Application of A4F-MALS for the Characterization of Polymers Prepared by Emulsion Polymerization: Comparison of the Molecular Structure of Styrene-Acrylate and Methyl Methacrylate-Acrylate Copolymers

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ABSTRACT: In this paper, organic asymmetric flow field flow fractionation coupled to a multi-angle light scattering detector is presented as a very efficient tool for the characterization of copolymers prepared by emulsion polymerization. The molar mass distribution and the extent of branching of styrene-acrylate copolymers have been compared with corresponding copolymers of methyl methacrylate. It has been found that the presence of acrylate monomer results in the increase of molar mass and formation of branched macromolecules due to intermolecular chain transfer to polymer similarly as in case of methyl methacrylate-acrylate copolymers. However, the effect is far less pronounced.

INTRODUCTION

Nowadays, the issues regarding environmental protection cause that technologies reducing or eliminating the application of organic solvents are appreciated. Therefore, waterborne polymers prepared via emulsion polymerization are of particular interest, especially in the coatings industry, offering a wide application range of products, starting from paints and plasters for the construction industry, through wood paints and varnishes to coatings for metal protection and decorative systems. Among the waterborne coatings, styrene/acrylic latex coatings play an important role due to their extraordinary properties including ease of modification, pigmentation and application as well as outstanding chemical resistance, resistance to atmospheric conditions and diversified mechanical features. By emulsion polymerization 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 [1].

During the polymerization of alkyl acrylates, both inter- and intramolecular chain transfer (back-biting) to polymer occurs yielding branched polymers [2,3,4,5]. The phenomenon

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of branching, being difficult to characterize, may affect both the colloidal stability of the polymerization system and the final properties of the product. The branching of emulsion polymers using a solid-state ^{13}C NMR was investigated by Plessis et al [6,7]. who studied the semi-continuous emulsion polymerization of n-butyl acrylate (*n*-BA) and 2-ethylhexyl acrylate (2-EHA), reporting that under starved conditions a highly branched polymer containing a significant amount of gel was formed. In further work,[5] Plessis et al. reported that the emulsion polymerization of *n*-BA with different amounts of styrene as a comonomer yielded a polymer varying in the gel content and molecular weight. They observed that the larger the amount of styrene, the smaller the gel content and the molecular weights. The addition of 10 % of styrene was found sufficient to avoid the gel formation. These results were confirmed by Yang et al. [8] who investigated the emulsion copolymerization of *n*-BA/styrene finding that in the range of styrene 10–90 % no gel occurred. Plessis[5] showed that only the hydrogen linked to the tertiary carbon of the backbone belonging to *n*-BA polymerized units was able to undergo the chain transfer reaction, whereas the hydrogen on the tertiary carbon belonging to polymerized styrene was very stable.

Until now, the asymmetric flow field flow fractionation (A4F) has been used successfully applied especially for the analysis of water-soluble polymers or aqueous suspensions of polymer particles [9,10,11,12,13]. By changing the carrier liquid from aqueous solution to organic solvent, it should be possible to utilize the advantages of A4F for high molar mass polymers soluble in organic solvents. In the literature dealing with A4F, however, very few articles report on the use of organic solvents as the carrier liquid. The first trials were made by Brimhall et al. [14] and Caldwell et al. [15] at the separation of

polystyrene samples in ethylbenzene. Later, several authors showed the possibility of using other organic solvents, terahydrofuran (THF) being the most frequent one [16,17,18]. Recently, Angoy and co-workers [19] published a paper on the structure characterization of branched poly(phenylacetylene) using THF as a mobile phase. Nevertheless, it becomes evident from the literature survey that no studies on the analysis of branched styrene/acrylic copolymers by means of A4F using THF as the carrier liquid have been published so far.

In our previous study [20] we focused on testing the applicability of organic A4F coupled with a multi-angle light scattering (MALS) detector for the characterization of molecular structure of copolymers of methyl methacrylate (MMA) with various acrylates prepared by semi-continuous non-seeded emulsion polymerization. It has been found that the weight-average (M_w) and the z-average (M_z) molar masses of MMA-acrylate copolymers increase with the increasing content of acrylate monomer; and that copolymers consisting of high amount of acrylate have a very broad molar mass distribution and contain ultra-high molar mass fractions of highly compact molecular structure. The A4F-MALS method has been proved as an efficient analytical tool for the characterization of these polymers that are often difficult to be analyzed by traditionally used size exclusion chromatography (SEC). In contrast to SEC, the separation by A4F is not limited by molar mass and in addition the technique offers more efficient separation of branched polymers [21,22]. The ability to separate large branched macromolecules is especially valuable in case of copolymers containing acrylate monomers that are prone to branching due to chain transfer to polymer. Besides the separation of soluble macromolecules, A4F can separate swollen nano-gel particles that can be created by

total crosslinking of the latex particles. Such nano-gels cannot be separated by SEC and their quantification can be achieved by analytical ultracentrifugation [23] that requires considerably longer analysis time than A4F-MALS.

