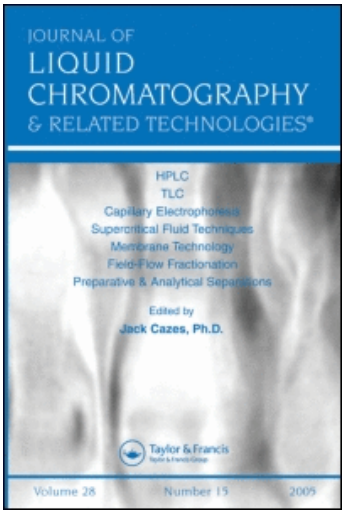

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Characterization of Polystyrene and Poly(Styrene-Glycidylmethacrylate) Copolymer Latexes by Sedimentation Field-Flow Fractionation

Josef Janča[a]; Dana Pibylová[a]; Karel Bouchal[b]; Vêra Tyráčková[b]; Eva ůrková[b]
[a] Institute of Analytical Chemistry Czechoslovak Academy of Sciences, Brno, Czechoslovakia [b] Institute of Macromolecular Chemistry Czechoslovak Academy of Sciences, Prague 6, Czechoslovakia

To cite this Article Janča, Josef , Pibylová, Dana , Bouchal, Karel , Tyráčková, Vêra and ůrková, Eva(1986) 'Characterization of Polystyrene and Poly(Styrene-Glycidylmethacrylate) Copolymer Latexes by Sedimentation Field-Flow Fractionation', Journal of Liquid Chromatography & Related Technologies, 9: 10, 2059 — 2072
To link to this Article: DOI: 10.1080/01483918608074135
URL: http://dx.doi.org/10.1080/01483918608074135

JOURNAL OF LIQUID CHROMATOGRAPHY, 9(10), 2059-2072 (1986)

CHARACTERIZATION OF POLYSTYRENE AND POLY(STYRENE-GLYCIDYLMETHACRYLATE) COPOLYMER LATEXES BY SEDIMENTATION FIELD-FLOW FRACTIONATION

Josef Janča[1], Dana Přibylová[1], Karel Bouchal[2], Věra Tyráčková[2], and Eva Žůrková[2]

[1]*Institute of Analytical Chemistry*
Czechoslovak Academy of Sciences
611 42 Brno, Czechoslovakia
[2]*Institute of Macromolecular Chemistry*
Czechoslovak Academy of Sciences
162 06 Prague 6, Czechoslovakia

ABSTRACT

Samples of polystyrene and styrene glycidylmethacrylate copolymer latexes were characterized by Sedimentation Field-Flow Fractionation (SFFF), electron microscopy and by the use of quasi-elastic light-scattering. SFFF makes possible the most complete characterization of particle size distribution of the analyzed samples. Its high selectivity, speed and casual possibility to use the obtained fractions for other analysis or for physico-chemical study belong to its advantages. A two-peak distribution curve was found for one of the studied samples by SFFF. The mechanism of polymerization of this sample could be deduced on the basis of this curve. No other of the compared methods was able to reveal the course of this distribution curve.

 0148-3919/86/0910-2059$3.50/0

INTRODUCTION

Sedimentation Field-Flow Fractionation (SFFF) has become a method of choice for the characterization of particles of different origin within a wide range of their sizes. Its advantages being high efficiency and selectivity of separations, speed of analysis, precision and accuracy of the obtained results and its ability to provide the absolute values of the analyzed particle sizes without previous calibration. It is also important that the obtained fractions of the analyzed samples can be used for further characterization and measurements and/or even for further physico-chemical study.

