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Characterization of Molecular Structure of Acrylic Copolymers Prepared via Emulsion Polymerization Using A4F-MALS Technique

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ABSTRACT: The study is primarily focused on the possibility to utilize organic asymmetric flow field-flow fractionation (A4F) coupled to a multi-angle light scattering (MALS) detector for the characterization of copolymers of methyl methacrylate with various acrylates prepared by emulsion polymerization. The effects of acrylate monomer type and content on the molar mass distribution and degree of branching of acrylic copolymers have been studied by A4F-MALS using tetrahydrofuran as a carrier solvent. It has been found that the growing amount of acrylate results in the increase of molar mass, polydispersity, and branching degree as a result of chain transfer to polymer. Highly branched compact macromolecules with ultra-high molar mass were identified in all copolymers containing a high level of acrylate. In contrast to size traditionally used exclusion chromatography, organic A4F-MALS has been proved as a very efficient technique for the characterization of high molar mass acrylic emulsion copolymers. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40995.

INTRODUCTION

The use of waterborne polymers prepared via emulsion polymerization has much increased over the past years. This is the consequence of their numerous successful applications, unique properties and the environmental concerns and governmental regulations to substitute solvent-based systems. Emulsion polymerization is a complex process that is affected by used monomers, surfactants and initiator selection and also by the polymerization process itself.[1] The latex particles originate either from micelles (in case of hydrophobic monomers and surfactant concentrations above the critical micelle concentration) according the Smith-Ewart theory[2] or by homogeneous nucleation in the case of more hydrophilic monomers as described by the Hansen-Ugelstad-Fitch-Tsai theory.[3] By this technique polymers can be prepared to meet the requirements of specific applications by variation of monomer composition, molar mass, cross-linking density, particle size or nature of surface charge. The most distinctive feature of emulsion polymerization refers to the fact that the radicals are distributed among different particles, thus losing the chance of terminating between them. This allows the simultaneous achievement of high polymerization rates and high molecular weights.[4]

During the emulsion polymerization of alkyl acrylates both secondary and tertiary carbon radicals are formed. Secondary radicals are produced by propagation reactions, and the tertiary radicals result from chain transfer to polymer.[5] It has been demonstrated in several research studies[6–8] that acrylic monomers are prone to suffer both inter- and intramolecular chain transfer (back-biting) to polymer yielding branched polymers. The mechanism is believed to involve abstraction of tertiary backbone hydrogen. Most of the branches are produced by intramolecular chain transfer, which yields short branches that do not contribute to the formation of cross-linked structure (gel). Gel can be formed in those systems if intermolecular chain transfer is predominant and long-chain branches are formed. The tertiary radicals are less reactive than the secondary ones, and hence the chains that suffer from backbiting will reach a shorter length in contrast to those that did not undergo any intramolecular chain transfer reaction. This phenomenon is more evident at high temperatures because the activation energy of the backbiting is higher than that of the propagation, and hence the fraction of tertiary carbon radicals sharply increases with temperature.[5] The extent of branching can be estimated by ^{13}C NMR measuring the number of long chain branches.[9] As NMR analysis relies on determining the branch points, a major

problem is distinguishing the long-chain branches from the short-chain branches formed by backbiting. The phenomenon of branching was documented by Plessis et al.[10] who studied the seeded semicontinuous emulsion polymerization of n-butyl acrylate (n-BA), finding that under starved conditions a highly branched polymer containing 50–60% of gel was formed. The branching was evaluated using a solid-state ^{13}C NMR. In further work, the emulsion polymerization of 2-ethylhexyl acrylate (2-EHA) was studied and the similarities to the polymerization of n-BA were proved.[11]

As aqueous polymeric dispersions are being more frequently utilized, there is a strong interest 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 shown as a powerful technique for the determination of molar mass distribution and branching of various synthetic and natural polymers. However, SEC may fail in case of polymer molecules containing ultra-high molar mass fractions that can be degraded by shearing forces in SEC columns.[12] In addition, acrylic polymers prepared by emulsion polymerization can contain branched molecules that in SEC often elute abnormally[13,14]; 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.[14,15]