In contrast to purely acrylic copolymers, styrene containing copolymers can be also characterized by the distribution of chemical composition. As a matter of fact, the obtainable information is not the true chemical distribution in the sense of fraction of molecules with a certain chemical composition, but the relation between the average chemical composition and molar mass. The analysis requires the use of a light scattering detector in conjunction with both a UV and a refractive index (RI) detector. The determination is based on the fact that styrene units are visible by both UV detector and refractive index detector whereas acrylate units can be monitored solely by the RI detector and are invisible in the UV detection. The determination requires the knowledge of extinction coefficient for polystyrene and specific refractive index (dn/dc) for styrene and acrylate homopolymers.

The goal of the current work was to compare the separation and characterisation of branched styrene/acrylic and methyl methacrylate/acrylic emulsion copolymers by means of A4F-MALS analytical system. The combination of UV and RI detection has enabled characterizing the distribution of chemical composition of styrene copolymers. The results from A4F-MALS have been completed by intrinsic viscosities determined using Ubbelohde capillary viscometer to further show the differences between styrene-acrylate and MMA-acrylate copolymers.

EXPERIMENTAL

Materials

Emulsion copolymers investigated in this research work were synthesized of styrene (S), methyl methactrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), acrylic acid (AA), ethyleneglykol dimethacrylate (EGDMA), and allyl methacrylate (AMA). 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) stabilized with 200 ppm butylated hydroxyl toluene was used as the A4F carrier and as the solvent for the determination of intrinsic viscosity by capillary viscometer.

Preparation of Emulsion Copolymers

Emulsion copolymers investigated in this work were synthesized from S, MMA, MA, EA, and BA. To improve the stability of acrylic dispersions, carboxyl functionalities were introduced by copolymerization with a constant amount (2 % wt) of acrylic acid (AA) into all the prepared copolymers. Two series of emulsion copolymers based on S and MMA, respectively, were synthesized. The contents of acrylate comonomer for both 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 samples containing cross-linked supermolecular structures, emulsion copolymers of S and MMA comprising AA (2 % wt) and EGDMA or AMA crosslinker in the amount of 0.2, 0.5, 1, 1.5, and 2 % wt were prepared. These samples can serve as models of highly branched and/or cross-linked polymers, and also can be used to modify the latex application

properties such as hardness, chemical and anticorrosion resistance of paint films. Note: to simplify the sample notation, AA content is not mentioned in further text and all the percentages are % by weight.

All emulsion copolymers were prepared in a 700 mL glass reactor by semi-continuous non-seeded 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 feeding rate of about 2 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

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 22. Both 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. THF was used as the A4F carrier at a 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. All prepared solutions were filtered with 0.45 µm filter before the injection into A4F channel. 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. 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 specific refractive index increments dn/dc used for data processing for individual homopolymers were 0.185 mL/g (PS), 0.084 mL/g (PMMA), 0.068 mL/g (PMA), 0.066 mL/g (PEA), and 0.064 mL/g (PBA). The extinction coefficient of PS at 254 nm of 1595 mL g^{-1} cm^{-1} was used for the determination of the fraction of styrene along the molar mass axis. 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.

Determination of Intrinsic Viscosity

The intrinsic viscosity was determined by the extrapolation of the viscosity number to zero concentration according to the Huggins extrapolation procedure. The measurements of the specific viscosity were carried out using a glass capillary viscometer of the Ubbelohde design in THF at 25 °C. Each sample was measured at 5 different concentrations that yielded the specific viscosity in the range of about 0.15 – 1.

RESULTS AND DISCUSSION

The chemical composition along the molar mass axis is depicted in Figure 1 for copolymers of S-MA, S-EA, and S-BA of different ratio of styrene/acrylate. The data for all prepared copolymers show that the average chemical composition remains approximately constant over the entire molar masses range, which coincides with the fact that the semi-continuous non-seeded emulsion polymerisation technique performed under so-called starved conditions generally ensures almost homogeneous statistical copolymers having the composition equal to the starting co-monomer ratio. During the continuous dosing of the monomer mixture in the course of emulsion polymerization the less reactive co-monomer becomes in excess and thus the lower reactivity is compensated by higher concentration. It may be worth mentioning that the average chemical composition determined by ASTRA software agrees within the experimental uncertainty with the composition of the monomer feed used for the emulsion polymerization.