The retention ratio R defined as

$$R = V_o/V_r \qquad (1)$$

i.e., the ratio of the unretained solute retention volume V_o and of the retained solute retention volume V_r, belongs among the basic parameters describing SFFF separation process. Provided, the retained solute is polydisperse, it holds for the retention ratio of the i-th fraction

$$R_i = V_o/V_i \qquad (2)$$

The retention ratio R is dependent on the dimensionless parameter λ characterizing the mean distance of centre of gravity of the retained solute concentration zone from the accumulation wall of the channel for SFFF by the equation

$$R = 6\lambda(\coth(1/2\lambda) - 2\lambda) \qquad (3)$$

The dimensionless parameter λ is determined by geometrical dimensions of the fractionation channel, its thickness, w, and its radius of rotation, r, as well as by the conditions under which the experiment is effectuated, i.e., rotation angular velocity, ω, the difference of densities of the carrier fluid and of the separated solute, $\Delta\rho$, the absolute temperature, T, and by the solute properties, i.e., explicitly by the particle diameter, d_p.

$$\lambda = 6kT/(\pi d_p^3 \omega^2 rw\Delta\rho) \qquad (4)$$

k in Equation (4) is the Boltzmann constant. Thus the curve of the particle size distribution and, eventually, also the mean value of particle diameter $\bar{d}_p$ can be calculated from the experimental fractogram employing Equations (1) - (4).

This paper deals with characterization of latex samples of polystyrene and polyglycidylmethacrylates and their copolymers that are important for medical diagnostics. These latexes are usually characterized by the method of electron microscopy or are measured by means of simple quasi-elastic light scattering (QELS) detector. Both these methods give, first of all, the mean particle size values. The evaluation of the particle size distribution is rather laborious. It concerns the case when the electron microscopy is used, or it gives only orientation results, i.e., if QELS detector is used. If the electron microscopy is employed, only a small number of particles is measured and this number need not to be representative. We utilized the mentioned methods for the characterization of our latex samples in order to compare critically both their advantages and drawbacks.

EXPERIMENTAL

A device manufactured in our laboratory was used for the separation and analysis by means of SFFF (1). Solution of 0.1 % Tween 60 surfactant (Fluka AG, Buchs SG, Switzerland) in distilled water was used as the carrier fluid. Prior to use, the solution was degassed by heating up to 90 ^{o}C and by ultrasound action. Latex samples were prepared by mixing with this solution, the resulting concentration was about 0.1 %. We injected 30 μl of emulsion of the latexes that were, before injection, stirred by ultrasound in order to destroy eventual aggregates. All measurements were performed under the temperature of 21 ^{o}C. The experimental conditions were chosen so that the undesirable zone broadening, caused by both nonequilibrium and relaxation processes would be suppressed (2). That is why the flow rate during injection was 50 μl/min, than it was stopped for the time of relaxation and restarted at 200 μl/min. Constant rotation was maintained in the whole course of the fractionation. The rotation speed, in revolutions per minute (rpm), and relaxation times t_r (min) are specified on fractograms of individual latex samples.

Electron Microscopy

Diluted emulsion of polymer latexes was layered on a glass plate face under the nitrogen stream and dried in the open air. The samples were coated with a layer of gold (about 10 nm thick) in a Sputtering Device (Balzers). The latex samples were photographed by means of a JSM - 35 scanning electron microscope

(Jeol, Japan) under 25 kV and 10,000 x eventually 20,000 x magnification. The average particle size was evaluated from the microphotographs by measuring of 20 to 30 individual latex particles.

Quasi-Elastic Light Scattering

A commercial device Nanosizer (Coulter Electronics, Ltd.) was utilized for measurements.

Studied Latex Samples

Various techniques of emulsion polymerization were applied for the preparation of latexes. Latex syntheses were performed in a glass reactor equipped with a jacket and a stirrer. Oxygen was removed from the reaction mixture before the polymerization that was performed in inert atmosphere. Potassium persulphate was used as the initiator (0.2 w/v % related to aqueous phase), styrene (ST) or glycidylmethacrylate (GMA) eventually their combinations were used as monomers. PGMA1, PS2 and PGMA5 latexes were prepared in the presence of surfactants, the others were polymerized without emulsifier (3). The conditions of individual latexes polymerizations are given in Table 1.

Samples of polystyrene standard latexes (PSS) (Duke Scientific, Palo Alto, California, U.S.A.) were used for calibration. Their parameters given by the producer and the values determined in our laboratory by means of SFFF and nanosizer are summarized in Table 2.

