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Molecular Characterization of Styrene / Butyl Acrylate / Acrylic Acid / Methacrylamide Copolymers Prepared by Emulsion Polymerization Using GPC-MALLS

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SUMMARY: Several samples of polystyrene and copolymer of styrene and butyl acrylate containing methacrylamide and/or acrylic acid synthesized by non-seeded semi-batch emulsion polymerization were characterized using gel permeation chromatography coupled with a multi angle laser light scattering photometer (GPC-MALLS). Molecular weight distribution varied with the polymer composition. The obtained GPC-MALLS data showed extraordinary GPC behaviour of the prepared samples. The data hint the presence of branched molecules and microgels in the measured samples.

Introduction

Many important properties of polymers and products on their basis depend on the molecular weight distribution (MWD) and average molecular weights. Moreover, the MWD contains the information about the polymerization kinetics and so provides insight into the manufacturing process. Several theoretical equations were developed which enable the MWD to be calculated for polymers prepared in emulsion polymerization1-3).

Reliable analytical tool is necessary for the verification of the theoretical assumptions and consequently improvement of polymerization process and synthesis of polymers with the desired MWD. Gel permeation chromatography coupled with a multi angle laser light scattering photometer (GPC-MALLS) is a practical and efficient way of the determination of the MWD4). In addition, the method provides the information about the root mean square (RMS) radius (radius of gyration) distribution and molecular architecture.

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The object of this article is to study the influence of the addition of water soluble monomer methacrylamide (MAAM) on the MWD of styrene (S), butyl acrylate (BA), acrylic acid (AA) containing copolymer prepared by emulsion polymerization and to demonstrate the benefit of combining GPC and light scattering techniques in characterizing molecular structure of polymers prepared in emulsion.

Experimental

The chromatographic system consisted of a 600 pump, a 717 autosampler, a 410 differential refractometer (all Waters) and a miniDAWN photometer (Wyatt Technology Corporation). Data were collected and handled by ASTRA software. A set of 3 Styragel HR 5E 300 x 7.8 mm columns (Waters) was used for the measurements. The samples were injected as solutions in tetrahydrofuran (THF) in the concentration about 0.25 w/v % and amount of 150 μl. THF was used as a mobile phase at a flow rate of 1 ml/min. Refractive index increment of polystyrene (PS) 0.185 ml/g was used for the calculation of results from the light scattering data. The value of dn/dc was validated by good agreement between the injected and calculated mass of PS standards. The value of dn/dc 0.064 ml/g for polybutylacrylate (PBA) was determined using a linear homopolymer and assuming 100 % sample mass recovery. The dn/dc value for S/BA copolymer of 0.115 ml/g was estimated from the copolymer composition and the dn/dc values of PS and PBA. The change of dn/dc due to the addition of AA and/or MAAM was neglected. GPC elution behaviour of emulsion polymers was compared with that of a broad linear polystyrene standard (PSL) to facilitate the data interpretation.

Samples were prepared by non-seeded semi-batch emulsion polymerization$^{5)}$ using Disponil AES 60 as emulsifier and $(NH_4)_2S_2O_8$ and $Na_2S_2O_5$ as initiators at a temperature of 80 °C. The dry weight was about 50 w %. Technical grade monomers were used for the polymerizations. The composition of prepared samples is given in Table 1. The mass ratio of S / BA in all copolymer samples was 42.5 / 57.5, MAAM and AA concentrations in Table 1 are expressed in percentage by weight of monomer mixture.

Results and Discussion

Number average (M_n) and weight average (M_w) molecular weights and weight average RMS radii (r_w) of the samples are scheduled in Table 1. The differential MWD curves of some samples are in Figure 1.

Table 1. Molecular weight and RMS radius averages of emulsion polymers.