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. Note that while A4F often provides superior separation of branched macromolecules over SEC, both techniques have common limitation given by the fact that they separate polymer molecules according to their hydrodynamic volume. In case of branched macromolecules, molecules of identical hydrodynamic volume may differ in their molar mass and degree and topology of branching. Consequently, the polydispersity of molecules eluting at a given retention time from a separation device (SEC column or A4F channel) is higher than the polydispersity of a corresponding linear polymer of the same molar mass. However, the abnormal SEC elution of branched macromolecules, which for many branched polymers represents the most serious source of polydispersity, is effectively eliminated by using A4F.[14,15]

So far the reported applications of A4F in the area of synthetic polymers represent a small fraction of papers devoted to proteins, polysaccharides, various nanoparticles, virus-like particles, plasmids, and environmental colloids. The applications for synthetic polymers include poly(N-vinyl-2-pyrrolidone),[16] hyperbranched AB2-type all-aromatic polyesters,[17] poly(acrylamide),[18] polyethylene,[19,20] poly-styrene,[20–22] glycomethacrylate hybrid stars,[23] poly(N-isopropylacrylamide),[24] functionalized styrene-butadiene rubber.[25] An interesting application in the area of synthetic polymers was the characterization of core-shell latexes and study of their swelling behavior as a function of pH and ionic strength.[26] Authors of Ref. 20 used narrow polystyrene standards to demonstrate the effect of cross flow, injected mass, and molar mass on the separation efficiency and peak broadening. They also compared the behavior of ceramic and cellulose membranes and investigated the sample loss through the membrane. Nevertheless, it becomes evident from the literature survey that no studies on the analysis of branched acrylic copolymers by means of A4F using tetrahydrofuran (THF) as the carrier liquid have been published so far. The only short comment demonstrating the feasibility of using A4F-MALS for the characterization of an acrylic copolymer in THF was reported in a review concerning possibilities of organic A4F-MALS for the characterization of natural and synthetic polymers.[27] To the best of our knowledge, no studies were published discussing the analysis of branching of acrylic emulsion copolymers by means of A4F-MALS analytical system.

In this article, we aimed to present A4F as a mature separation technique capable of providing separation efficiency comparable to SEC, and in addition, solving several traditional SEC drawbacks. We demonstrated and compared the separation and characterization of branched acrylic emulsion copolymers by means of A4F-MALS and SEC-MALS analytical systems. THF, a potent solvent for a wide range of polymers and an environment, in which the applications of A4F have so far been sporadic, was chosen as a carrier liquid for all the A4F and SEC experiments.

EXPERIMENTAL

Materials
Emulsion copolymers investigated in this research work were synthesized of methyl methacrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), 2-ethylhexyl acrylate (2-EHA), acrylic acid (AA), and ethyleneglykol dimethacrylate (EGDMA). All the monomers were purchased from Roehm (Germany). Disponil FES 993 IS (Henkel, Czech Republic) was used as a surfactant and ammonium persulfate (Lach-Ner Company, Czech Republic) was utilized as an initiator of the polymerization reaction. THF (Sigma-Aldrich, Czech Republic) was used as the mobile phase in A4F-MALS measurements.

