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Gel Permeation Chromatography, Dynamic Light Scattering and Viscometry Studies of NaEPSS Polyelectrolytes Obtained from Polystyrene Wastes

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Summary: The determination of the physicochemical properties of polyelectrolytes in water solution has fundamental importance for the description of their possible application. Gel permeation chromatography (GPC), dynamic light scattering (DLS) and viscosimetry studies of the polyelectrolytes were performed for this goal.
The polyelectrolytes were obtained from polystyrene waste. Waste polystyrene foam (EPS) as reference material was converted into polymeric flocculants (NaEPSS) in chemical reactions.[1–3] Products with determined molecular weight and number of sulphonic group per monomer unit were divided into several fractions by fractional precipitation with 0.5 M aqueous NaOH as the solvent and 2-propanol as the precipitant. Viscosity measurements of water solutions of obtained polyelectrolytes NaEPSS were performed and the results were used for the calculation of the viscosity average molecular weights. The obtained results were then compared with the data from GPC (gel permeation chromatography) measurements and DLS (dynamic light scattering) results. It was stated that the changes of the molecular weights for the fractions of the NaEPSS values may be the result of side reactions occurring during the sulphonation process and of the irregular course of the fractionation process.

Keywords: dynamic light scattering DLS; flocculants; gel permeation chromatography GPC; molecular weight distribution; polyelectrolyte; polystyrene waste; viscosity

Introduction

Flocculation is an essential stage in many solid/liquid separation processes, especially in wastewater treatment or sludge conditioning, when the solid particles are too small to be effectively removed during the coagulation process. Polymeric flocculants are widely used to make flocculation more efficient.[4–6] Over the last several years research of the possible mechanisms of the flocculation processes was extended and it is commonly known that the processes, which occur in the system, are quite complicated.[6–10] The mechanism of flocculation was studied and the properties of the synthesized polymersin solution together with the viscosity average molecular weights M_η were determined. The obtained data made it possible to find the dependence between the structure of the molecules of the synthesized flocculants in solution and the course of the flocculation processes.[3] The study of the sulphonation process was conducted to find the best conditions for the sulphonation process with the use of concentrated sulphuric(VI) acid as sulphonation agent. The water soluble polyelectrolytes of the anionic type, with the average value of sulphonic group per one monomer unit equal to one were obtained. However, it was stated

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that probably the undesirable reactions (crosslinking, degradation) occur during the processes carried out longer than 2 hours, in the temperature range of 100–110 °C.[3] Viscosity molecular weights M_η were compared with the relative molecular weights obtained from the Gel Permeation Chromatography (GPC) measurements.[12–18] The experiments with the use of Dynamic Light Scattering (DLS) were also performed for the polymers. In spite of the methods applied the interpretation of obtained data still remains incomplete.[19–21]

Materials and Methodology

Sulphonated derivatives of expanded polystyrene waste, sodium poly(styrenesulphonate) (NaEPSS) were obtained by sulphonation of waste expanded polystyrene (EPS) $M_{\eta EPS} = 230\,000$ with concentrated sulphuric acid. Sulphuric acid, calcium carbonate, and sodium carbonate produced by Chemical Company POCh in Gliwice Poland were used in the synthesis. The dried sample of polystyrene was pulverized in a mill and fraction of the size 0.40–1.04 mm was separated. It was sulphonated by mixing with concentrated sulphuric acid (5 times EPS weight) and silver sulphate (1% of EPS weight) as a catalyst. The amount of Ag_2SO_4 was dissolved in H_2SO_4 (95–97%) in a glass flask equipped with mechanical agitator, vertical condenser and thermometer. Then polystyrene (EPS) was added at 80 °C and the reaction mixture was stirred in the temperature range 80–90 °C, during the period of the reaction from 15 minutes to 8 hours. The results of the research showed that there is no need to perform the synthesis for longer than 2 hours. Therefore the product of the synthesis, performed for 2 hours, was then fractionated in fractional precipitation. The content of sulphur and carbon in products of PS sulphonation was determined using Perkin Elmer CHNS/O elementary analyzer. The content of sulphur and carbon was then used for calculations of the number of sulphonic groups per one monomer unit (*n.sulph*).[3] The quotient of sulphur and carbon contents is linearly dependent on *n.sulph* for the theoretical structures of NaPSS.