Label in Figures	Polymer Composition	10^{-3} M_n	10^{-3} M_w	r_w [nm]
S	S	223	516	34
S-3min	S, after 3 min of reaction	285	465	32
S+2M	S, 2 % MAAM	369	805	41
-	S, 2 % AA	197	508	36
S/BA	S, BA	196	312	25
S/BA+2M	S, BA, 2 % MAAM	511	1,070	45
-	S, BA, 2 % AA	242	345	25
-	S, BA, 3 % MAAM, 2 % AA	529	1,185	44

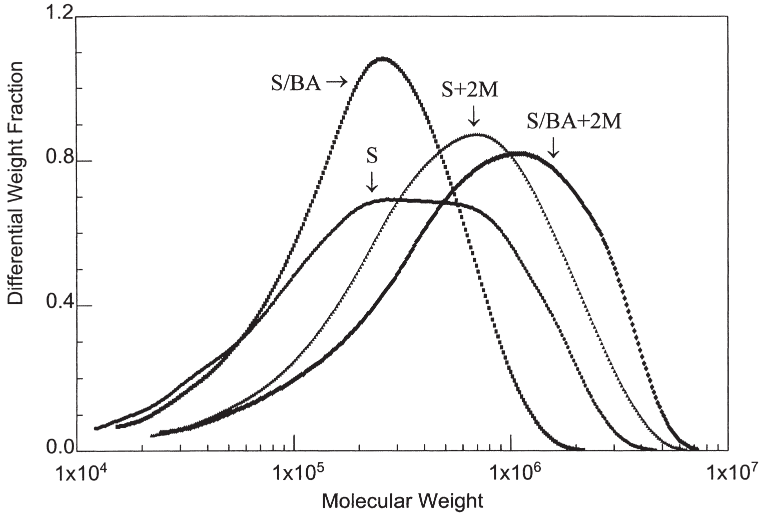

Fig. 1: Differential distribution curves of polymers prepared by emulsion polymerization.

Compared to PS the MWD of S/BA copolymer is shifted towards lower molecular weights while the addition of MAAM results in the opposite trend. Copolymer S/BA is more affected by the MAAM addition than PS. Addition of acrylic acid (AA) does not have significant effect on the MWD of either PS or S/BA copolymer. In case of MAAM content ≥ 5 w % the obtained samples were partially insoluble in THF.

Figure 2 contrasts molecular weight vs. elution volume plots of PSL and samples prepared by emulsion polymerization. PS prepared by emulsion polymerization shows an extraordinary elution behaviour. The entire curve is shifted towards higher molecular weights. Moreover, there is a deviation from the straight line in the region of higher elution volumes. This behaviour was found even for molecules arisen at the initial stage of reaction (S-3min, PS sample taken after 3 min of reaction). The extraordinary elution behaviour is emphasized by the addition of MAAM and the effect is more significant for the copolymer S/BA than for PS. The elution behaviour of emulsion PS and S/BA copolymer is nearly identical. The addition of 2 % of AA did not have any significant effect on the elution behaviour of PS or S/BA copolymer (data are not shown in Fig. 2).

The shift of the molecular weight vs. volume curve to higher molecular weights can be explained by a presence of branched molecules the structure of which is more compact. Chain branching of polymers produced in emulsion was theoretically predicted and described in papers[1-3]. The bowing of the curves at the higher elution volume range can be caused by the presence of small, but highly compact species (microgels). The presence of microgels can be inferred from the RMS radius vs. molecular weight plots that are for emulsion PS and copolymer S/BA both containing 2 % MAAM compared with the plot of PSL in Figure 3. The similar unusual U-shaped RMS radius vs. molecular weight plots were reported by Johann and Kilz for polystyrene microgels[6].

It is worth mentioning that conventional GPC lacking a MALLS detector would miss the presence of both branched molecules and microgels and so provide erroneous information about the molecular structure of emulsion polymers. Nevertheless, even GPC-MALLS cannot provide fully correct number average molecular weights and MWDs as there is a mixture of species with different molecular weights along the elution profile. However, M_w values are always correct.