Preparation of Emulsion Copolymers
Emulsion copolymers investigated in this work were synthesized from MMA, MA, EA, BA, and 2-EHA. To improve the stability of acrylic dispersions, carboxyl functionalities were introduced by copolymerization with a constant amount (2 wt %) of acrylic acid (AA). Four series of emulsion copolymers were synthesized. They consisted of AA, MMA and MA or EA or BA or 2-EHA. The contents of acrylates for all series were 0, 5, 10, 25, 49, 73, and 98 wt %. That means the acrylate homopolymer containing only 2 wt % AA was prepared in each series as well. To obtain model branched structures, six emulsion copolymers of MMA, AA (2 wt %) and EGDMA cross-linker (0.2, 0.4, 0.8, 1.2, 1.6, 2 wt %) were prepared varying in the EGDMA content. To simplify the sample notation, AA content is not mentioned in further text and all the percentages are % by weight.
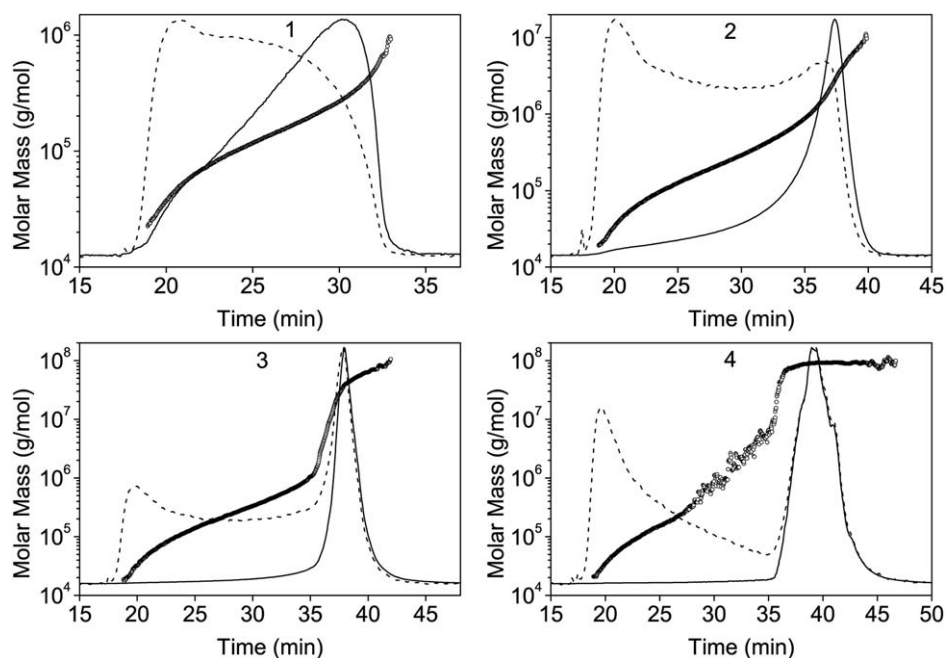
Figure 1. Molar mass versus retention time plots overlaid on MALS @ 90° (solid line) and RI (dashed line) fractograms for MMA-EA copolymers containing (1) 0 % EA, (2) 25 % EA, (3) 49 % EA, and (4) 98 % EA.

All the emulsion copolymers were prepared in a 2500-mL glass reactor by semi-continuous nonseeded emulsion polymerization under nitrogen atmosphere at 85°C. This procedure should ensure nearly homogeneous statistical copolymers. The reactor charge (99 g water, 1.8 g Disponil FES 993 IS, and 0.5 g ammonium persulphate) was put into the reactor and heated to the polymerization temperature. Then the monomer emulsion (185 g water, 19 g Disponil FES 993 IS, 1 g ammonium persulphate, 200 g monomer mixture) was fed into the stirred reactor during 3 hours (at a feeding rate of about 10 mL/min). After that, during 2 hours of hold period the polymerization was completed and the aqueous polymeric dispersion was cooled to room temperature.

A4F-MALS and SEC-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). Both detectors operated at 658 nm. A set of two PLgel Mixed-B 300 × 7.5 mm columns (Agilent) was used for comparative SEC measurements. 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 were injected as solutions in THF in the volume of 100 μL and the concentration of about 0.2% w/v. Note that the maximum concentrations of the molecules eluting from the A4F channel were around 0.03 mg/mL. A long channel with a wide 350 μm spacer and a regenerated cellulose 5 kDa membrane was used for the A4F separation. The A4F separation was achieved 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 fol-

lowed by additional 10 min focusing. That means the elution started at 17 min.

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 branching ratio (g) and number of branch units per molecule (m) were calculated with ASTRA 6 using well known definitions[28]:

$$g = \left(\frac{R_{br}^2}{R_{lin}^2} \right)_M \tag{1}$$

$$g = \left[\left(1 + \frac{m}{7} \right)^{\frac{1}{2}} + \frac{4m}{9\pi} \right]^{-\frac{1}{2}} \tag{2}$$

where R^2 is the mean square radius of linear *lin* and branched *br* macromolecules at common molar mass M. Note that eq. (2) is valid for three functional branch units corresponding to the formation of branch units by chain transfer to polymer.