Our previous study on the molecular structure of copolymers of MMA with acrylate monomers showed a shift of molar mass distribution towards higher molar masses with increasing content of the acrylate monomer [20]. The formation of high molar mass fractions was associated with the formation of branched macromolecules formed by the intermolecular chain transfer to acrylate units of polymer chain. The mechanism is believed to involve abstraction of tertiary backbone hydrogen. The A4F-MALS results obtained for styrene-acrylate copolymers show the same tendency, but markedly less pronounced in the range of acrylate comonomer 5 − 75 %. Figure 2 contrasts molar

mass distribution of poly(methyl methacrylate) (PMMA) and polystyrene (PS) prepared under identical conditions and styrene-acrylate copolymers containing 50 % and 75 % acrylate. In comparison with PMMA, the molar mass distribution of PS is shifted significantly to higher molar masses. In spite of the higher propagation rate constant for the PMMA polymerization in the homogenous media [24], the possible explanation of higher molar mass of emulsion PS may be represented by the effect of different initiation and termination rate constants of S and MMA and also by the fact that emulsion polymerization is performed in a heterogeneous system where different water solubility of S and MMA monomers may play the crucial role.

Figure 2 also shows that even a high level of acrylate monomer results in a moderate shift of molar mass distribution towards higher molar masses. The shift of molar mass distribution with increasing content of acrylate is much less pronounced than that in copolymers with MMA, as can be seen in Figure 3. The molar mass distribution of MMA copolymers containing 10 % acrylate is shifted to lower molar masses compared to that of styrene-acrylate copolymers containing 25 and 50 % acrylate. This reveals that the intermolecular chain transfer to polymer (leading to the formation of fractions with high molar mass) occurred at a low level. The increase of acrylate level in MMA copolymers to 25 % results in appearance of a higher-molar-mass tail and the molar mass distributions of MMA copolymers containing 50 % acrylate become markedly shifted to high molar masses. In this case, the effect of lower molar mass of PMMA compared to PS (Figure 2) is overcompensated by the increase of molar mass due to intermolecular chain transfer to acrylate units.

Branched macromolecules formed by intermolecular chain transfer to polymer were identified in the previously studied MMA-acrylate copolymers [20]. Branched macromolecules can be also found in S-acrylate copolymers, but the presence of styrene markedly decreases the degree of branching likely due to steric hindrance by large phenyl groups. Several examples are depicted in Figure 4 that contrasts the root mean square (RMS) radius versus molar mass plots (conformation plots) of S-acrylate with corresponding MMA-acrylate copolymers. It is well recognized that the slope of the conformation plot can reveal branching. The typical values for linear random coils in thermodynamically good solvents are around 0.58 while lower values are indicative of branching in the sense of the lower the slope the higher the degree of branching [21,25]. In the examples depicted in Figure 4, all the MMA based copolymers have lower slopes than the analogous styrene based copolymers, i.e., they can be considered to be more branched; whereas the slopes of the corresponding S-acrylate copolymers indicate moderately branched or even linear molecular structure. Figure 4 shows further that in the case of MMA-acrylate copolymers, the slopes of conformation plots are not to be affected by the acrylate type, whereas in the case of S-acrylate copolymers, differences between slopes of concentration plots with respect to the type of alkyl acrylate appear. Slightly higher slopes of S-copolymers containing 10 % BA might indicate that this monomer is less prone to chain transfer than MA and EA and moderately branched or even linear molecular structure was formed. This phenomenon is in a good accordance with results presented in Figure 2.

The intrinsic viscosity [η] is a fundamental property of colloidal systems that is extensively used for the analysis and characterization of synthetic and biological

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polymers, nanoparticles, and other colloids [26]. It provides information about fundamental properties of the solute and its interaction with the solvent. As [η] is related to the volume occupied by macromolecules in solution, it can be used in combination with molar mass to characterize the branching of polymer chains. The difference between the molecular structure of S-acrylate and MMA-acrylate copolymers is further demonstrated in Figure 5 that depicts the intrinsic viscosity versus M_w plot. The solid lines indicate [η] versus M_w relations for linear PS and PMMA calculated using the literature parameters of the Mark-Houwink equations for PS and PMMA [27,28]. The data show significantly larger difference of [η] from the linear models for MMA-acrylate copolymers which confirms their more compact, i.e., branched structure.