The molecular weights (M_η) were calculated from the viscosity data (η) with the use of the parameters $\boldsymbol{K} = 1.86 \times 10^{-4}$ and $\boldsymbol{a} = 0.64$ (from Mark-Houwink equation), determined by light-scattering measurements for these conditions.[11]

The theoretical molecular weight (M_{cal}) was calculated from the formula [1]:

$$M_{cal} = \frac{[(n.sulph \times 102) + M_{PS}] \times M_{\eta EPS}}{M_{PS}} \tag{1}$$

where: *n.sulph* – number of sulphonic groups per one monomer unit, M_{PS} – molecular weight of the monomer unit of polystyrene equal to 104, $M_{\eta EPS}$ – molecular weight of polystyrene used as a reagent of the sulphonation process equal to 230 000, Number 102 - the difference between molecular weights of the monomer unit of NaEPSS.

The sodium salts of poly(styrenesulphonic acids) (NaEPSS) were fractionated in the process of fractional precipitation. They were dissolved in aqueous 0.5 M NaOH solution and fractionated into several fractions by stepwise precipitation with a suitable volume of 2-propanol as a precipitant.[3] The measurements of the viscosities of the synthesised polymer and their fractions dissolved in 0.5 M NaCl solutions were carried out using the Ubbelohde viscometer placed in a water bath (Julabo). The measurements, made at 25 °C, were controlled thermostatically with a precision of ±0,1 °C. The concentration of the solutions of the fractions of NaEPSS were of 0.25% to 1.00%.

To confirm the presence of the sulphonic groups in the structures of the obtained derivatives of polystyrene wastes the Magnetic Nulear Resonance (NMR) spectroscopy was used. The experiments were performed on the Bruker 400 MHz Ultra Shield Spectrometer.

Gel Permeation Chromatography experiments were performed on the Waters 600 apparatus with the use of the column TSK gel G5000 PWXL 7.8 mm ID*30.0 cm and guard column 7.5 mm ID*7.5 cm. The flow rate was 0.5 ml/min and the injection volume 4 μl. The detection was performed on UV224 nm. From the obtained retention time [min] values molecular weights were than calculated. For the preparation of the calibration curve the standards of the sodium poly(styrenesulphonate) were used for the values of molecular weights: 49 000, 77 000, 150 000, 350 000, 990 000, 260 0000 (Sigma-Aldrich).

Dynamic Light Scattering experiments were performed on the Zetasizer nano series apparatus. The sample of the polymer was dissolved in 0.5 M NaCl water solutions and filtrated on a microfilter of the diameter of 0.2 μm. The obtained values of the diameter of the molecule [nm] can be used for the calculation of the molecular weights. For the preparation of the calibration curve the standards of the sodium poly(styrenesulphonate) were used for the values of molecular weights: 49 000, 77 000, 150 000, 350 000, 990 000, 260 0000 (Sigma-Aldrich).

Results and Discussion

The sodium salts of poly(styrenesulphonic acids) (NaEPSS) were obtained in the process of modification of EPS. The values of *n.sulph*, M_η and M_{cal} were calculated (Table 1).

The obtained NMR spectra confirmed the structure of the obtained products. It is highly probable that the sulphonic groups were present in the para position of the aromatic rings of the polyelectrolyte sodium salt of the poly(styrenesulphonic acid) (Fig. 1).