Table 1 Conditions of preparation of studied latex samples

Latex	Monomers	Emulsifier	H_2O/Monomer	Conversion[a] %
PGMA 1	ST-GMA (15%)	DDSNa[b]	2	92
PS 2	ST	UDNa[c]	2	89
PGMA 3	ST-GMA (50%)	-	10	96
PGMA 4	ST-GMA (75%)	-	10	95
PGMA 5	ST-GMA (50%)	UDNa	3	91
PGMA 6	GMA-MA (25%)[d]	-	10	95

[a] conversion after 24 hours at 70 °C

[b] sodium dodecylsulphate (2 % w/v related to aqueous phase)

[c] sodium undecylenan (2 % w/v related to aqueous phase)

[d] methacroleine (MA)

Table 2 Summary of characteristics of the studied polystyrene latex standards (PSS) and copolymers on the basis of polyglycidylmethacrylate (PGMA)

Sample	Mean particle diameter (nm)			Density (g/cm^3)	Standard deviation of the distribution (%)
	Producer's data	SFFF	QELS		
PSS 1	109	113	110	1.05	
PSS 2	261	248	274	1.05	
PSS 3	364	352		1.05	
PSS 4	500	477		1.05	
PGMA 1	-	(100)[x)]	102	1.06	19.6
PS 2	-	(131)	130	1.11	6.3
PGMA 3	-	(160)	160	1.17	6.5
PGMA 4	-	(176)	175	1.24	5.9
PGMA 5	-	(251)	250	1.20	bimodal distribution
PGMA 6	-	(285)	280	1.27	12.3

x) The values in parenthesis as well as the values of densities of PGMA samples have no absolute meaning. Only their product $\bar{d}_p \cdot \bar{\varrho}_p$ is absolute. See the text regarding the used procedure of SFFF data interpretation.

RESULTS AND DISCUSSION

Physico-chemical characteristics of the analyzed latex samples are summarized in Table 2. The mean values of particle diameter of the individual samples were obtained by SFFF and QELS. The results of the SFFF analysis were calculated using the above mentioned relationships. However, it follows from Equation (4), that the particle diameter d_p can be calculated only if the difference in densities $\Delta\varrho$ between the carrier fluid and the separated sample is known or, on the contrary, $\Delta\varrho$ can be calculated if the value of d_p is known. If the density of the studied sample is not known beforehand, it is possible to calculate the mean values of particle masses, i.e., product of $\bar{\varrho}_p\bar{d}_p$ (where $\bar{\varrho}_p$ is the mean particle density) and, of course, also the distribution curve of the particle masses. Employing SFFF only, the density of particles $\bar{\varrho}_p$ and also their mean diameter $\bar{d}_p$ can be measured and calculated providing the measurement is performed in two or more liquids differing in their densities. However, we did not use this experimentally complicated procedure. We only measured a number of reference polystyrene standard latexes of known values of $\bar{d}_p$ and ϱ_p using SFFF and QELS. The mean values of $\bar{d}_p$ obtained from measurements performed by both these methods coincided, which confirmed the reliability of the mean values of $\bar{d}_p$ obtained by measurement employing QELS. The values of $\bar{d}_p$ of other analyzed samples measured by means of QELS were used for calculation of the sample densities from SFFF data and the density values were used for the calculation of the d_p values scale on original fractograms.

Figures 1 and 2 show the fractograms of individual latex samples prepared in our laboratory. The