A commercial sample of linear high molar mass poly(methyl methacrylate) (PMMA) prepared by suspension polymerization was used for the comparison with the synthetized samples. The specific refractive index increments (dn/dc) were determined by the measurements of homopolymers of MMA, MA, EA, BA, and 2-EHA with Optilab rEX. The homopolymers were prepared by solution radical polymerization in toluene using azobisisobutyronitrile as an initiator. The obtained values were 0.084; 0.068; 0.066; 0.064; and 0.064 mL/g, respectively. The uncertainties of measurements were ± (0.002–0.003) mL/g.

Note that the accuracy of molar mass of copolymers determined by light scattering can be affected by possible chemical heterogeneity. In our case the effect of chemical heterogeneity was
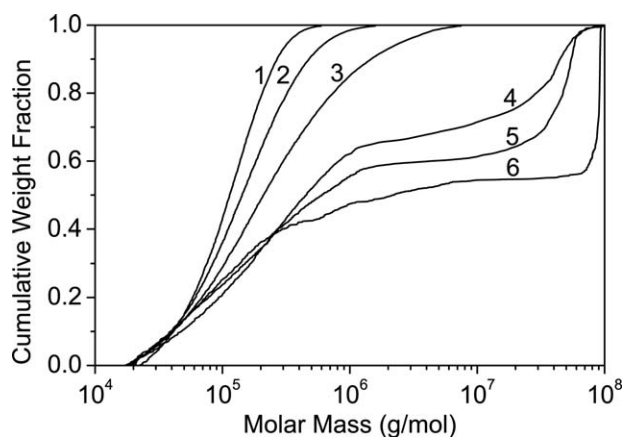
Figure 2. Cumulative molar mass distribution curves of MMA-EA copolymers containing (1) 0 % EA, (2) 10 % EA, (3) 25 % EA, (4) 49 % EA, (5) 73% EA, and (6) 98 % EA.

neglected and average dn/dc values corresponding to the overall chemical composition were used for processing the MALS data. Neglecting the chemical heterogeneity simplifies the data processing and is justified by relatively small dn/dc differences of parent homopolymers and employing the semi-continuous non-seeded emulsion polymerization that minimizes the chemical heterogeneity.

RESULTS AND DISCUSSION

The repeatability of polymer synthesis was tested by six preparations of PMMA. The average values of the number-average molar mass (M_n), the weight-average molar mass (M_w), and the z-average-molar mass (M_z) were 89,000 ± 3000 g/mol; 147,000 ± 8000 g/mol; and 228,000 ± 19,000 g/mol, respectively. Molar mass versus retention time plots for samples containing various weight fractions of MMA and EA are shown in Figure 1. The plot of PMMA indicates unimodal molar mass distribution while the plots of MMA-EA copolymers show bimodal distribution that becomes more obvious with increasing content of EA. The molar mass distribution curves of MMA-EA copolymers (Figure 2) shift towards ultra-high molar masses with increasing content of EA. Similar data were obtained for other MMA-acrylate copolymers. The molar mass averages as a function of acrylate content for all the prepared copolymers are shown in Figure 3. The values of M_w and M_z show significant increase with growing content of acrylate while M_n remains approximately identical with no obvious dependence on the acrylate content. This can be explained by the formation of high molar mass fractions as a result of chain transfer to polymer. The molar mass increases with increasing acrylate content as acrylates are markedly more prone to the chain transfer than methacrylates. As the chain transfer has a minimum effect on the fractions with lower molar mass, the values of M_n do not depend on the acrylate amount significantly while the averages M_w and M_z which count mainly the high molar mass fractions, strongly increase.

