

Investigation of the Effect of Molar Mass on Coating Properties of Self-Crosslinking Latexes based on Acrylic Microgels

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Abstract

The effect of reducing the molar mass of the shell layer of core-shell latex particles on film-forming and final coating properties of self-crosslinking latexes was investigated. Latex particles were prepared by the semi-continuous non-seeded emulsion polymerization of methyl methacrylate, butyl acrylate and methacrylic acid as main monomers. The particle core was slightly crosslinked (using a constant amount of allyl methacrylate as a comonomer) to prevent the copolymers forming the core phase from migration into the shell phase. For interfacial 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 varied by isooctyl 3-mercaptopropionate chain transfer agent included in the synthesis of each of the shell layers and the molar mass distribution was determined using size exclusion chromatography coupled with a multi-angle light scattering detection. Fundamental properties of latexes and cast films were systematically compared. These properties included minimum film-forming temperature, pendulum hardness, adhesion, impact resistance, stress-strain properties as well as the characterization of water absorption. The results confirmed theoretical predictions and described empirically the effects of reducing the molar mass of the shell layer copolymer on final properties of coating films.

Keywords: Emulsion polymerisation; Self-crosslinking latex; Core-shell latex; Molar mass distribution; Diacetone acrylamide

1. Introduction

A growing interest in waterborne polymer coatings has been driven by increasing environmental pressures, particularly the loss of volatile organic solvents to the atmosphere. Therefore, waterborne polymers, i.e. “latexes”, prepared via emulsion polymerization are of particular interest. In order to improve water resistance and film hardness of common latex coatings, the applications of the core-shell structured latexes, intra-particle crosslinking and self-crosslinking chemistry in emulsion polymers have been studied significantly in recent years [1–6].

The incorporation of crosslinking chemistry in waterborne coatings is recognized to provide a particularly effective means of enhancing the mechanical

strength, chemical stability, and solvent resistance of the final film [7–11]. Recently, a system based on the reaction of a carbonyl pendant group on the dispersed polymer backbone with a diamine, especially where the diamine is the adipic acid dihydrazide (ADH), has been the subject of increased interest [12–19]. This chemistry, termed the keto-hydrazide reaction, offers the advantage of fast, ambient-temperature crosslinking in functionalized acrylic latex, when the dihydrazide is incorporated in the aqueous phase of the latex. Among the carbonyl functionalized monomers, diacetone acrylamide (DAAM) has attracted the most significant attention [20,21]. The network formation mechanism based on the keto-hydrazide crosslinking reaction is depicted schematically in Fig. 1.

The molar mass distribution can strongly influence many physical properties of an emulsion coating polymer (e.g., glass transition temperature, gel content, extent of polymer chains inter-diffusion during the coalescence period) [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]. 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. As a result, a precise control of latex copolymer particles structure from the point of view of the molar mass and its distribution is particularly important in the case of self-crosslinking latexes. By varying the molar mass of emulsion copolymers, desired film properties like hardness, adhesion, or minimum film forming temperature can be tuned. To the best of our knowledge, no investigations on the dependence of molar mass on fundamental coating properties of self-crosslinking latexes were performed. This lack of information has motivated this present work.

The goal of the current work was to explore the coating properties of self-crosslinking latexes in relation to molar mass of the model shell copolymer (without core-shell structure) having the identical composition of monomer feeds as the shell layer of structured acrylic microgels. The strategy was to have structured particles composed of an internally crosslinked soft core (to prevent the copolymers forming the core phase from migration into the shell phase) and a hard shell layer comprising DAAM repeat units (to provide for interfacial crosslinking by reaction with ADH added during latex formulation). The molar mass of the copolymer forming the shell phase was gradually reduced with different amounts of the chain transfer agent included in the synthesis of the shell layers and was determined using the size exclusion chromatography (SEC) combined with a multi-angle light scattering (MALS) detector.

2. Materials and Methods

2.1. Materials

Self-crosslinking 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 carrier. All the chemicals were utilized as received without any further purification.

2.2. 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 [24]) 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-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 model shell copolymers (without core-shell structure) having the identical composition of monomer feeds 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 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-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 (DLS) experiments performed using a Coulter N4 Plus instrument (Coulter, Corp., UK). 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.

2.3. Gel Content and Glass Transition Temperature Measurements

For the glass transition temperature (T_g) and the gel content measurements, specimen were prepared by pouring the latexes into a silicone mould. Films were formed by water evaporation firstly at 35 °C overnight, secondly at room temperature (23 °C) 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 °Cmin⁻¹ with N₂

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-hr extraction with tetrahydrofuran (THF) 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.

