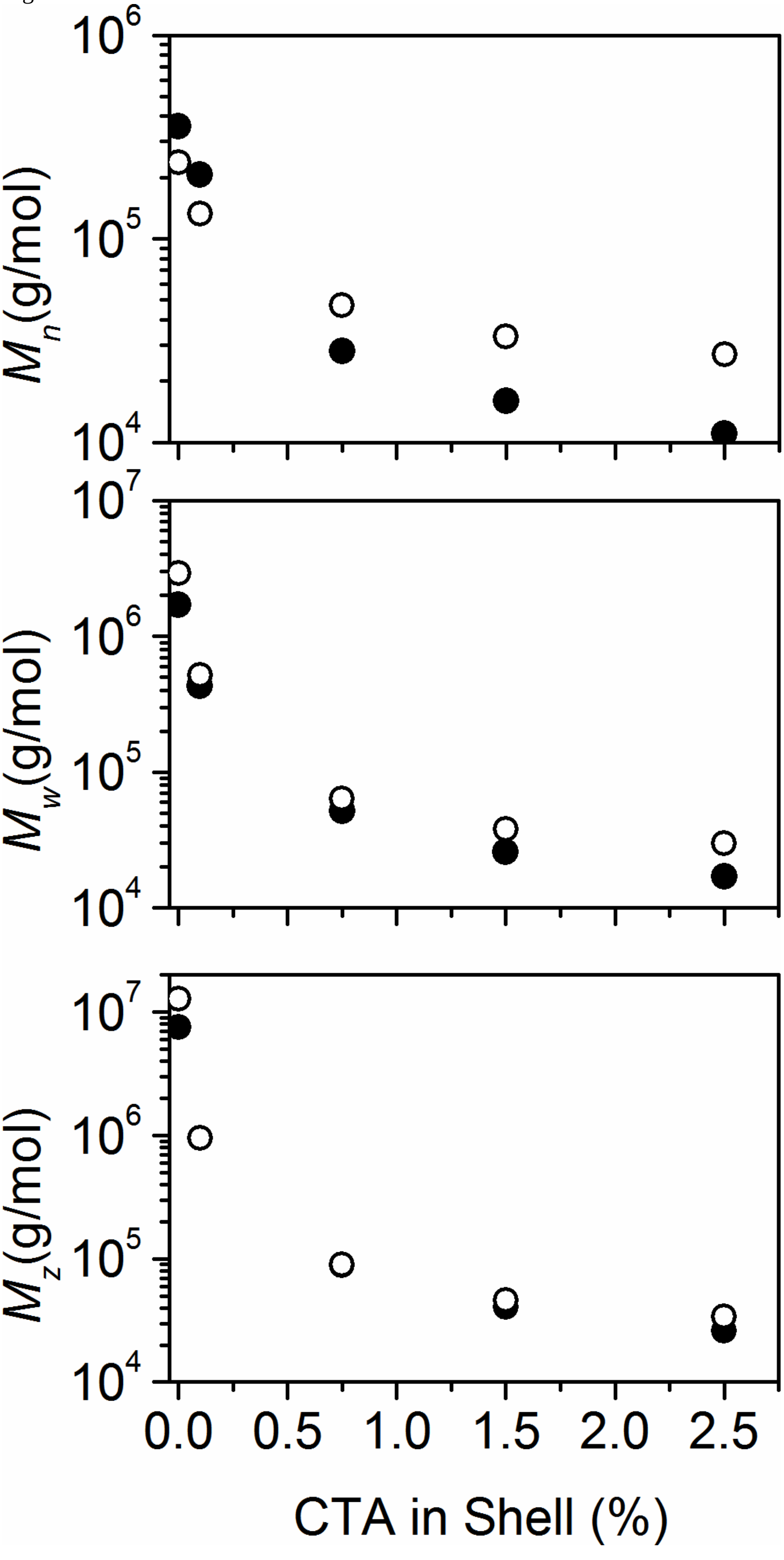
10^6
10^5
10^4
M_n (g/mol)
10^7
10^6
10^5
10^4
M_w (g/mol)
10^7
10^6
10^5
10^4
M_z (g/mol)
0.0
0.5
1.0
1.5
2.0
2.5
CTA in Shell (%)