The ability of A4F to separate cross-linked particles is demonstrated in Figure 6 for PS prepared with the addition of 1% EGDMA or 1% AMA. The relative peak areas corresponding to soluble macromolecules and cross-linked particles shows that AMA is a more efficient cross-linking agent than EGDMA. The molar mass of particles cross-linked with AMA is higher compared to those cross-linked with EGDMA whereas their RMS radius is smaller, which gives the evidence of their higher compactness. The finding allows concluding that the latex P(S-AMA) particles are more cross-linked and thus in THF swell less than the particles cross-linked with EGDMA. Furthermore, the data show that EGDMA cross-linked PS contains a substantial fraction of almost linear fractions, as can be seen from the slope of the conformation plot ≈ 0.56 for lower molar mass part of the molar mass distribution. The slope of conformation plot ≈ 0.15 for higher molar mass part of the molar mass distribution is lower than the value for compact spheres (slope = 0.33). This may be explained by the fact that the addition of

monomer into the crosslinked particle occurs without the additional growth of the particle size.

CONCLUSIONS

Similarly as in the case of MMA-acrylate copolymers, A4F-MALS was demonstrated as an efficient analytical tool capable of detailed characterization of molecular structure of styrene-acrylate copolymers prepared by emulsion polymerization. The method can provide molar mass distribution as well as to identify the presence of branched macromolecules. In addition, combination of UV and RI detection yields the fraction of styrene as a function molar mass. The chemical composition of all analyzed styrene copolymers was approximately constant over the entire molar mass range. The presence of acrylate units results in the formation of branch units by intermolecular chain transfer to polymer and to the shift of molar mass distribution towards high molar masses. However, in contrast to corresponding MMA containing copolymers, the effect is significantly less pronounced probably due the steric hindrance by phenyl groups. A4F can also separate soluble macromolecules from cross-linked particles formed by the addition of multifunctional monomers or by the excessive chain transfer to polymer. The information about the degree of crosslinking can be estimated from the molar mass and RMS radius data. AMA was found to be more efficient cross-linking monomer for the polymerization with styrene than EGDMA.

REFERENCES

1. Asua, J.M. Emulsion Polymerization: From Fundamental Mechanisms to Process Developments. J. Polym. Sci., Part A: Polym. Chem. **2004**, *42*, 1025-1041.

2. Plessis, Ch.; Arzamendi G.; Leiza, J.R.; Schoonbrood, H. A.; Asua, J.M. A decrease in effective acrylate propagation rate constants caused by intramolecular chain transfer. Macromolecules **2000**, *33*, 4-7.

3. Plessis, Ch.; Arzamendi G.; Leiza, J.R.; Schoonbrood, H. A.; Asua, J.M. Seeded semibatch emulsion polymerization of poly(n-butyl acrylate). Kinetics and structural properties. Macromolecules **2000**, *33*, 5041-5047.

4. Lovell, P. A.; Shah, T. H. Chain transfer to polymer in emulsion polymerization of n-butyl acrylate studied by carbon -13 NMR spectroscopy and gel permeation chromatography. Polym. Commun. **1991**, *32*, 98-103.

5. Plessis, Ch.; Arzamendi, G.; Alberdi, J. M.; Agnely, M.; Leiza, J.R.; Asua, J.M. Kinetics and polymer microstructure of the seeded semibatch emulsion copolymerization of n-butyl acrylate and styrene. Macromolecules **2001**, *34*, 5147-5157.

6. Plessis, Ch.; Arzamendi G.; Leiza, J.R.; Alberdi, J. M.; Schoonbrood, H. A.; Charmot, D.; Asua, J.M. Seeded semibatch emulsion polymerization of butyl acrylate: Effect of the chain-transfer agent on the kinetics and structural properties. J. Polym. Sci., Part A: Polym. Chem. **2001**, *39*, 1106-1119.

7. Plessis, Ch.; Arzamendi G.; Alberdi, J. M.; Agnely, M.; Leiza, J.R.; Asua, J.M. Seeded semibatch emulsion polymerization of butyl acrylate: Effect of the chain-transfer agent on the kinetics and structural properties. Macromolecules **2001**, *34*, 6138-6143.

8. Yang, H. Y.; Yang, C. H. Statistical experimental strategies approach to emulsion copolymerization of styrene and n-butyl acrylate. J. Appl. Polym. Sci. **1998**, *69*, 551-563.

