

GPC-MALS vs. A4F-MALS: STANOVENÍ MOLEKULOVÉ HMOTNOSTI SAMOSÍŤUJÍCÍCH AKRYLÁTOVÝCH POJIV NA BÁZI EMULZNÍCH KOPOLYMERŮ

GPC-MALS vs. A4F-MALS: MOLAR MASS DETERMINATION OF SELF-CROSSLINKING ACRYLIC BINDERS BASED ON EMULSION COPOLYMERS

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Summary

Self-crosslinking core–shell latexes 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. 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.

Keywords: Emulsion polymerization, core–shell latex, keto-hydrazide crosslinking, molar mass distribution, A4F, chain transfer

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]. The reaction between the carbonyl functionalities of DAAM and hydrazide 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 [3]. 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 due to suppressed inter-diffusion and entanglement of polymer chains during the particle coalescence stage [4,5].

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 [6,7] as a consequence of the coupling of propagating branches generated through chain transfer to a

polymer [8,9]. 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. 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 [10]. 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 [11,12]. Hence, the desired film properties 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; 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. 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.

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

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 of approximately 6 – 8 °C. 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.

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 10 ml/min in two steps (1. core preparation, 2. shell preparation). After that, during 2 hours of hold period the polymerization was completed. 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.

Table 1. Composition of self-crosslinkable latexes based on structured microgels

Sample	Composition of monomer feeds (wt.%)	
	MMA/BA/MAA/AMA/DAAM/CTA	
	<i>Core</i>	<i>Shell</i>
L0	48.5/48.5/1.5/1.5/0/0	47.5/47.5/1.5/0/3.5/0
L0.1	48.5/48.5/1.5/1.5/0/0	47.45/47.45/1.5/0/3.5/0.1
L0.75	48.5/48.5/1.5/1.5/0/0	47.12/47.13/1.5/0/3.5/0.75
L1.5	48.5/48.5/1.5/1.5/0/0	46.75/46.75/1.5/0/3.5/1.5
L2.5	48.5/48.5/1.5/1.5/0/0	46.25/46.25/1.5/0/3.5/2.5

Molar mass determination

An instrumental setup of A4F-MALS 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 [Chyba! Zálóžka

není definována.]. 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.

An instrumental setup of SEC-MALS 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 μ L and the concentration of about 0.2 % w/v. All prepared solutions were filtered with 0.45 μ m 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.

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. 1 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 2,3. 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 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 and A4F separations showed (see Tables 2 and 3) 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.

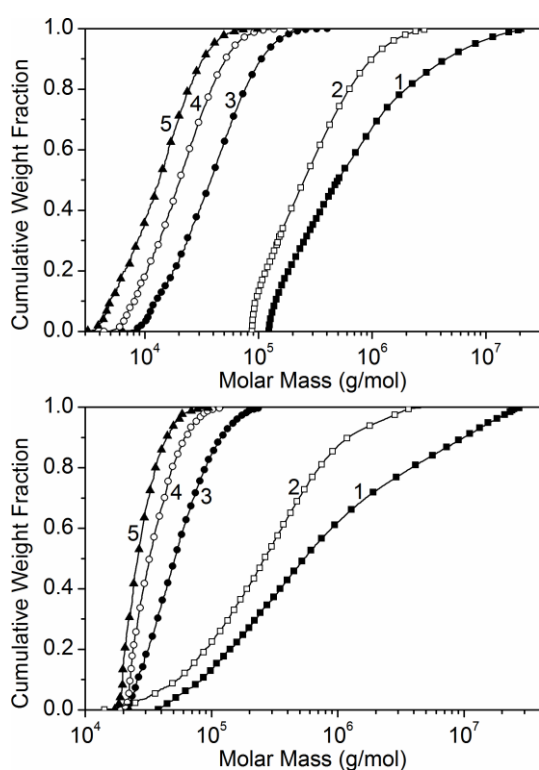


Figure 1. Comparison of cumulative molar mass distribution curves of shell copolymers obtained from SEC-MALS (top) and A4F-MALS (bottom). The content of isoctyl 3-mercaptopropionate (CTA) in the copolymer: 0 wt.% (1), 0.1 wt.% (2), 0.75 wt.% (3), 1.5 wt.% (4), 2.5 wt.% (5).

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 intermolecular chain transfer to polymer. 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.

Table 2. 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 (10^3 g/mol)	M_w (10^3 g/mol)	M_z (10^3 g/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

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 A4F-MALS

Sample	CTA content (wt. %)	M_n (10^3 g/mol)	M_w (10^3 g/mol)	M_z (10^3 g/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

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. 2. The molar mass versus

retention time plots of all microgel samples showed a bimodal molar mass distribution 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.

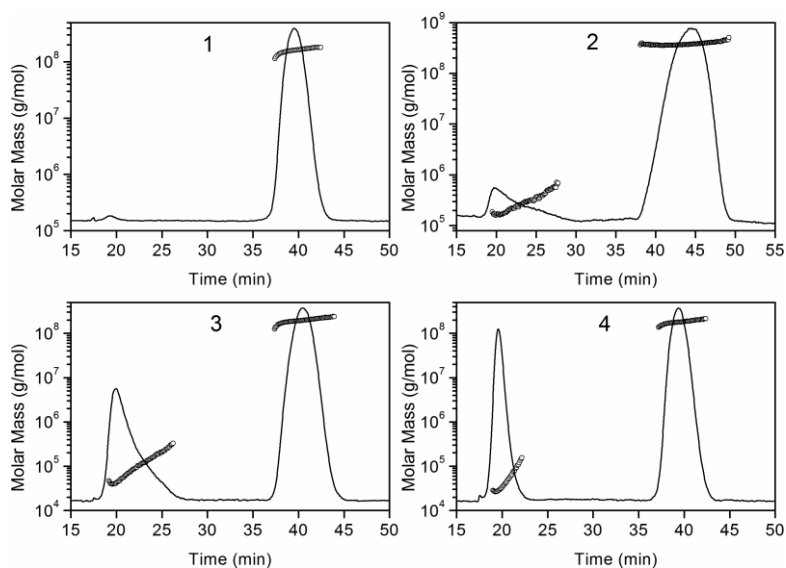


Figure 2. Molar mass versus retention time plots overlaid on RI fractograms for the core microgel (1) and core-shell microgels containing different amounts of CTA in the shell copolymer layer: 0 wt. % (2), 0.75 wt. % (3), and 2.5 wt. % (4).

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.

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