The NaEPSS sample obtained during 2 hours with the highest M_η and *n.sulph* was chosen for fractionation.[3] The molecular weight values for the obtained product were equal to $M_\eta = 495\,000$, $M_{cal} = 447\,000$ and $n.sulph = 0.96$. For the fractions obtained during the fractionation of the NaEPSS the values of *n.sulph* were of the range from 0.78 to 1.51. The values of M_{cal} equal 406 000–571 600 were significantly higher than the values of M_η equal 289 000–520 000 (Table 2).

The differences between the values of M_η and M_{cal} can be the result of different molecular structures, caused by the possible intramolecular and/or intermolecular sulphone-type cross-linked structure or oxidative degradation of polymer during the sulphonation process of polystyrene.[3] Probably the fractionation process proceeds not only with the change of M_η but also in agreement the structure of sodium poly(styrenesulfonate). The other factor possibly affectingthe process is the intramolecular and/or intermolecular cross-linking of macromolecules. The intramolecular cross-linking effect was probably the main reason for the worse precipitation of the fractions with lower M_η (M_η equal to 289 000 and 310 000) than in other synthesized polyelectrolytes. It should be pointed out that the values of M_η were determined with the use of parameters ($\boldsymbol{K} = 1.86 \times 10^{-4}$ and $\boldsymbol{a} = 0.64$ from Mark-Houwink equation) for sodium salt of poly(styrenesulphonic)acid although the M_{cal} values (calculated from the values of concentration of

Table 1.
The properties of the NaEPSS obtained in the sulphonation process at temperature 80–90 °C with the use of sulphuric acid (VI) as the sulphonation process agent.

Reaction time [h]	*n.sulph*	M_η/M_{cal}	Retention time [min],obtained from GPC measurements	M_{GPC}
0.50	0.89	430 000/431 000	15.86	380 000
0.75	0.95	450 000/444 000	15.99	355 000
2.00	0.96	495 000/447 000	15.95	363 000
5.00	0.82	420 000/415 000	16.24	313 000
8.00	0.85	370 000/422 000	17.06	210 000

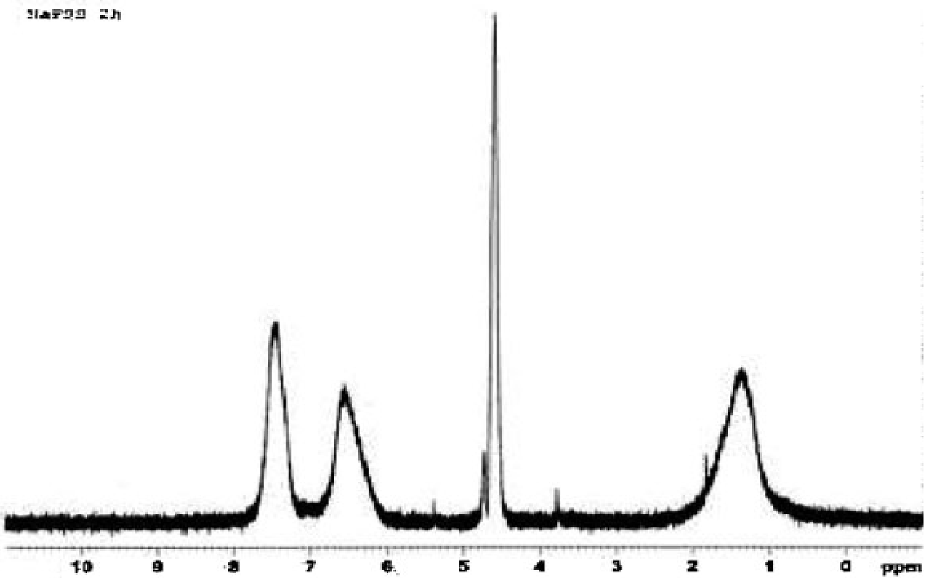

Figure 1.
^{1}H NMR spectrum of NaEPSS obtained during a 2 h synthesis at temperature 80–90 °C.

sulphur in the obtained fractions) were calculated at lower values than M_η. It may be supposed that the intramolecular cross-linking prevents the untwisting of the macromolecule chains in the solutions resulting their delayed precipitation or caused them to remain in the solution. The twisted macromolecules, with numerous intramolecular cross-linking, remained in the solution even though the volume of the precipitant became higher in the whole solution. The presence of the intramolecular cross-linking should not be precluded for the molecules with higher values of M_η. Then the use of $K = 1.86 \times 10^{-4}$ and $a = 0.64$ from Mark-Houwink equation for calculations of the fraction with lower M_η values are probably would be unfounded.