The root mean square (RMS) radius (R) is another important piece of information yielded by a MALS detector. The plot of RMS radius against molar mass (conformation plot) can pro-

vide the information about polymer chain conformation and most often is used to study polymer branching. The branching information can be revealed from the slope of the conformation plot. The typical values for linear random coils in thermodynamically good solvents are around 0.58 while lower values are indicative of branching presence. The value of 0.33 corresponds to homogeneous spheres and values less than 0.33 imply that the increase of molar mass is not associated with the corresponding increase of RMS radius. That is the case of reactions when the added mass is absorbed inside the macromolecular domains and the macromolecules become denser in their centers.

Figure 4 compares conformation plots of linear PMMA, copolymer of MMA with 25% EA and polyEA. The linear sample has a slope corresponding to a linear random coil configuration while the slope of the copolymer is very much smaller and proves the presence of branched macromolecules. The probability of chain transfer to a macromolecular chain increases with
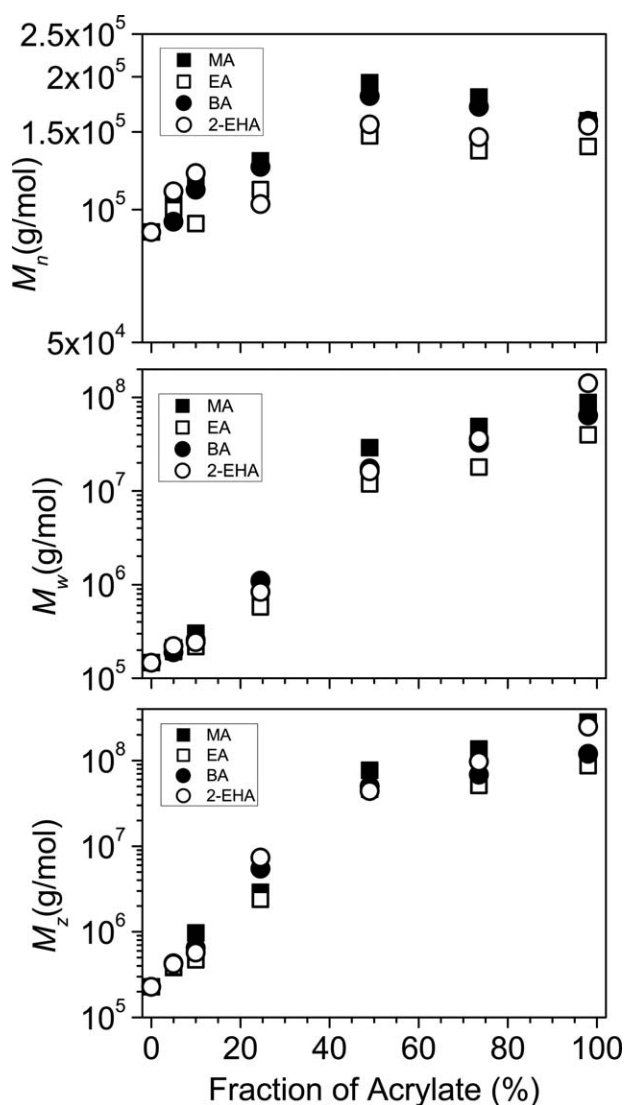