2.4. Molar Mass Determination of Shell Copolymers

The average molar masses and molar mass distribution curves of emulsion copolymers were 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), a HELEOS MALS photometer and an Optilab rEX refractive index (RI) detector (both Wyatt Technology Corporation, USA). Both detectors operated at 685 nm. THF was used as the mobile phase at the 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 0.45µm filter before the injection into SEC columns. The data acquisition and processing were carried out by ASTRA 6 software (Wyatt Technology Corporation, USA). The MALS data were processed using Berry light scattering formalism. The specific refractive increment dn/dc of 0.74 ml/g was used for data processing. The value was calculated from the dn/dc values of parent homopolymers and the average copolymer composition.

2.5. Coating Preparation and Evaluation

The coating films with a wet thickness of 120 µm were cast at room temperature on glass and metallic panels by drawing the self-crosslinking latexes using a blade

applicator. Immediately after the casting, the film-formation process was performed by warming the films at 35 °C (well above the T_g of the latex particles) for 24 h in a hot air oven 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, adhesion, 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 Gauge (Sauter, Germany). The pendulum hardness of test films was measured by the pendulum hardness tester with “Persoz” pendulum (BYK-Gardner, Germany) following CSN EN ISO 1522. The scratch hardness was performed following the procedure of ISO 15184 using the set of twenty pencils from grade 9B to 9H with a standard holder. 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 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 $50 \times 5 \times 0.75$ mm³. Five specimen 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 $20 \times 20 \times 0.75 \text{ mm}^3$ were tested and averaged values of the results were collected as a function of time.

3. Results and Discussion

3.1. Molar Mass and Properties of Shell Copolymers

Molar mass distribution curves of model shell copolymers (without core-shell structure) determined using SEC-MALS are presented in Fig. 2 and the number-average, weight-average and z -average molar masses (M_n , M_w , M_z , respectively) compared to the results of measurements of gel content and glass transition temperature of the shell copolymers are shown in Table 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 molar mass averages of shell copolymers. It is evident that a sharp drop in 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 the effect of molar mass regulation remained similar. The phenomenon 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.

According to gel content and mass recovery from SEC columns, it can be assumed that shell copolymers M0 (polymerized without CTA) contained a significant amount of ultra-high molar mass fractions of branched or crosslinked macromolecules.

As alkyl acrylates are prone to 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 and termination by combination [25]. Such species can be removed by sample filtration with 0.45 μm filter and/or filtered out by SEC columns, which explains lowering the mass recovery from SEC columns. In addition, macromolecules of very high molar mass are prone to shearing degradation in SEC columns, which results in the decrease of M_w and especially M_z . Therefore, the molar mass averages M_w and M_z of shell copolymers M0 are probably markedly underestimated. On the other hand, the other shell copolymers prepared using various levels of CTA, were found to exhibit negligible gel content, as the chain transfer to short polymer chains does not result in complete crosslinking. Consequently, the values of mass recovery in SEC measurements are close to 100 % and the values of molar mass averages M_w or M_z may be approaching the reality.

Further, Table 3 demonstrates the effect of molar mass of model shell copolymer on the glass transition temperature. It was found that T_g of shell copolymers was affected significantly by their molar mass, 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.

3.2. Latex and Microgel Properties vs. Molar Mass of Shell Copolymer

Latexes with negligible amount of coagulum (0.1 – 0.8 %) were synthesized by the semi-continuous non-seeded emulsion polymerization process with varying levels of chain transfer agent in shell layer compositions and were stable for over 6 months. Their compositions and characteristic properties are listed in Table 1. The results showed 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 formulation of shell layer of latex particles (more precisely by the molar mass of the shell copolymer), a demonstration is given in Fig. 2. 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.

Glass transition temperatures and gel content values of model shell copolymers (without core-shell structure), core-shell microgels without and with the addition of ADH crosslinker into the aqueous dispersion were studied simultaneously (see Tables 3 and 4). Latex particles of the core copolymer (without core-shell structure) 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 40 % of gel (suggesting that no keto-hydrazide crosslinking reaction takes place). The consistent gel content value of 41.9 % was determined only in the case of microgels M2.5 composed using the highest CTA content in the shell layer composition. 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 model shell copolymers without core-shell structure (see Table 3) and core-shell microgels without ADH (see Table 4), it can be assumed that higher than predicted gel content of microgels M0, M0.1, M0.75 and M1.5 is related to swelling of the crosslinked core by monomers fed in the second stage of emulsion polymerization and polymerization of these monomers inside the polymer network of the pre-formed core structure. A polymer in the “shell stage” containing ultra-high molar mass or even crosslinked material might be present, since unreacted AMA pendant double bonds are present