9. Leeman, M., Islam, M.T.; Haseltine, W. G. Asymmetrical flow field-flow fractionation coupled with multi-angle light scattering and refractive index detections for characterization of ultra-high molar mass poly(acrylamide) flocculants. J. Chromatogr. A **2007**, *1172*, 194-203.

10. Roessner, D.; Kulicke, W.M. Online coupling of flow field-flow fractionation and multi-angle laser-light scattering. J. Chromatogr. A **1994**, *687*, 249-258.

11. Leeman, M.; Wahlund, K.G.; Wittgreen, B. Programmed cross flow asymmetrical flow field-flow fractionation for the size separation of pullulans and hydroxypropyl cellulose. J. Chromatogr. A **2006**, *1134*, 236-245.

12. Andersson, M.; Wittgren, B.; Schagerlöf, H.; Momcilovic, D.; Wahlund, K.G. Size and structure characterization of ethylhydroxyethyl cellulose by the combination of field-flow fractionation with other techniques. Investigation of ultralarge components. Biomacromolecules **2004**, *5*, 97-105.

13. Knappe, P.; Bienert, R.; Weidner, S.; Thünemann, A.F. Characterization of poly(N-vinyl-2-pyrrolidone)s with broad size distributions. Polymer **2010**, *51*, 1723-1727.

14. Brimhall, S.L.; Myers, M.N.; Caldwell, K.D.; Giddings, J.C. Polymer characterization by flow field-flow fractionation. Polym. Mater. Sci. Eng. **1984**, *50*, 48-51.

15. Caldwell, K.D.; Brimhall, S.L.; Gao, Y.; Giddings, J.C. Sample overloading effects in polymer characterization by field-flow fractionation. J. Appl. Polym. Sci. **1988**, *36*, 703-719.

16. Kirkland, J.J.; Dilks, C.H. Flow field-flow fractionation of polymers in organic solvents. Anal. Chem. **1992**, *64*, 2836-2840.

17. Bruijnsvoort, M.; Kok, W. T.; Tijssen, R. Hollow-fiber flow field-flow fractionation of synthetic polymers in organic solvents. Anal. Chem. **2001**, *73*, 4736-4742.

18. Bang, D.Y.; Shin, D.Y.; Lee, S.; Moon, M. H. Characterization of functionalized styrene–butadiene rubber by flow field-flow fractionation/light scattering in organic solvent. J. Chromatogr. A **2007**, *1147*, 200-205.

19. Angoy, M.; Bartolomé, M.I.; Vispe, E.; Lebeda, P.; Jiménez, M.V.; Pérez-Torrente, J.J.; Collins, S.; Podzimek, S. Branched poly(phenylacetylene). Macromolecules **2010**, *43*, 6278-6283.

20. Podzimek, S.; Machotova, J.; Snuparek, J.; Vecera, M.; Prokupek, L. Characterization of molecular structure of acrylic copolymers prepared via emulsion polymerization using A4F-MALS technique. J. Appl. Polym. Sci. **2014**, *131*, 11178-11185.

21. Podzimek, S. Light Scattering, Size Exclusion Chromatography and Asymmetric Flow Field Flow Fractionation; Wiley: New Jersey, **2011**; p. 318.

22. Podzimek, S. Asymmetric Flow Field Flow Fractionation in Encyclopedia of Analytical Chemistry; Meyers, R. A., Ed.; John Wiley: Chichester, **2012**. DOI: 10.1002/9780470027318.a9289.

23. Müller, H.; Schmidt, A.; Kranz, D. Determination of the degree of swelling and crosslinking of latex particles by analytical ultracentrifugation. Prog. Coll. Polym. Sci. **1991**, *86*, 70-75.

24. Gilbert, R.G. Critically-evaluated propagation rate coefficients in free radical polymerizations I. Styrene and methyl methacrylate (Technical Report). Pure Appl. Chem. **1996**, *68*, 1491-1494.

25. Wyatt, P.J. Light scattering and the absolute characterization of macromolecules. Anal. Chim. Acta **1993**, *272*, 1-40.

26. Kulicke, W. M.; Clasen, C. Viscosimetry of Polymers and Polyelectrolytes; Springer: Berlin, **2004**; p. 156.

27. Kolinsky, J.; Janca J. Introduction to Modern Liquid Chromatography. J. Polym. Sci: Polym. Chem. Ed. **1974**, *12*, 1181-1191.

28. Podzimek, S. The use of GPC coupled with a multiangle laser light scattering photometer for the characterization of polymers. On the determination of molecular weight, size and branching. J. Appl. Polym. Sci. **1994**, *54*, 91-103.