Figure 3. Molar mass averages (from top to bottom M_n, M_w, M_z) of MMA-acrylate copolymers a function of acrylate content.
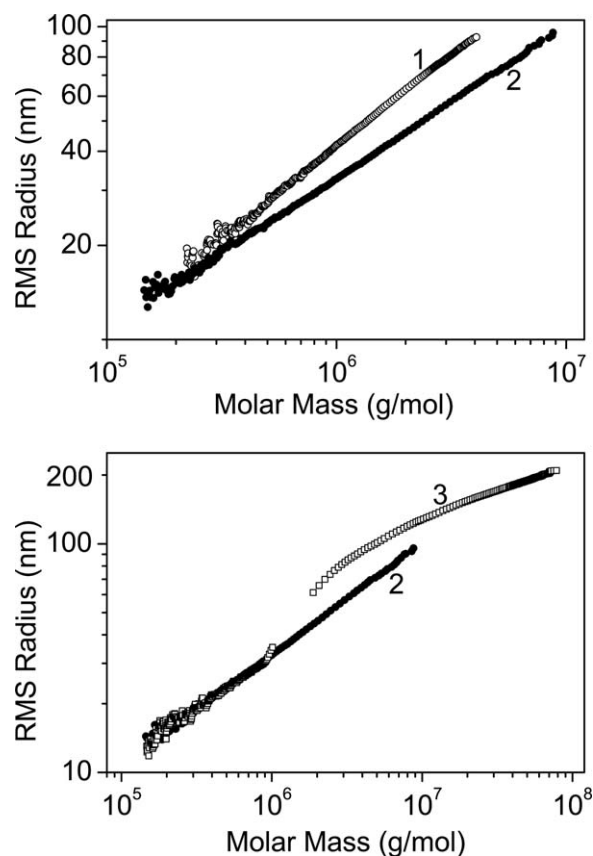
Figure 4. Conformation plots of: top – linear PMMA (1, ●) and copolymer containing 25 % EA (2, ●); and bottom – copolymer containing 25 % EA (2, ●) and polyEA (3, ▢). Slopes: linear PMMA ≈ 0.59; MMA-EA copolymer ≈ 0.49; and polyEA in the range of about $8 \times 10^6 – 8 \times 10^7$ g/mol ≈ 0.24.

increasing polymerization degree and consequently the high molar mass fractions are more branched. This causes the growing deviation of the two plots toward high molar masses. The plots of PMMA and copolymer MMA-EA (73/25) allow direct calculation of branching ratio assuming that a hypothetical linear MMA-EA copolymer has the identical conformation plot as PMMA homopolymer. Although this assumption may not be completely fulfilled, it simplifies the data processing and permits estimating the branching characteristics of MMA-EA copolymer. The plots of branching ratio and number of branch units versus molar mass are shown in Figure 5. The assumption that a hypothetical linear copolymer PMMA-EA has the same RMS radius versus molar mass relation as the linear PMMA is necessary as it is impossible to prepare the linear PMMA-EA copolymer because of a strong tendency of EA to chain transfer to polymer. Consequently, the data in Figure 5 represent only a rough estimation of branching in PMMA-EA copolymer. Despite the limitation, such plots can be used to demonstrate the trends in the molecular structure and compare samples of similar composition prepared under different reaction conditions. The plots in Figure 5 show that the molecules with molar mass up to about 1×10^5 are mostly linear, which is typical of randomly branched polymers where the lower molar mass part of distribution consists mostly of linear molecules. Glancing at distribu-

tion curve (Figure 2) one can see that linear molecules represent about 1/3 of the sample. The conformation plot of polyEA (Figure 4) shows two different sections. The one in the region of lower molar masses overlap with that of copolymer containing 25% EA, the second section is shifted towards higher radii, which indicates different structure than branched polymer coils, likely swollen cross-linked particles, with the slope indicative of compact structure.