[26,27] and BA units in the core polymer are prone to suffer intermolecular chain transfer to polymer that followed by termination by combination might yield further gel [28,29]. Obviously, as CTA concentration was increased in the formulations of shell layer copolymers, the probability of intermolecular chain transfer to polymer and propagation of pendant double bonds decreased and hence the amount of gel approached to that produced in the synthesis of core polymer without core-shell structure. 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 reduction of shell layer copolymers on glass transition temperature of structured microgels was investigated as well. Similarly as described in the previous section dealing with model shell copolymers without core-shell structure, the T_g of microgels decreased with reducing the molar mass of shell copolymers. The exception is represented by microgels M0.1 that exhibited higher T_g than microgels M0 (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 M0.1. 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 final polymer structure was decreased causing the elevation of microgel T_g . 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-crosslinking latexes leading to intra- or inter-particle crosslinking.

3.3. Coating Properties vs. Molar Mass of Shell Copolymer

The subject of our 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 without core-shell structure were not the subject of the present study. Nevertheless, in contrast to latexes of model shell copolymers, the latex comprising model core particles is not supposed to form transparent high-quality films even at elevated temperatures, as the crosslinked structure hinders the inter-diffusion of polymer chains and particle deformation at the stage of particle coalescence [30–33].

The effect of molar mass reduction of copolymers forming the shell layer of acrylic microgels on final coating properties of self-crosslinking latexes is presented in Table 5 and Figs. 4 and 5. Note that the molar masses of shell copolymers mentioned in all tables and figures represent only model shell polymers without core-shell structure but not those real shell polymers produced in the core-shell process. All the self-crosslinking latexes 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 particles. As expected, the tested mechanical properties and MEK resistance 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. The decrease in MEK resistance and adhesion by cross-

cut test may be apparently associated with the drop in number of inter-particle chain entanglements due to shortening the polymer chain length.

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 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 (given in Fig. 5). 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].

4. Conclusions

In this study, we aimed to describe empirically the optimization possibility of desired coating properties of self-crosslinking latexes based on keto-hydrazide crosslinking system by affecting the microstructure of the emulsion polymers from the point of view of their molar mass. The structured microgel particles were prepared by semi-continuous emulsion polymerization of acrylic monomers, forming an internally crosslinked core and a shell layer containing DAAM repeat units within the polymer chains. Molar mass of shell copolymers was gradually reduced with different amounts of isooctyl 3-mercaptopropionate included in the synthesis of the shell layers. 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, stress-strain properties 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. The decrease in MEK resistance and adhesion by cross-cut test 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 uptake 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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Table 1

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

Sample	Composition of monomer feeds (wt.%)		Particle size in the water phase (nm)	MFFT (°C)
	MMA/BA/MAA/AMA/DAAM/CTA			
	<i>Core</i>	<i>Shell</i>		
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

Table 2

Recipe of emulsion polymerisation

<i>Reactor charge:</i>	
Water (g)	80
Disponil AES 60 (g)	0.5
Ammonium persulfate (g)	0.4
<i>Monomer emulsion (core):</i>	
Water	50
Disponil AES 60 (g)	5.84
Ammonium persulfate (g)	0.32
Monomers (g)	80
<i>Monomer emulsion (shell):</i>	
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 model shell copolymers (without core-shell structure) on their molar mass averages (M_n , M_w , M_z), gel content and glass transition temperature

Sample	CTA content (wt. %)	M_n (10^3 g/mol)	M_w (10^3 g/mol)	M_z (10^3 g/mol)	Mass recovery * (%)	Gel content (%)	T_g (°C)
M0	0	356	1,704	7,519	90.5	8.5	32.9
M0.1	0.1	206	433	952	99.8	1.9	27.4
M0.75	0.75	28	52	89	99.9	0.8	24.1
M1.5	1.5	16	26	41	99.3	0.3	20.4
M2.5	2.5	11	17	26	99.9	0.3	16.6

* 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

Glass transition temperatures and gel content values of core-shell microgels without and with post-crosslinking using ADH as a function of weight average molar mass of the corresponding model shell copolymers (without core-shell structure)

