ONLINE MULTI-STAGE MEMBRANE FILTRATION OF SYNTHETIC POLYDISPERSED WATER-SOLUBLE POLYMERS WITH UV VISIBLE ABSORPTION AS A MODE FOR THEIR DETECTION

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ABSTRACT

This paper reports the application of online membrane filtration with UV visible absorption as a mode of polydispersed substances detection for poly(acryloyl morpholine-co-2-acrylamido-2-methyl-1-propane sulfonic acid), poly[2-acrylamido-2-methyl-1-propane sulfonic acid-co-(3-acryloylamidopropyl) trimethylammonium nitrate], and poly(vinyl alcohol-co-crotonic acid) 10 % of crotonic acid which can be used in medicine and technology. The mass balance in all the cases was not below $100 \pm 7\%$. The calibration curve are linear at λ_{opt} 245, 230, and 220 nm in the interval 0.1–4.0 mg/mL, 0.2–3.0 mg/mL and 0.2–6.0 mg/mL, respectively.

It was also used the combination of microfiltration, MF, and gel permeation chromatography, GPC to provide more complete information about the molecular weight distribution of the obtained fractions.

Keywords: Water-soluble polymers, ultrafiltration membranes, analysis.

INTRODUCTION

In the last few years, control of the polymer production process has become especially important due to increased demands for specific qualities by industry as well as for their use in the environment and in medical practice.

Addition polymerization, particularly radical initiation is a synthesis method to obtain polycationic polymers, where oligomers and polymers are at different degrees of polymerization, which can vary in a wide range depending on the synthesis conditions. Additionally, polymers or copolymers often contain other components that cause problems, especially since the investigated polymers were previously designed and tested as metal ion remover and could be used in water purification for either drinking water or residual water. Moreover, they have been tested as biocide against Gram negative and Gram positive bacteria [1-3]. Generally, impurities of the initial monomers, additives, and residual monomers can migrate to the tissue and, depending on the chemical reagent, can cause various tissue responses. The additives may themselves contain various levels of impurities resulting in a potentially large number of compounds available for diffusion into tissue or into a drug solvent system. Additionally, the leached compound can introduce an ingredient that in itself can elicit a pharmacological response. Even, when the leached impurity may not have any appreciable biological activity in other instances, but it may interact with one of the components in the product [4]. The normally used anionic and non-ionic polymers are low toxic, while cationic types are more toxic, especially for aquatic organisms [5, 6]. The health significance of possible contaminants has been reviewed in detail [7, 8]. Generally, the monomers are more toxic than other polymers [6]. Limits on the level of residual monomer are strictly controlled, especially with acrylamide products, where as a general rule the maximum permitted content of free acrylamide is 0.025 % and the residue in drinking water is limited to 0.5 mg/L [4].

Due to a broad spectrum of polar groups and non-polar fragments, polymers interact between themselves. To better understand the mechanism of these reactions and thus be able to predict the polymer behavior, more detailed information is needed about molecules, structural constituents, molecular size, and degree of polymerization. The better characterization of polydispersed substances, which are complex mixtures of polymers and other products that are sometimes obtained after synthesis, can hardly be achieved without the application of fractionation techniques based on different properties of macromolecules, and especially their size [9, 10].

Various separation procedures have been employed for polymers: gel permeation chromatography, membrane filtration to fractionate polymers by their size (molecular weight), electrophoresis, and others. Specially designed online membrane filtration devices were recently tested on polydispersed substances, namely for aquatic humic substances [11-14].

In this paper, we describe the ability of the on-line membrane filtration technique (MF) separation with UV-visible absorption as a mode to detect polydispersed polymers with varying substitutes at main chain.

EXPERIMENTAL

Reagents

The following chemicals were used in the experiments: NaOH, HCl, NaCl, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (Reakhim, Russia); Tris (Reanal, Hungary); sodium dodecyl sulphate (SDS) (Serva, Germany); Blue dextran 2000 (Pharmacia, Sweden). Acryloyl morpholine, 97%, Aldrich; 2-acrylamido-2-methyl-1-propane sulfonic acid, 99%, Aldrich; (3-acryloylamidopropyl) trimethylammonium chloride, 75%, Aldrich. Aqueous solutions of all reagents were prepared using Milli-Q (Millipore) distilled water. Poly(vinyl alcohol-co-crotonic acid) 10 % of crotonic acid was purchased from Sigma-Aldrich. The stock 5 mg mL⁻¹ polymer solution was prepared by dissolving an exact weighted sample of each polymer in deionized water.