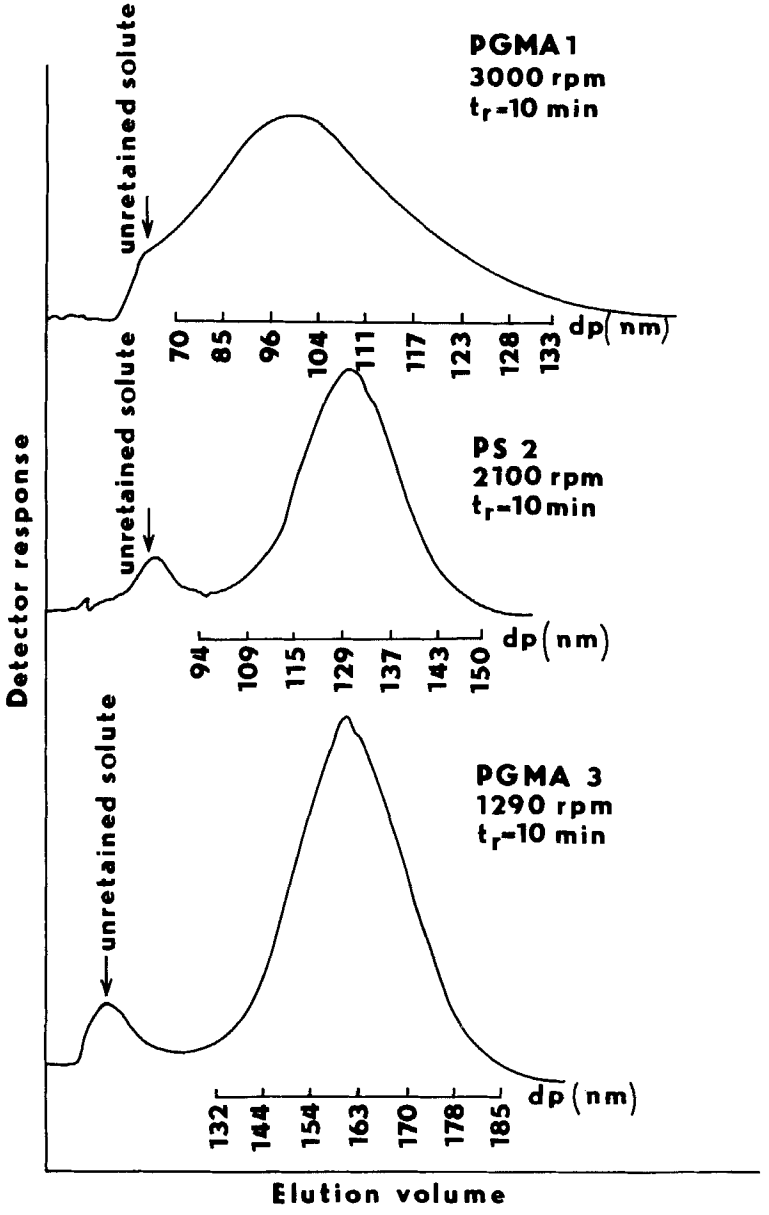

Figure 1 Fractograms of the prepared latex samples

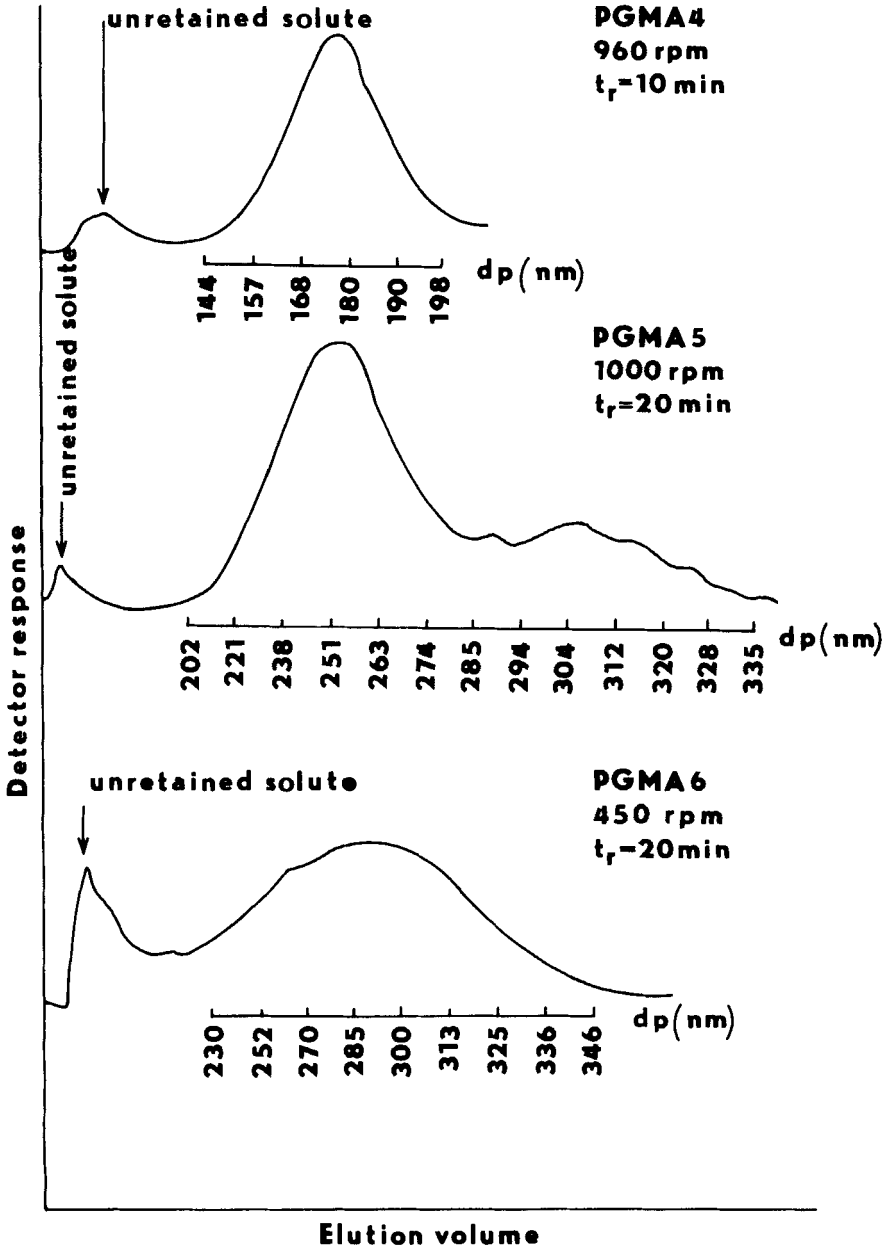

Figure 2 Fractograms of the prepared latex samples

scales of d_p values are plotted parallelly with the axis of elution volumes. The fractograms in these coordinates are unnormalized particle size distribution curves of the analyzed samples. The distribution widths of all the samples were evaluated from these fractograms and they were expressed as relative percentual standard deviation of the particle size distribution. These values are also summarized in Table 2.

Figure 3 shows photographs of latex samples taken by the electron microscope. It can be seen, by a mere comparison of these photographs with the calculated distribution widths that the clear differences in sizes of the illustrated particles cannot be found from photographs for samples with narrow distribution, i.e., for samples having low values of standard deviations. Evaluating quantitatively the distribution width of particle sizes from electron microscopy photographs a distortion due to the presence of particle aggregates (see Fig. 3) would interfere. The aggregates may appear during the preparation of the sample for measurement by the electron microscopy. Such problems do not appear with SFFF where samples are treated by the action of ultrasound before measurement and so the casual aggregates are destroyed. If a part of aggregates remained in the sample, a clear individual peak, corresponding to these aggregates, would appear in the fractogram. Such a separation of aggregates is due to the high selectivity of SFFF. However, the peaks of aggregates did not appear in any of the fractograms.

Photographs of samples PGMA 1, PGMA 5 and PGMA 6, see Figure 3, demonstrate the presence of particles of different sizes. This qualitative evaluation co-