Sample	M_w of shell copolymer (10^3 g/mol)	Microgels without ADH		Microgels after crosslinking with ADH	
		T_g (°C)	Gel content (%)	T_g (°C)	Gel content (%)
M0	1,704	26.7	87.3	32.0	90.7
M0.1	433	28.7	87.0	32.2	91.2
M0.75	52	25.1	54.1	30.1	71.5
M1.5	26	21.5	46.7	24.4	62.3
M2.5	17	17.4	41.9	22.9	48.9

Table 5

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 (10^3 g/mol) [*]	Pendulum hardness (%)	Scratch hardness (pencil grade)	Adhesion (degree of flaking)	MEK resistance (number of strikes)	Impact resistance (mm)	Tensile modulus (MPa)
M0	1,704	55.8	4H	0	19	15	1020 ± 1
M0.1	433	51.6	4H	0	16	22	705 ± 1
M0.75	52	49.5	3H	0	13	16	607 ± 5
M1.5	26	46.1	3H	1	12	14	386 ± 2
M2.5	17	44.3	3H	2	11	13	374 ± 3

* Data represent the weight average molar masses of model shell copolymers (without core-shell structure).

Figure Captions

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

Fig. 2. Cumulative molar mass distribution curves of model shell copolymers (without core-shell structure). 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. Dependence of minimum film-forming temperature of self-crosslinking latexes on weight average molar mass of corresponding model shell copolymers (without core-shell structure).

Fig. 4. Dependence of coating properties: tensile strength (1), pendulum hardness (2), impact resistance (3), and elongation at break (4) on weight average molar mass of

model shell copolymers (without core-shell structure). 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. 5. Water absorption of films cast from self-crosslinking latexes: M0 (1), M0.1 (2), M0.75 (3), M1.5 (4), and M2.5 (5) as a function of duration of immersion in water. Latex films were warmed at 35 °C overnight and then aged 30 days at 23 °C before testing.