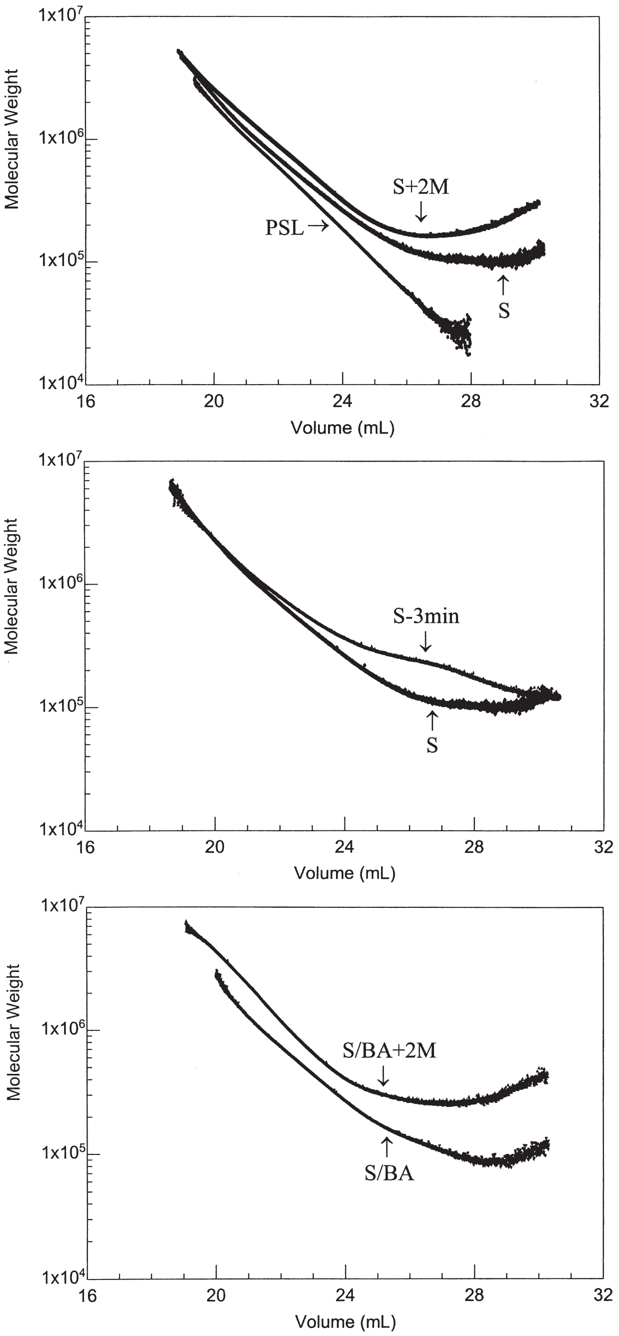

Fig. 2: Molecular weight vs. volume plots of PSL and emulsion polymers.

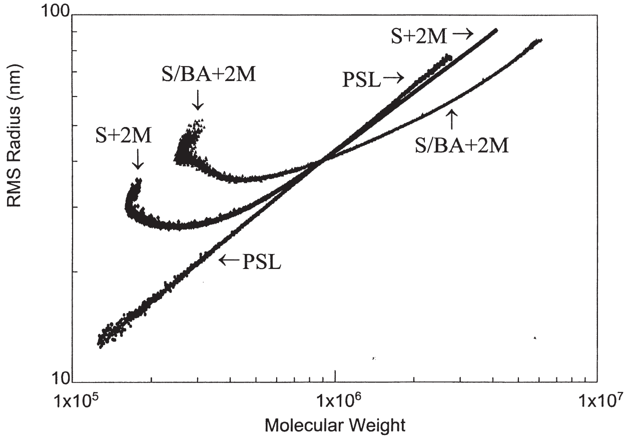

Fig. 3: RMS radius vs. molecular weight plots of PSL and emulsion polymers.

Conclusions

Branched molecules and microgels were found in polymers prepared by non-seeded semi-continuous emulsion polymerization. These species arise from the beginning of the polymerization. The formation of branched molecules and microgels is pronounced by the addition of MAAM while AA does not have similar effect.

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