Polydisperse substances. Poly(acryloyl morpholine-co-2-acrylamido-2-methyl-1-propane sulfonic acid) and poly[2-acrylamido-2-methyl-1-propane sulfonic acid-co-(3-acryloylamidopropyl) trimethylammonium nitrate] were synthesized by radical polymerization as previously described [15,16]. Molar masses for both polymers were determined means light scattering, using a Wyatt Dawn DSP-F photometer with a argon laser, and an interferometric refractometer Wyatt Optilab 903. 0.5 M HCl and NaNO₃ solution was used as electrolyte.

Copolymer of a) acryloylmorpholine and 2-acrylamido-2-methyl-1-propane sulfonic acid, Mw = $4.10 \pm 0.60 \cdot 10^6$ g/mol (Sample 1)

Copolymer of b) 2-acrylamido-2-methyl-1-propane sulfonic acid and (3-acryloylamidopropyl) trimethylammonium nitrate) $M_w = 9.65 \pm 1.00 \cdot 10^5$ g/mol (Sample 2).

Copolymer of c) of vinyl alcohol and crotonic acid (Sample 3).

Figure 1. Formula of the studied polymers.

Apparatus

The membrane filtration studies were made in a completely closed online fractionation device that, after the replacement with the first portion of the sample, provides constant gas balance. The device consisted of five poly(methacrylate) discs with non-spiral channels and bearing 47 mm Millipore polysulphone membranes with pore sizes of 0.22, 0.1, 0.05, 0.03 and 0.005 μm in the upper part (Eschborn, Germany). The total inner volume of the fractionation device with the pump and connecting tubings was about 15 mL (Figure 2).

Figure 2. Flow diagram and photo of multistage fractionation device. M-membrane; F-fraction, R-retentate.

The whole fractionation system also included reservoirs for test samples and washing liquids and a multistage peristaltic pump (Gilson Minipuls 3, France), which was equipped with TYGON® tubes of 2.06 mm I.D. The discs had spiral channels in the upper part, and a drainage system connected with the under-membrane space of the next disc in the lower part. A test sample

was fed from a reservoir to the first (lowest) filtration step, where it partially moved in parallel to the membrane surface (tangential flow) before returning to the reservoir and partially through the membrane (filtration flow). The filtrate penetrated into the chamber of the next (upper) disc also partially filtered and partially recirculated; the process was repeated at each next step with a membrane of smaller pore sizes. Special regulating valves were used to control the relatively fast recirculation streams, thus minimising concentration polarisation of solutes at the membrane surfaces [11– 12].

Specord UV-VIS was used for UV visible absorption as a mode of detection for polydispersed polymer concentration.

PROCEDURES

The fractionation system was rinsed with deionized water before each filtration run. The remaining water was displaced from the device by air using the pump applied in all other experiments. After that, the solution was pumped in membrane system. Size classification of polydispersed substances depended on chosen operation parameters. It was found that optimal filtration and circulation flow rates were for speed rotation of pump head equal 60 and 90 rpm. Then, filtration and circulation flow rates are determined (Figure 3). So the sample solution was pumped through the device at a filtration rate of 1.4 – 1.6 mL/min and a circulation rate of 0.2 – 0.6 mL/min for 45 min. The ultimate filtrate was again pumped through for another 40 min to provide better equilibrium between the fractions. Portions of liquid fractions from every filtration stage (2 mL each) were taken from reservoirs after obtaining 30 mL of the filtrate.

Figure 3. Conditions for fractionation analysis, (u) Rotation speed of pump head 60 rpm; (n) Rotation speed of pump head 90 rpm.

Molecular weight distributions of polydispersed substances fractionated by GPC were obtained in the K 1.6 cm $\times$ 70 cm column ("Pharmacia", Sweden) filled with Sephadex G-75 gel (eluent 0.025 M Tris-HCl buffer (pH 8.2) + 0.05 M NaCl + 0.1 % SDS + 0.02 % NaN_3 , elution rate 8 mL/h). Each column was calibrated by blue dextran 2000 and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ solutions in the eluent buffer to determine a column void volume and a total gel bed volume, respectively.

To obtain the calibration curves for the UV visible spectrophotometric determination of the polymers series, solutions for each stock solution of initial polymer were prepared in 5 mL volumetric test tubes. Between 0.1 and 1.0 mL of stock solutions of 2 mg mL^{-1} at pH 5-6 were added and diluted to 5 mL with deionized water, mixed thoroughly, and the optical density of obtained solution was measured at optimum for each polymer I, relative to deionized water. It was carried out in a 1 cm cuvette.