Fig. 4

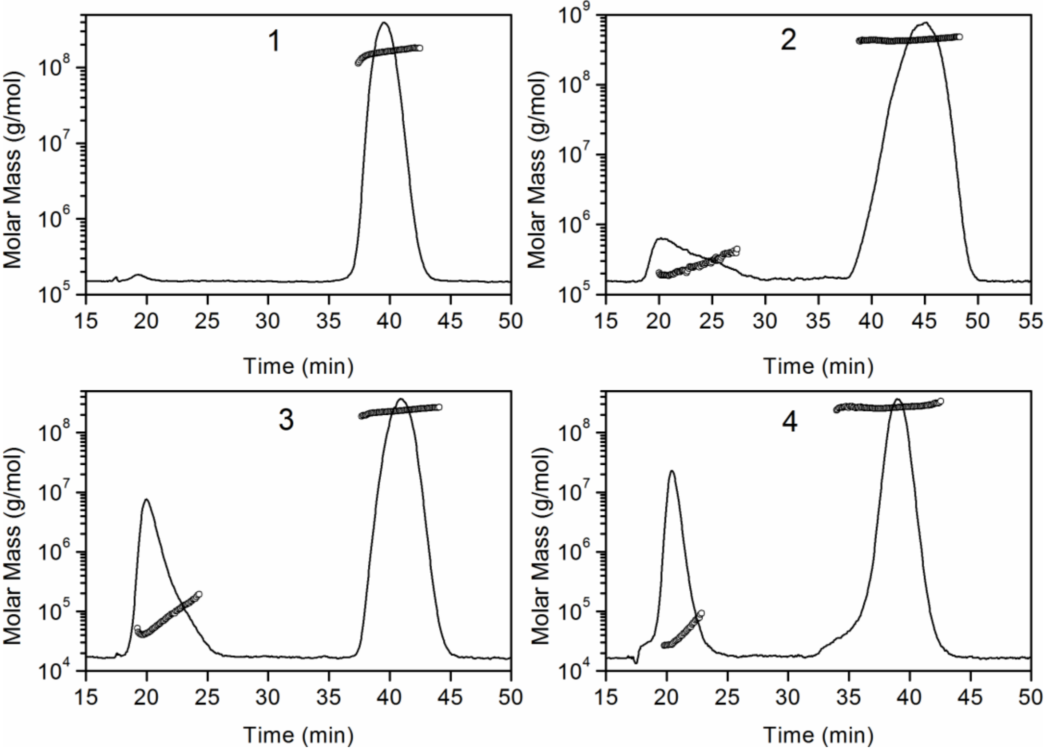
1
2
3
4
Molar Mass (g/mol)
10^5
10^6
10^7
10^8
10^9
10^4
Time (min)
15
20
25
30
35
40
45
50
55

Fig. 5

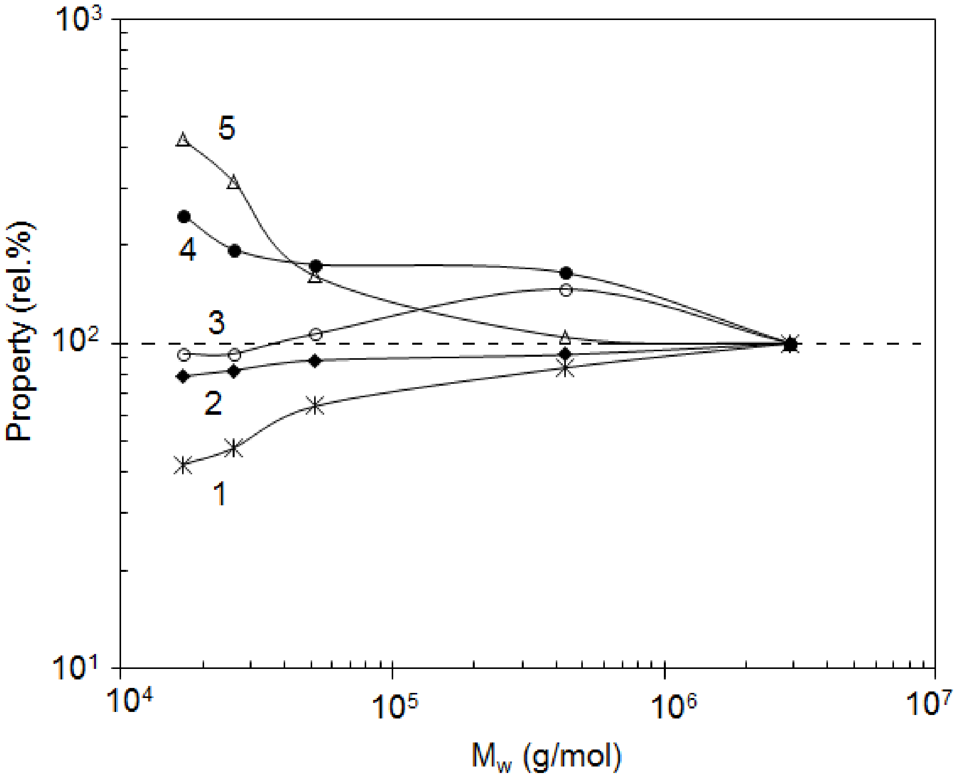
10^3
10^2
10^1
Property (rel.%)
10^4
10^5
10^6
10^7
M_w (g/mol)
5
4
3
2
1