FIGURE 1: Plots of styrene fraction versus molar mass for copolymers prepared by emulsion polymerization of styrene-acrylate mixtures containing 23 % (1), 48 % (2) and 73 % styrene (3). The average styrene fractions calculated from the signal of UV detector: 21.9 %, 43.5 % and 70.2 % for P(S-MA) copolymers; 22.6 %, 45.4 % and 73.5 % for P(S-EA) copolymers; and 22.0 %, 46.3 % and 70.7 % for P(S-BA) copolymers.

FIGURE 2: 1 - Cumulative molar mass distribution curves of PS (○) and PMMA (●) prepared by emulsion polymerization under identical conditions, two sample preparations for each polymer; 2,3,4 - PS (○) and styrene-acrylate copolymers containing 50 % (half right circle) and 75 % (●) acrylate.

FIGURE 3: Cumulative molar mass distribution curves of styrene-acrylate copolymers (○) containing 25 % and 50 % styrene and MMA-acrylate copolymers (●) containing 10 %, 25 % and 50 % acrylate. Numbers indicate acrylate fraction in MMA-acrylate copolymers. The curve representing styrene-acrylate copolymers containing 25 % styrene is always slightly shifted to lower molar masses.

FIGURE 4: RMS radius versus molar mass plots of S-acrylate (○) and MMA-acrylate (●) copolymers. The slopes of styrene versus MMA copolymers: 0.55 versus 0.49 (10 % MA), 0.55 versus 0.48 (25 % MA), 0.52 versus 0.48 (25 % EA), 0.60 versus 0.51 (10 % BA).

FIGURE 5: Intrinsic viscosity determined by Ubbelohde viscometer versus M_w of styrene-acrylate copolymers (○) and MMA-acrylate copolymers (●) containing 25 %, 50 % and 75 % acrylate. Lines ☆ and ★ are the intrinsic viscosity versus molar mass plots for linear PS and PMMA, respectively. The numbers indicate the contents of acrylate monomers in MMA-acrylate

copolymers: 1, 2, 3 ≈ 25 %, 50 % and 75 % MA, respectively; 4, 5, 6 ≈ 25 %, 50 % and 75 % EA, respectively; 7, 8, 9 ≈ 25 %, 50 %, 70 % BA, respectively. The error bars are smaller than the point size.