Figure 1

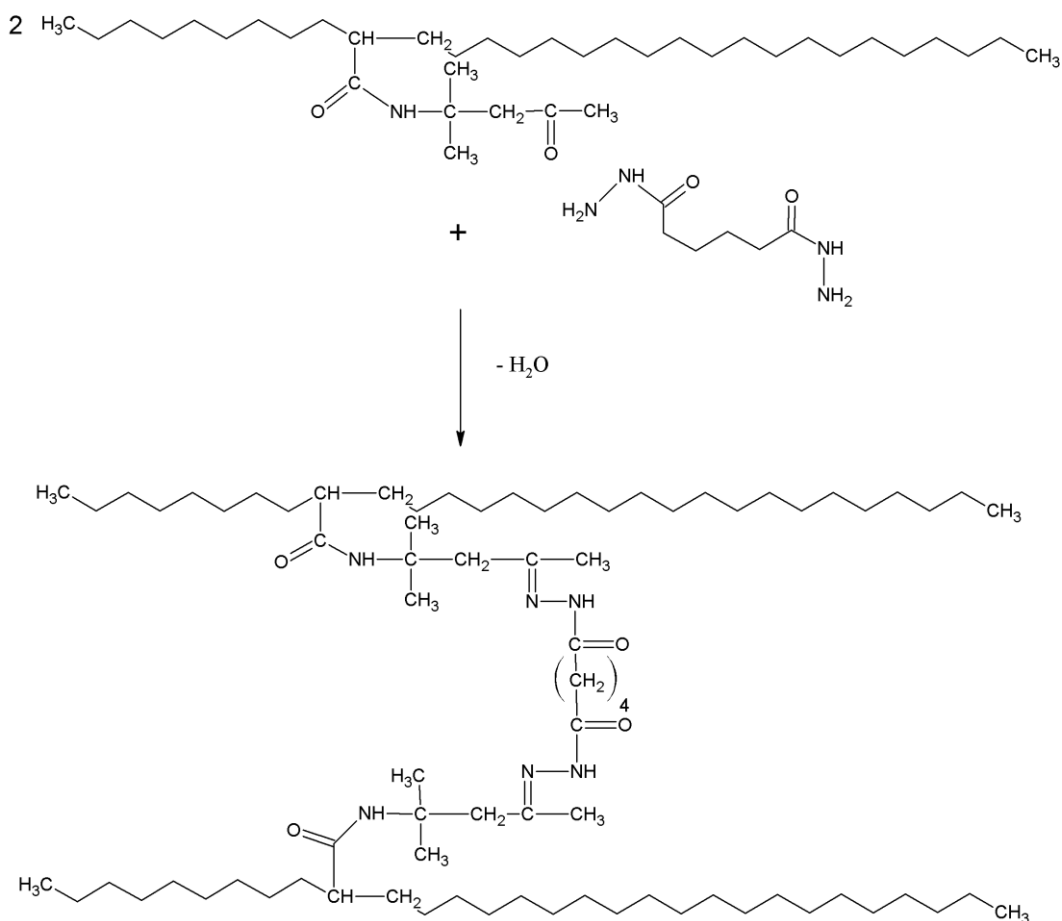


Figure 2

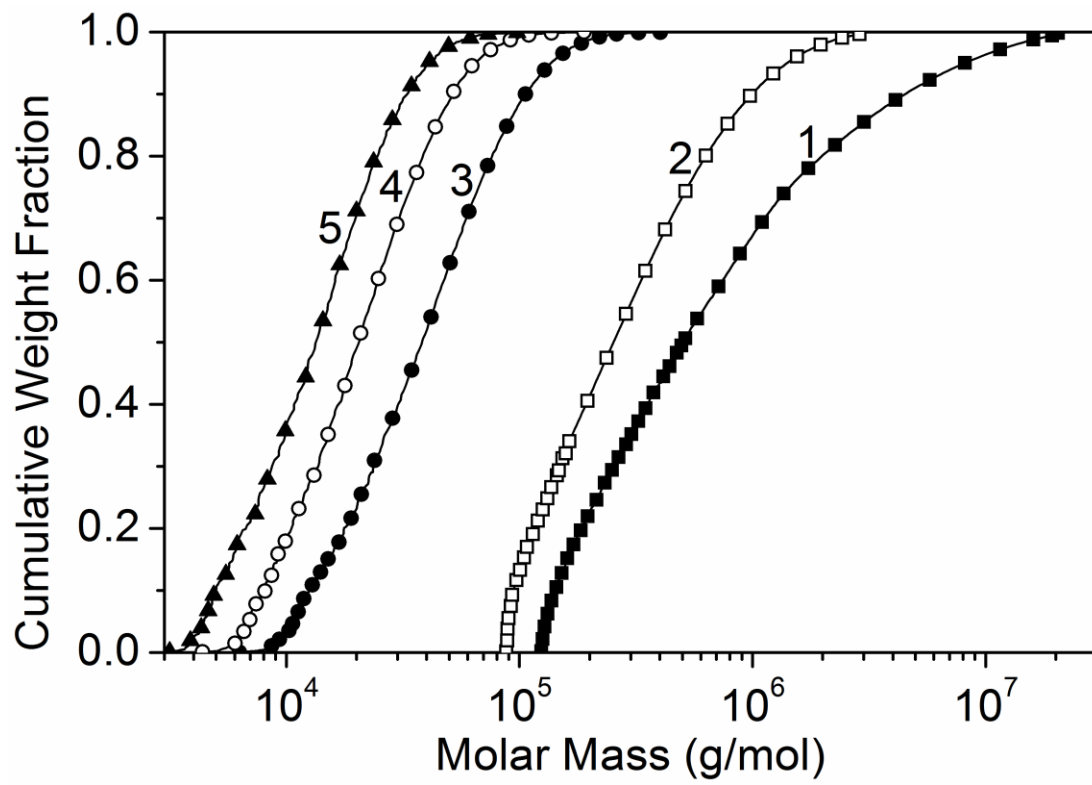