It was stated that the M_{GPC} values obtained on the basis of the GPC measurements for the NaEPSS were lower than the molecular weights obtained from the viscosity measurements, although the changes were similar (Table 1, Fig. 2).

The differences between the obtained molecular weights were probably the result of the differences between of the method used for their determination. It is also possible that the changes of the molecular weight values were the due to the side

Table 2.
The properties of the NaEPSS obtained in the sulphonation process at temperature 80–90 °C with the use of sulphuric acid (VI).

No	*n.sulph*	M_η/M_{cal}	Retention time [min], obtained from GPC measurements
F1	1.51	520 000/571 000	16.46/316 000
F2	1.01	490 000/458 000	16.45/317 000
F3	1.12	478 000/483 000	17.20/204 000
F4	1.20	450 000/501 000	15.51/468 000
F5	1.09	420 000/476 000	15.27/536 000
F6	0.78	310 000/406 000	16.00/371 000
F7	1.33	289 000/530 000	15.25/525 000
F8	1.48	290 000/564 000	16.90/235 000

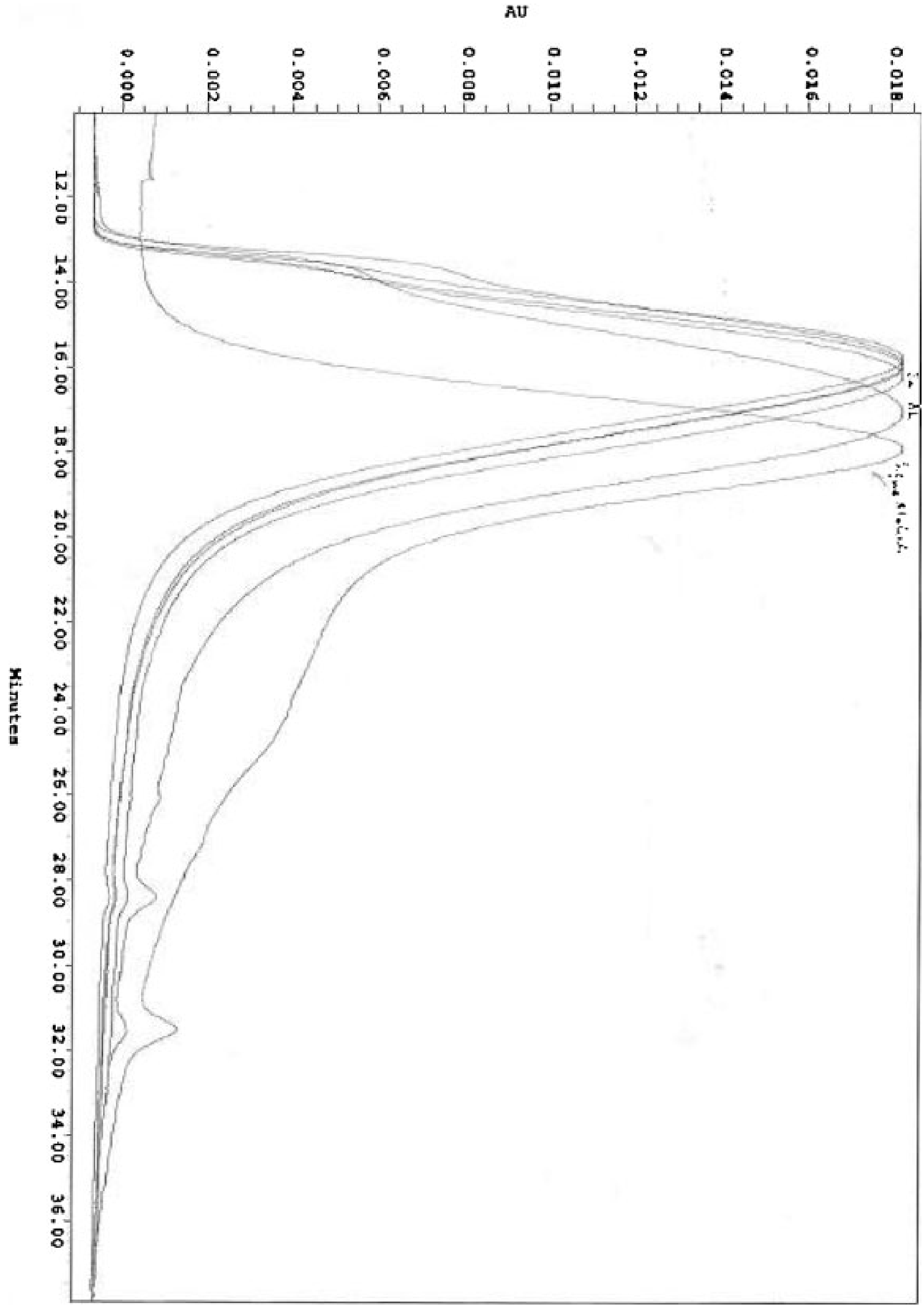

Figure 2.
Chromatograms GPC for the NaEPSS samples, obtained during the synthesis time of: 30 min, 2 hours, 5 hours, 8 hours and for the NaPSS (Aldrich).

reactions occurring during the sulphonation process. The molecules having lower molecular weights are soluble in the sulphuric acid and probably undergo the sulphonation process first. Also the molecules having higher molecular weight may be soluble in the sulphuric acid (but next, according to their higher values). The molecules having higher molecular weights undergo the sulphonation process as well as smaller molecules, although the undesirable cross-linking (intermolecular and intramolecular) between molecules is more probable.

The comparison of the peaks of the chromatograms obtained for NaEPSS show that their values are almost equal to the values of the standards which was confirmed by the results of the fractionation