FIGURE 6: Molar mass (top) and RMS radius (centre) versus retention time plots overlaid on RI fractograms for samples of PS cross-linked with 1% EGDMA (○, dash line) and AMA (●, solid line). The peaks starting at retention time of ≈ 37 min correspond to cross-linked particles. The bottom plot is the conformation plot of PS cross-linked with 1 % EGDMA. The numbers are the slopes of the conformation plot.
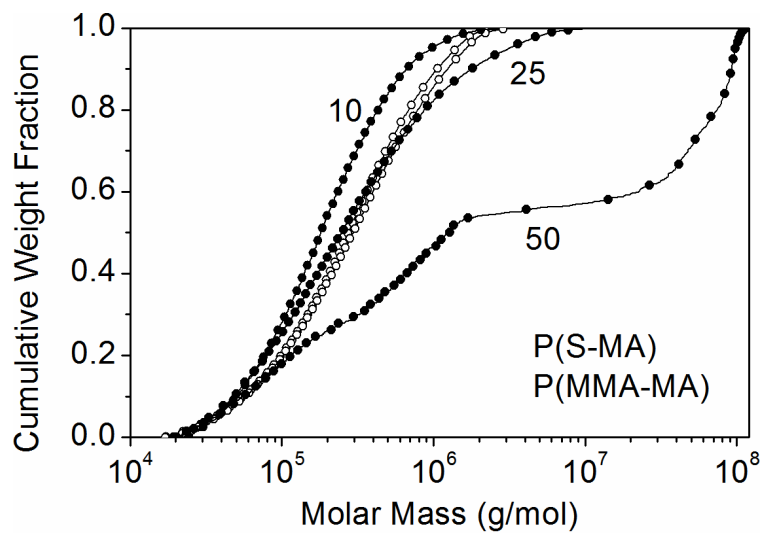