RESULTS AND DISCUSSION

Results for the three different fractionated samples and their metrological evaluation are shown in Table 1. The mass balance was calculated as a ratio of the polymer's total concentration in all fractions to its initial concentration in the corresponding sample. The mass balance in all the cases presented was not below $100 \pm 7\%$.

The calibration curves are linear at λ_{opt} 245, 230, and 220 nm in the interval 0.1 – 4.0 mg/mL, 0.2 – 3.0 mg/mL and 0.2 – 6.0 mg/mL for samples 1, 2, and 3 respectively. The equations of calibration graphs and regression coefficients (R) for sample number 1, 2, and 3 are: $A_1 = 0.206c + 0.046(0.9)$,

$A_2 = 0.511c + 0.066(0.9)$, and $A_3 = 0.186c + 0.013(0.9)$ respectively.

Table 1. Results of polyvinyl determination in fractions F_1 (<0.003 μm), F_2 (0.003-0.03 μm), F_3 (0.03-0.05 μm), F_4 (0.05-0.1 μm), F_5 (0.1-0.22 μm), F_6 (>0.22 μm), $n = 3$, $P = 0.95$).

Sample number		1	2	3
Added, mg		55.0	90.0	25.0
Found in fractions	F_1	0.0	35.0 ± 5.9	0.0
	S_r	-	0.10	-
	F_2	2.00 ± 0.26	12.60 ± 3.64	1.40 ± 0.52
	S_r	0.06	0.13	0.16
	F_3	2.98 ± 0.30	2.10 ± 0.39	5.63 ± 0.90
	S_r	0.045	0.080	0.074
	F_4	3.55 ± 0.65	6.40 ± 2.34	6.13 ± 0.65
	S_r	0.083	0.160	0.057
	F_5	5.10 ± 0.90	24.43 ± 3.38	1.45 ± 0.35
	S_r	0.14	0.06	0.11
	F_6	40.6 ± 6.50	2.27 ± 1.17	8.43 ± 1.69
	S_r	0.07	0.23	0.10
Found in sum, mg		54.2 ± 4.5	82.8 ± 8.4	23.2 ± 2.3
S_r		0.04	0.05	0.04

A supplementary size classification by a reference method (e.g. GPC) is recommended [8-10]. We use the combination of MF and GPC to provide more complete information about the molecular weight distribution of the obtained fractions. Due to the large dilution of samples during MF, only quality characteristics for sample 2 were obtained. Their concentration appears to be outside of the GPC method's limit of sensitivity. The initial sample concentrations could not be increased due to the large increase in viscosity. Qualitative GPC analysis of sample No 2 fractions showed a relative homogeneity increase from the initial sample to the filtrate.

Table 2. Polyvinyl content (%) in the fractions after membrane filtration.

Fraction (No)	Pore size Mkm	Polymer content in fractions (%)		
		Sample No 1	Sample No 2	Sample No 3
F_6	<0.003	0.0	42.3	0.0
F_5	0.003 – 0.03	3.9	15.2	6.7
F_4	0.03 – 0.05	5.9	2.5	26.7
F_3	0.05 – 0.1	7.0	7.7	24.5
F_2	0.1 – 0.22	10.0	29.5	6.9
F_1	>0.22	79.9	2.7	35.4

According to the data of MF (Table 2), the polymer in sample 2 is the only one of three investigated that was determined in the fraction $\text{MM} < 30$ kDa. Analysis of this fraction by the GPC method showed that there are not only molecules with $\text{MM} < 30$ kDa, but also molecules with $\text{MM} > 75$ kDa. This phenomenon might be explained by considering the possibility of molecule conformation changes during the MF process. Thus, molecules ($\text{MM} > 75$ kDa) with long-chain substitutes have the architecture to penetrate through the membrane corresponding to $\text{MM} < 30$ kDa.

As can be seen in the MF data (Table 2), approximately 80 % of the sample 1 polymer was determined in the fraction corresponding to an MM about 2200 kDa, which could be explained as a result of synthesis. However, it cannot be excluded the explanation that the molecule conformation changed when it contains some morpholine substitutes.

MF analysis of polymer sample 3 showed that its molecules are equally distributed between first, third, and fourth fractions (Table 2). Thus, one could assume that polymer sample 3 consists of a mixture of polymers with MM from 300 to 2200 kDa and greater.

CONCLUSIONS

On-line membrane filtration method and following it spectrophotometric analysis is very useful for the purposes of water-soluble polymer separation and fractionation and their spectrophotometric analysis because of its reliable and reproducibility.

It is very important establish that this procedure was used by the first time for analysis of real water-soluble polymer synthetic samples.

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