Figure 3

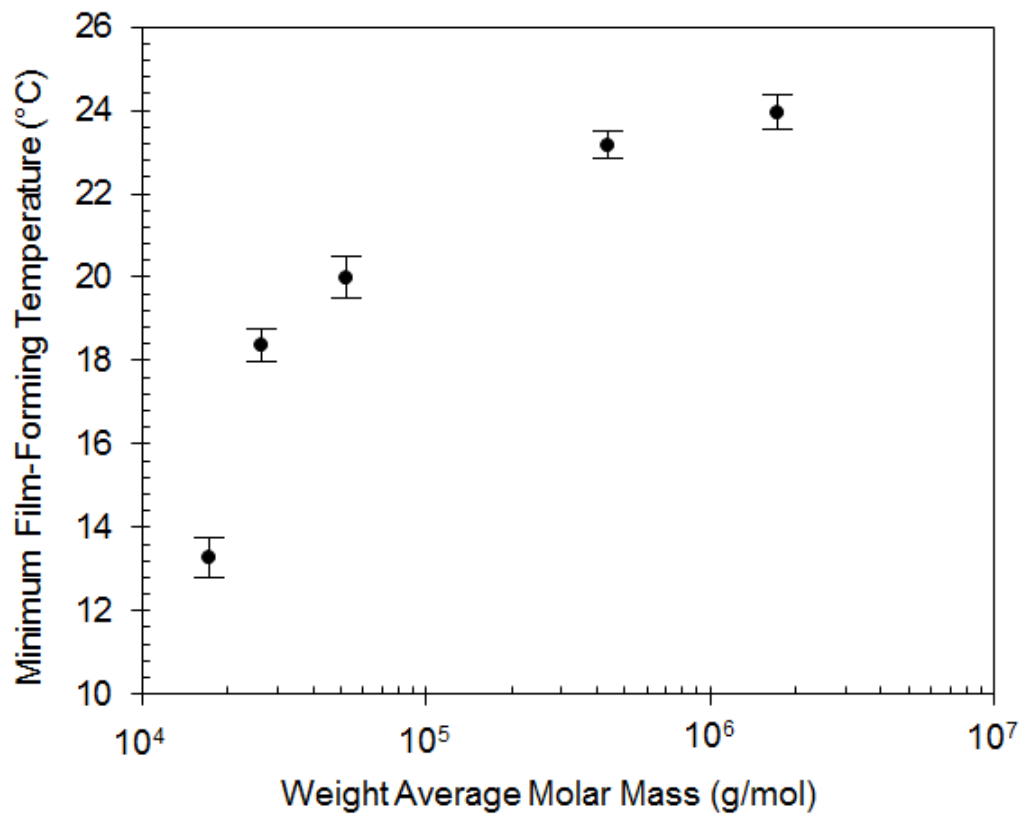


Figure 4

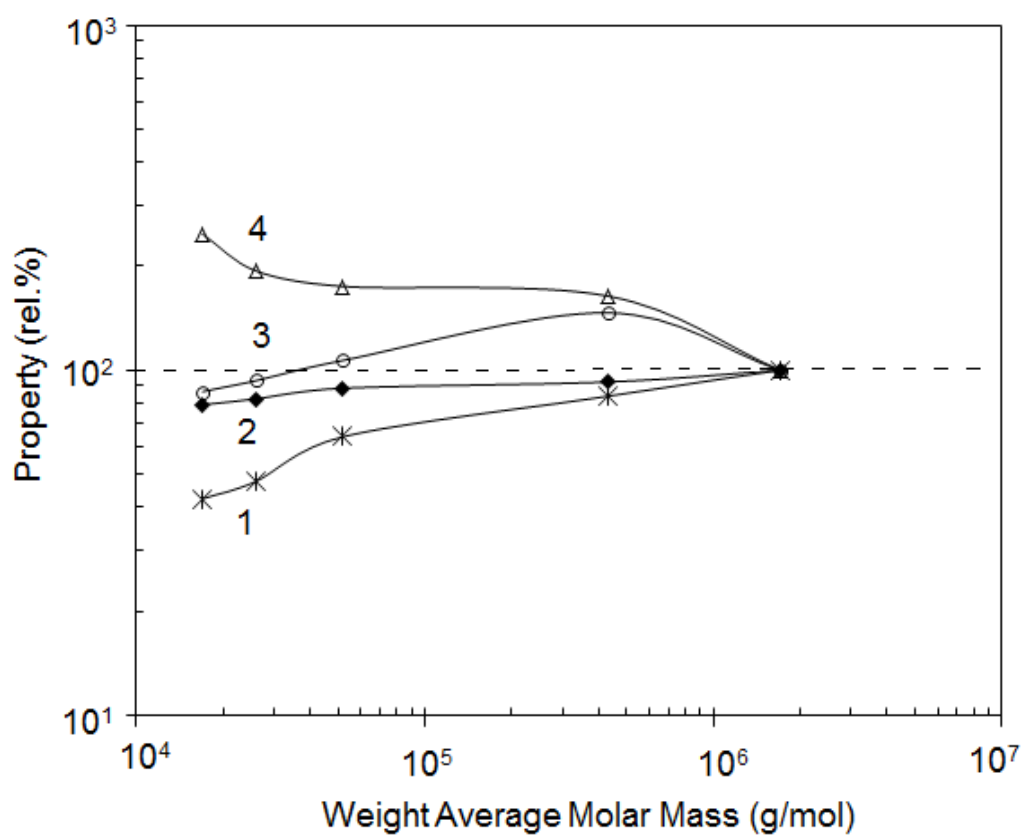


Figure 5