Cumulative distribution curves of RMS radius depicted in Figure 6 show a slightly different pattern compared to molar mass distributions. The plots are shifted towards higher radii with increasing acrylate content as in the case of molar mass distributions. However, in the region of the highest radii the trend is opposite to the molar mass. The largest radii can be found in the copolymer containing 49% EA, and then the plots of copolymer containing 73% EA and polyEA move back to smaller radii. This indicates that the compactness of the very high molar mass fractions increases with increasing quantity of acrylate. Using a high amount of acrylic monomer, i.e., high concentration of monomer segments capable of chain transfer to polymer, a highly branched or even cross-linked macromolecular structure having suppressed swelling ability in THF is formed, which is manifested by smaller radii of gyration. Cross-linking of the very high molar mass fractions is supposed to be achieved predominantly by the intermolecular chain transfer to
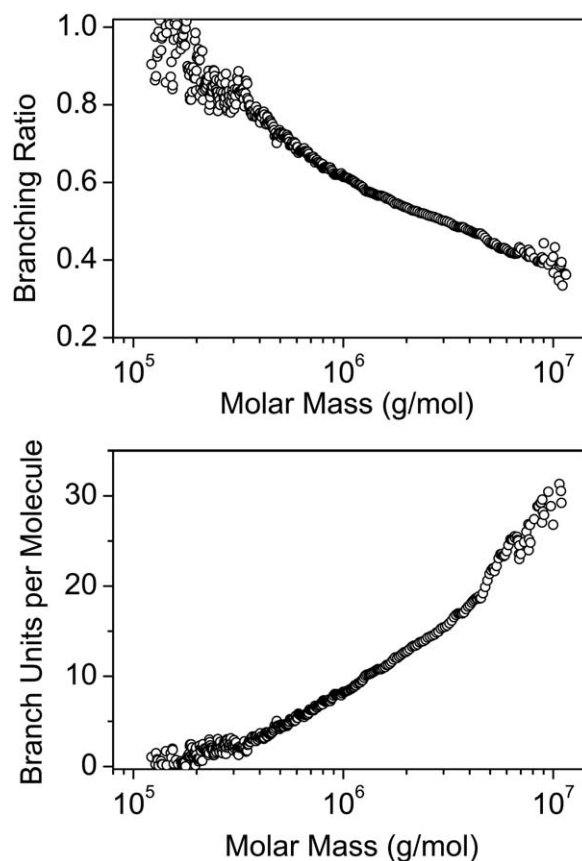

Figure 5. Branching ratio (top) and number of branch units per molecules (bottom) as a function of molar mass for copolymer MMA with 25 % EA.
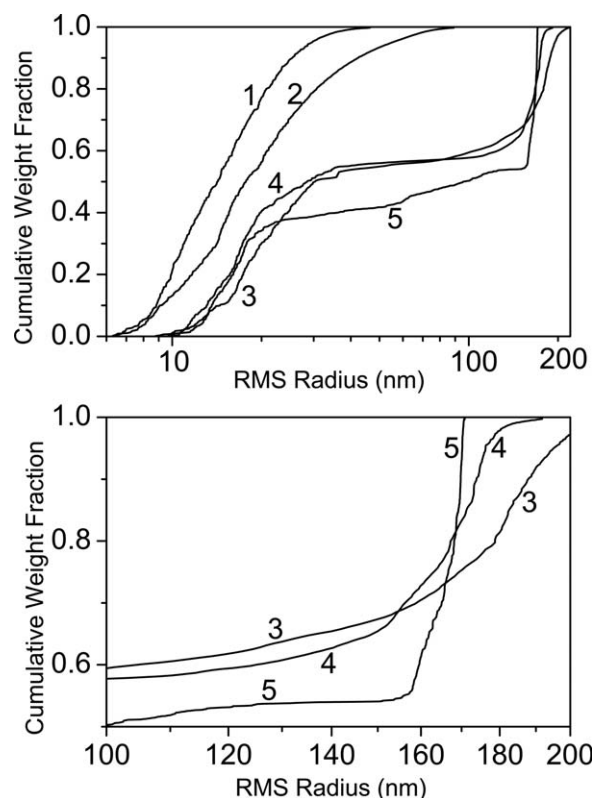
Figure 6. Cumulative distribution curves of MMA-EA copolymers containing (1) 10 % EA, (2) 25 % EA, (3) 49 % EA, (4) 73 % EA, and (5) 98 % EA. Full (top) and zoomed (bottom) view.

polymer yielding long-chain branches. The other possible reaction contributing to gel formation in a small way may include the termination of polymeric radicals by combination.[4]

As the polymerization and chain transfer reactions occur in a dense domain of a single micelle, they may cross-link the macromolecules in the micelle into one large structure. When latex containing a high amount of acrylate is dissolved in THF, the uncross-linked linear and branched molecules diffuse out of the latex particles and the remains are swollen particles formed by
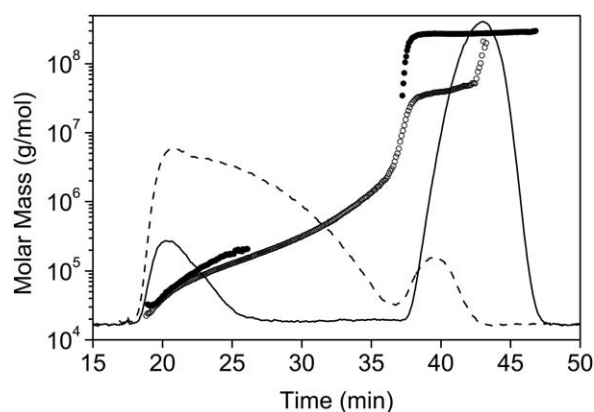