Table 1 Composition and characteristics of self-crosslinking 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*		
M0	48.5/48.5/1.5/1.5/0/0	57/38/1.5/0/3.5/0	117	24.0
M0.1	48.5/48.5/1.5/1.5/0/0	56.95/37.95/1.5/0/3.5/0.1	114	23.2
M0.75	48.5/48.5/1.5/1.5/0/0	56.62/37.63/1.5/0/3.5/0.75	115	20.0
M1.5	48.5/48.5/1.5/1.5/0/0	56.25/37.25/1.5/0/3.5/1.5	118	18.4
M2.5	48.5/48.5/1.5/1.5/0/0	55.75/36.75/1.5/0/3.5/2.5	119	13.3

The self-crosslinking latexes contained ADH in the amount corresponding to the molar ratio ADH:DAAM = 1:2.

Table 2 Recipe of emulsion polymerisation

Reactor charge:	
Water (g)	80
Disponil AES 60 (g)	0.5
Ammonium persulfate (g)	0.4
Monomer emulsion (core):	
Water	50
Disponil AES 60 (g)	5.84
Ammonium persulfate (g)	0.32
Monomers (g)	80
Monomer emulsion (shell):	
Water (g)	90
Disponil AES 60 (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) and polydispersity of shell copolymers determined using SEC-MALS analytical system

Sample	CTA content (wt. %)	M_n (10^3g/mol)	M_w (10^3g/mol)	M_z (10^3g/mol)	M_w/M_n	Mass recovery[*] (%)
M0	0	356	1,704	7,519	4.8	90.5
M0.1	0.1	206	433	952	2.1	99.8
M0.75	0.75	28	52	89	1.9	99.9
M1.5	1.5	16	26	41	1.6	99.3
M2.5	2.5	11	17	26	1.5	99.9

[*] 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 the A4F-MALS technique

Sample	CTA content (wt. %)	M_n (10^3g/mol)	M_w (10^3g/mol)	M_z (10^3g/mol)	M_w/M_n	Mass recovery[*] (%)
M0	0	237	2,917	12,852	12.3	99.8
M0.1	0.1	132	516	955	3.9	98.7
M0.75	0.75	47	64	90	1.4	73.8
M1.5	1.5	33	38	46	1.2	53.9
M2.5	2.5	27	30	34	1.1	34.6

[*] 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 M0 – M2.5 determined using the A4F-MALS technique

Sample	CTA content (wt. %)	M_w (10^6g/mol)	R_z (nm)	$R_{h,z}$ (nm)	$R_z/R_{h,z}$	Mass recovery (%)	Mass fraction[*] (%)
Core	-	166	53	53	1,00	99.7	2 : 98
M0	0	436	69	86	0,80	99.6	14 : 86
M0.1	0.1	405	74	73	1,01	99.2	16 : 84
M0.75	0.75	266	55	71	0.77	91.7	42 : 58
M1.5	1.5	277	65	63	1.03	80.6	36 : 64
M2.5	2.5	234	63	62	1.02	69.5	34 : 66

[*] Mass fraction is defined as the ratio of the total concentration of low molar mass fractions to the total concentration of high molar mass fractions.

Table 6 Comparison of final properties of coating films cast from self-crosslinking latexes differing in molar mass of shell copolymers

Sample	M_w of shell copolymer (10^3g/mol)	Impact resistance (mm)	Pendulum hardness (%)	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Water absorption[**] (%)
M0	2,917[*]	15	55.8	1020 ± 182	29.0 ± 0.7	3.7 ± 0.5	22.6
M0.1	433	22	51.6	705 ± 113	24.4 ± 2.3	6.1 ± 0.3	23.6
M0.75	52	16	49.5	607 ± 58	18.6 ± 2.0	6.5 ± 0.2	36.4
M1.5	26	14	46.1	386 ± 28	13.8 ± 1.6	7.2 ± 0.8	71.1
M2.5	17	14	44.3	374 ± 39	12.3 ± 1.5	9.2 ± 1.1	95.9

[*] The value obtained using A4F-MALS analytical system.

[**] Water uptake after a 70-days-long immersion in distilled water at 23 °C.