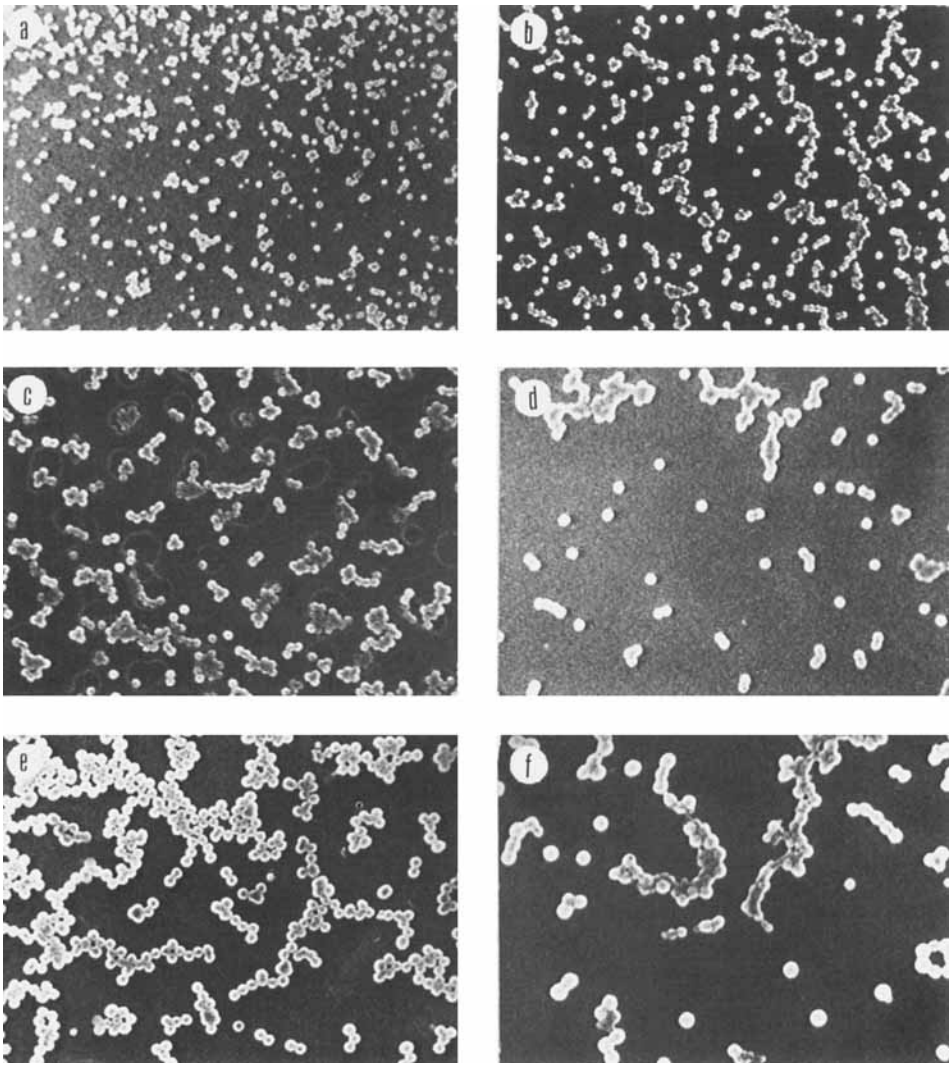

Figure 3 Photographs of the prepared latex samples taken by the electron scanning microscope, magnification 10 000 x.
(for printing purposes these were reduced by 27%)
a: PGMA 1, b: PS 2, c: PGMA 3, d: PGMA 4, e: PGMA 5, f: PGMA 6.

incides with the results of SFFF measurement that showed a substantially wider particle size distributions, expressed as standard deviations in Table 2 and apparent also from the fractogram courses of samples PGMA 1, PGMA 5 and PGMA 6 (see Figures 1 and 2). It is not simple to evaluate quantitatively the distribution width from the electron microscopy photographs regarding the tendency of the particles to form aggregates. Moreover the fractogram of the sample PGMA 5 (see Figure 2) exhibits clearly two peaks in the particle size distribution. It means that the polymerization reaction had probably a two--phase course during the preparation of this sample. It is impossible to reveal this course of the distribution curve by QELS measurement or from an electron microscopy photograph. The higher peak of the fractogram does not correspond to aggregates of particles. The largest fractions (the second, lower peak) should be at least twice as large as those having the minimal size (the first, higher peak), that is not the case.

It follows, from the mentioned results, that SFFF is a very suitable method for the high-speed and highly selective characterization of the latexes on the basis of copolymers of glycidylmethacrylates. The results of SFFF provide more information compared with QELS measurement and with electron microscopy, moreover the influence of possible artefacts, such as the aggregations that appear during the sample preparation for electron microscopy measurements is eliminated. SFFF is the only among the compared methods that makes it possible to find even very small irregularities in particles size distribution of the analyzed samples.

REFERENCES

1. Janča, J., Janíček, M., Přibylová, D. and Klesnil, M., Chem. Anal.Instrumentation, in press.

2. Janča, J., Chmelík, J. and Přibylová, D., J. Liq. Chromatogr., in press.

3. Žůrková, E., Bouchal, K., Zdeňková, D., Pelzbauer, Z., Švec, F. and Kálal, J., J. Polym. Sci. Polym. Chem. Ed., 21, 2949 (1983).