Figure 7. Molar mass versus retention time plots overlaid on RI fractograms for PMMA containing 0.4 % EGDMA (●, dashed line) and 1.6 % EGDMA (●, solid line).
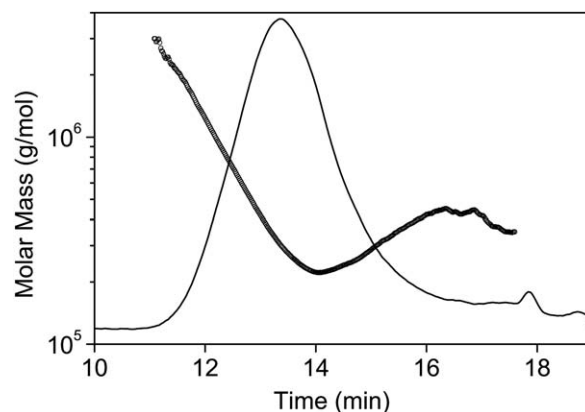

Figure 8. Example of SEC-MALS analysis: Molar mass versus elution time and RI chromatogram for copolymer of MMA with 25 % EA. Compare with Figure 1, plot 2.

the macromolecules cross-linked into supermolecular structures of the dimensions comparable with those of latex particles. These two different populations are separated by A4F into two more or less overlapping peaks. To support this hypothesis model PMMA samples containing different levels of EGDMA cross-linker were prepared. The molar mass versus retention time plots and fractograms of two samples are shown in Figure 7. The plots show two polydisperse species of highly different molar mass and resemble the results for copolymers containing high amounts of acrylates.

The prepared copolymers were also measured by SEC-MALS to demonstrate the superior separation of A4F for the acrylic emulsion copolymers. An example of SEC-MALS shown in Figure 8 clearly indicates that SEC fails to characterize acrylic emulsion copolymers containing high molar mass branched molecules. The comparison of molar mass versus time plots from A4F-MALS (see Figure1) and SEC-MALS shows not only the difference in the region of very high molar masses as a result of shearing degradation and/or filtering effect of SEC columns, but in the region of lower molar masses as well. The upturn on the plot of molar mass from SEC incorrectly suggests that the sample does not contain molecules with molar mass lower than about 200,000 g/mol. However, A4F-MALS analysis clearly reveals molecules with molar masses much below this value. The upturn on the plot obtained from SEC analysis is due to the anchoring of large branched macromolecules in the pores of column packing and their delayed elution. The delayed macromolecules increase the polydispersity of fractions eluting in the region of higher elution volumes. For polydisperse fractions the MALS detector measures the weight average molar masses, which count more the molecules with very high molar mass. As a consequence of this fact, the plot of molar mass shows increasing trend in the region of higher elution times.[13,14]

CONCLUSIONS

In contrast to SEC, A4F allows efficient separation of macromolecules present in acrylic copolymers prepared by emulsion polymerization. The molar mass of these copolymers increases

with the increasing content of acrylate monomer with no obvious effect of the type of the acrylate monomer. Copolymers containing higher level of acrylate are composed of two different species, namely by soluble linear and branched macromolecules that can dissolve at molecular level, and by completely cross-linked latex particles. A4F was proved as a more efficient separation technique than commonly used SEC. Combination of A4F with a MALS detector yields not only correct molar mass distribution, but information about the branching and ratio of soluble macromolecules and cross-linked latex particles. The copolymers containing high quantity of acrylate have similar molecular structure as polyMMA containing small quantity (≈ 1 %) of EGDMA cross-linker.

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