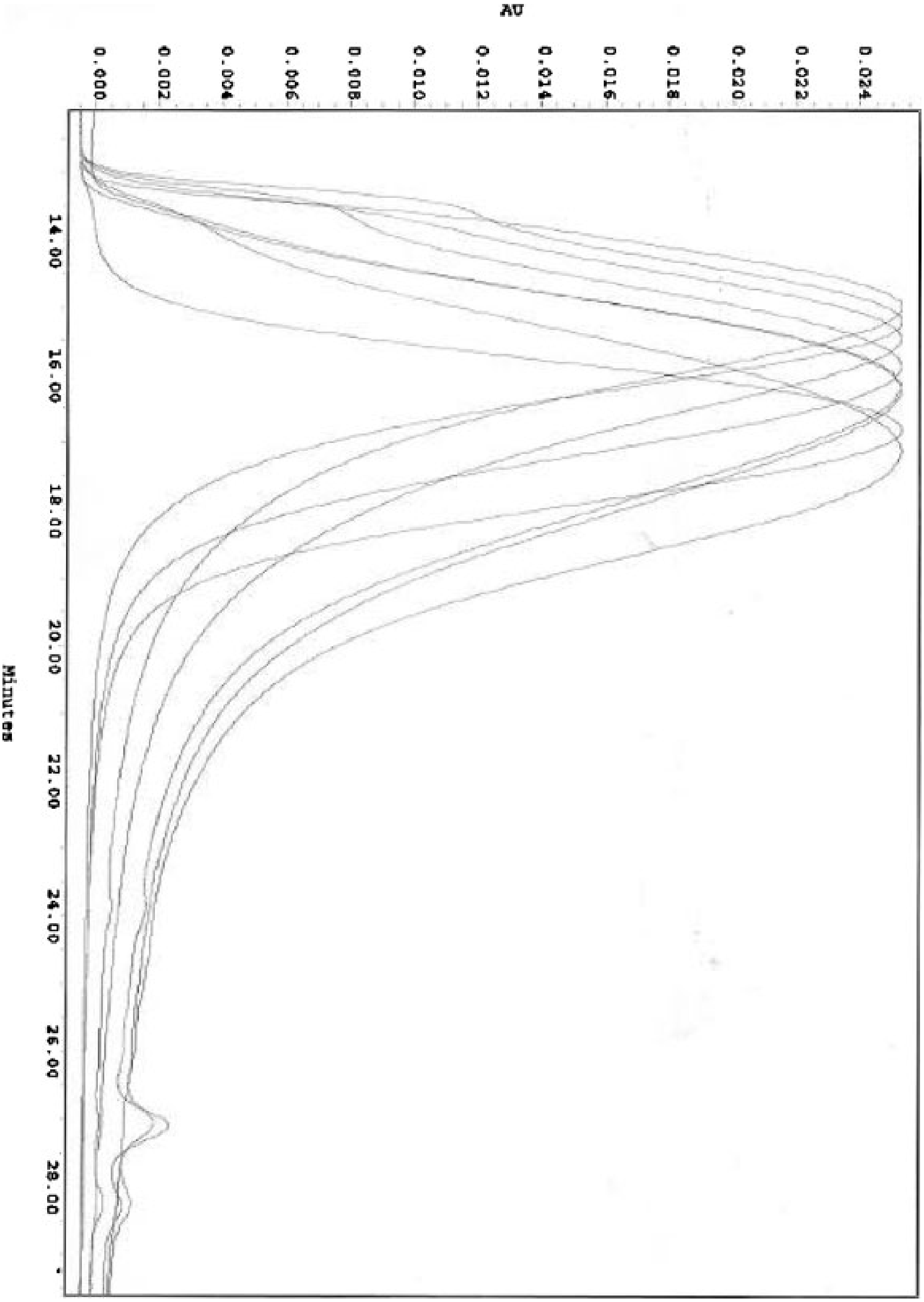

Figure 3.
Chromatograms GPC for the NaEPSS fractions.

process. The obtained results are in agreement with the conclusion concerning the narrow molecular weight distribution of the NaEPSS (Fig. 2, 3).

The results of the determination of molecular weights for the fractions of NaEPSS show that the values of M_{GPC} do not decrease with the decrease of the values of M_η. As expected the changes of the M_{GPC} values for fractions were similar to the results obtained for the samples (Fig. 3).

The unexpected results obtained may be the effect of the abnormal course of the fractionation process. It is possible that the obtained fractions contain molecules of different sizes and small molecules of the other substances.

It also can be stated that some of the samples have a bimodal character. The bimodal character of NaEPSS obtained during 0.5 hour suggest that all molecules (with different sizes) are sulphonated at the same time. This is in agreement with the conclusion drawn above. It is also observed that the longer the time of the synthesis the more probable the occurrence of the cross-linking processes is.

The results for the products obtained during the synthesis performed for not longer than 2 hours show that the products have almost equal values of molecular weights. To find the reasons for the observed phenomenon the continuation of the research is required.

Conclusions

The changes of the molecular weights for the fractions of the NaEPSS values may be the result of side reactions occurring during the sulphonation process and of the irregular course of the fractionation process. It was also possible that the obtained fractions contained molecules of different sizes and small molecules of other substances. The differences between the features of the molecules of the obtained polyelectrolytes and the possibility of the presence of sulphone type cross-linking in some of them influenced the fractionation process.

The differences between the molecular weights of the synthesized polymers were probably due to the type of the method used for their determination. However the GPC technique can be used to the determine the molecular weights of the obtained products.

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