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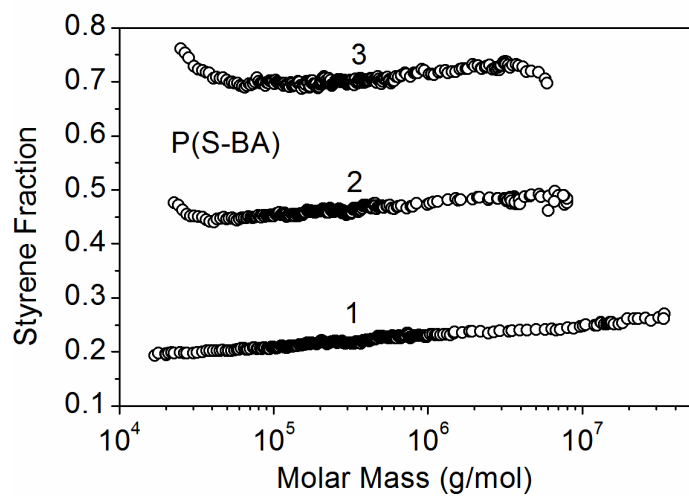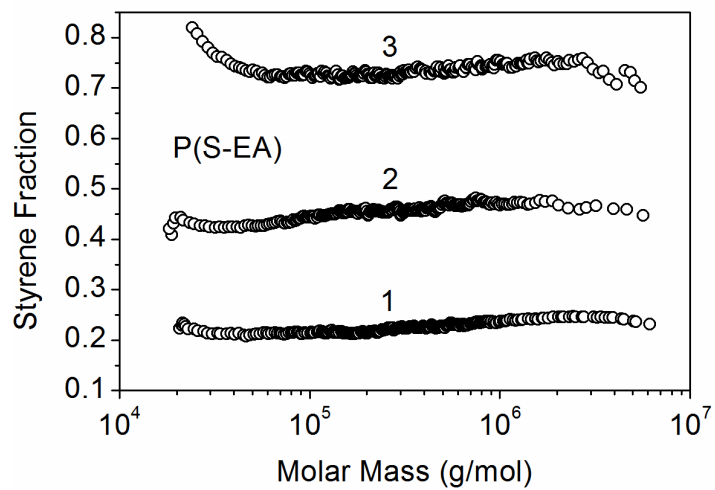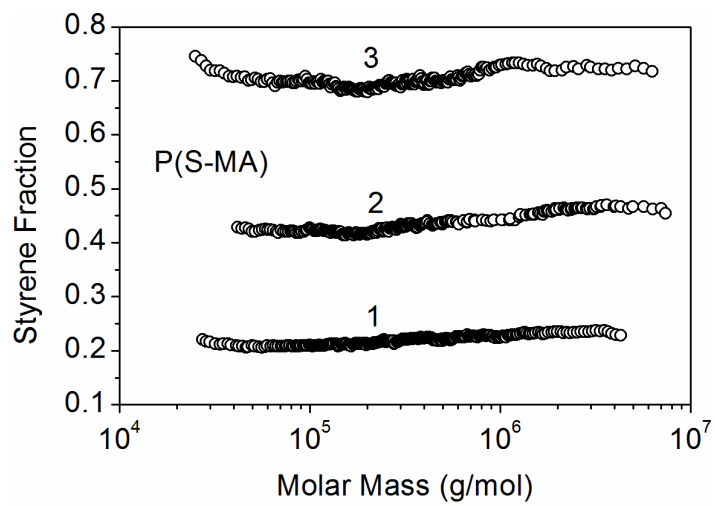
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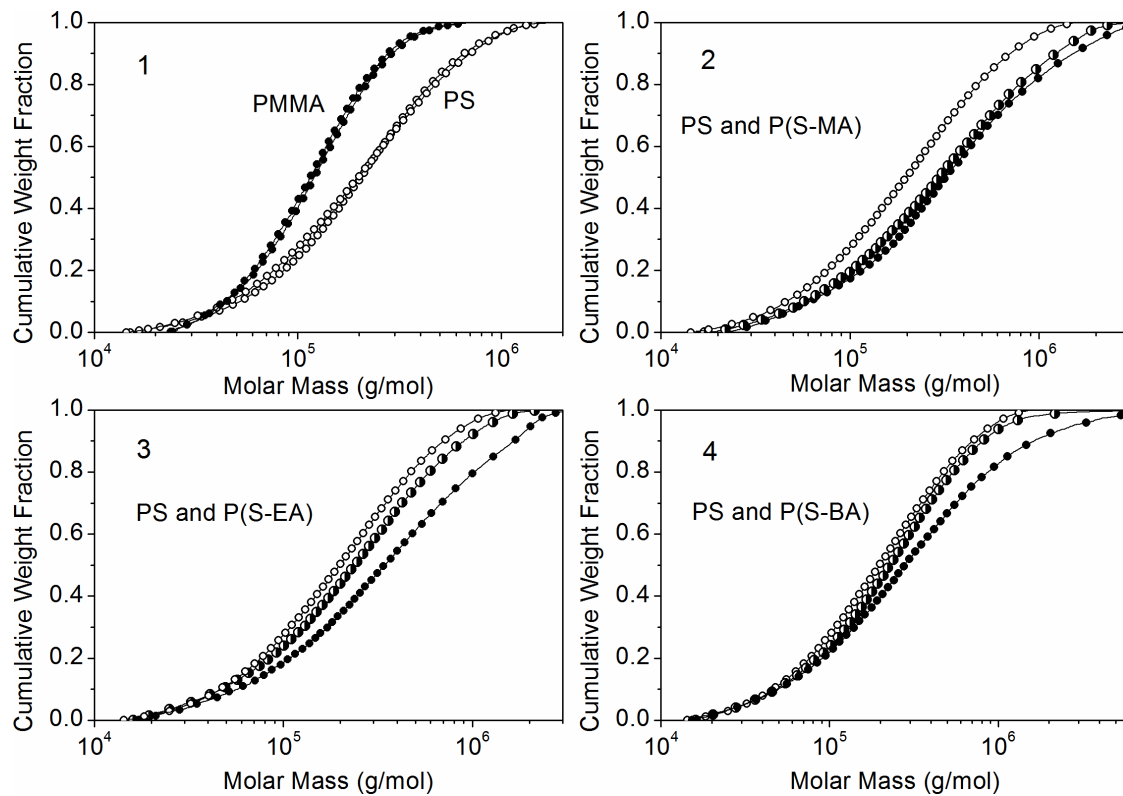
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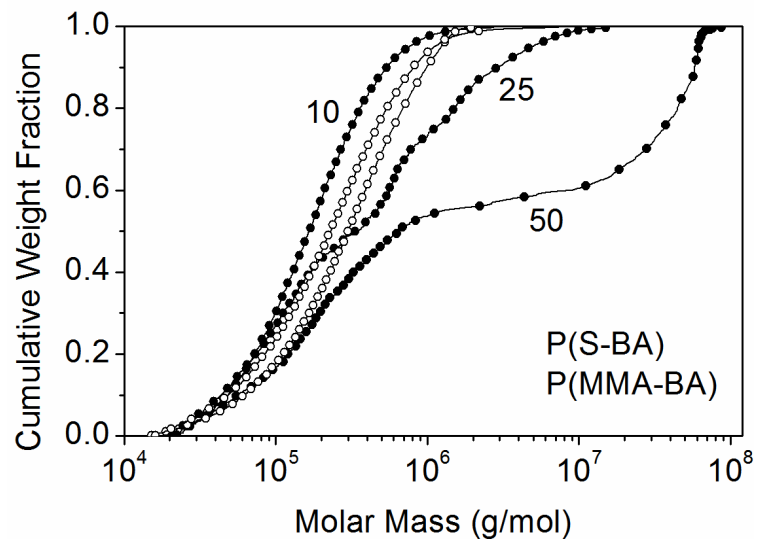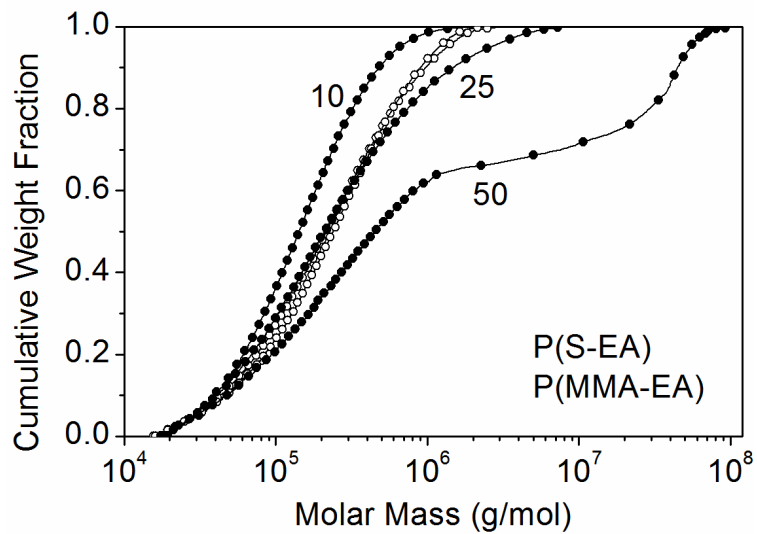
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Figure 6