Polymolecularity of the extremely high molecular mass polymer prepared by emulsion polymerization with a macromolecular initiator forming a heterogeneous phase

[a]L. ŠOLTÉS, [b]D. MIKULÁŠOVÁ, [c]J. SUSLA, and [b]I. HUDEC

[a]*Institute of Experimental Pharmacology, Slovak Academy of Sciences,
881 05 Bratislava*

[b]*Department of Chemical Technology of Plastics and Fibres,
Slovak Technical University, 880 37 Bratislava*

[c]*Matador, 811 60 Bratislava*

Extremely high molecular mass polymer samples (polystyrenes with $\bar{M}_w$ between 8.84×10^6 and 29.4×10^6) have been prepared by emulsion polymerization with a macromolecular initiator forming a heterogeneous phase. The dependences of the monomer conversion (Y_1), $\bar{M}_w$ (Y_2), and $\bar{M}_w/\bar{M}_n$ (Y_3) on the concentrations of the initiator (x_1), of the activator (x_2), and of the emulgator (x_3) as well as on the polymerization temperature (x_4) were tested by a factor experiment of the half-replica type $2^{(4-1)}$. The true functional dependences of the studied output parameters on x_1, x_2, and x_3 were mathematically approximated by the rotatable factor experiment. At conditions under which the prepared extremely high molecular mass polystyrene samples attained a local minimum of the polymolecularity ($\bar{M}_w/\bar{M}_{n,\text{calc}} = 1.552$) a polymethylmethacrylate sample was also synthesized.

Полимеризацией в эмульсии с макромолекулярным инициатором, образующим вторую фазу, были приготовлены образцы экстремально высокомолекулярного полимера (полистиролов с $\bar{M}_w$ между $8{,}84 \cdot 10^6$—$29{,}4 \cdot 10^6$). Зависимости конверсии мономера (Y_1), $\bar{M}_w$ (Y_2) и $\bar{M}_w/\bar{M}_n$ (Y_3) от концентрации инициатора (x_1), активатора (x_2) и эмульгатора (x_3), а также от температуры полимеризации (x_4) были испытаны при помощи факторного эксперимента с половинной репликой типа $2^{(4-1)}$. Настоящие функциональные зависимости изученных выходных параметров от x_1, x_2 и x_3 были апроксимированы математически при помощи ротабельного факторного эксперимента. Был синтезирован образец по-

лиметилметакрилата в условиях, когда были приготовлены образцы высокомолекулярного полистирола с минимальной полимолекулярностью ($\bar{M}_w/\bar{M}_{n,\,\text{рассч.}} = 1,552$).

In the last decade the number of reports dealing with extremely (E) high molecular mass (HMM) polymers ($\bar{M}_w \gtrsim 10 \times 10^6$) increased markedly both in the field of the measurements of their molecular characteristics in solution [1—3] and the methods of their preparation [3—6]. While EHMM polystyrene (PS) samples are prepared mainly by anionic polymerization [1, 3] and reference materials with $\bar{M}_w \geqslant 10.0 \times 10^6$ ($\bar{M}_w/\bar{M}_n \leqslant 1.2$) are commercially available [7, 8], new polymerization methods have been searched for monomers that do not polymerize ionically [4—6].

One of convenient methods for preparation of EHMM polymers is the radical emulsion polymerization with a macromolecular initiator forming a heterogeneous phase [4, 9, 10]. The further-described EHMM PS and polymethylmethacrylate (PMMA) samples were synthesized by this method, using oxidized isotactic polypropylene powder (OIPP) as a macromolecular initiator. The choice of styrene as the monomer was determined by the availability of PS reference materials needed for calibration of the gel permeation chromatographic instrument which was used for characterization of all synthesized samples [10, 11]. In view of the number of investigated variables x, the approximation of the true functional dependence $y = f(x_1, x_2, \ldots x_k)$ was done by mathematico-statistically planned and evaluated experiments [12—14].

Experimental

Materials and methods

The OIPP used, mesh size of 0.1—0.2 mm, contained nominally I: 0.95×10^{-2} mol O_2/kg OIPP, and II: 1.54×10^{-2} mol O_2/kg OIPP iodometrically determined as the hydroperoxide groups [15]. Other chemicals:

aqueous solution (4.0×10^{-2} mol dm^{-3}) of Chelaton III (disodium ethylenediamine tetraacetate);

aqueous solution (4.0×10^{-2} mol dm^{-3}) of FeSO$_4$, acidified with a drop of H$_2$SO$_4$;

aqueous solution (100 g dm^{-3}) of Slovasol 2430 (Slovasol 2430 is an emulsifier of nonionic type produced by W. Pieck Chemical Works, Nováky);

redistilled styrene and methylmethacrylate.

Polymerization was performed [9, 10] in glass ampoules under nitrogen atmosphere. The monomer conversion was expressed in mass %. The molecular mass average $\bar{M}_w$ and the polymolecularity coefficient $\bar{M}_w/\bar{M}_n$ of EHMM PS samples were determined by g.p.c. [11].

Factor experiment of the half-replica type $2^{(4-1)}$

The preparation conditions of EHMM PS samples $1e$—$8f$, according to planned experiments (Table 1), are given in Table 2. In addition to the components listed in

Table 1

Plan of factor experiment of the half-replica type $2^{(4-1)}$ (— — —) and rotatable factor experiment (———)

Experiment No.	Level of factor			
	x_1	x_2	x_3	x_4
1	−1	−1	−1	−1
2	1	−1	−1	1
3	−1	1	−1	1
4	1	1	−1	−1
5	−1	−1	1	1
6	1	−1	1	−1
7	−1	1	1	−1
8	1	1	1	1
9	−1.682	0	0	
10	1.682	0	0	
11	0	−1.682	0	
12	0	1.682	0	
13	0	0	−1.682	
14	0	0	1.682	
15—20	0	0	0	

Table 2 (and also in Table 4), the polymerization system contained styrene (3 cm³) and water up to 18 cm³. The time of polymerization was 1 h. The achieved monomer conversions, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$ are given in Table 3. The following first-order regression equations were calculated by numerical evaluation of the experimental data

$$Y_1 = 53.7 + 7.95x_1 - 1.85x_2 + 10.7x_3 + 7.06x_4 + 1.83x_1x_2$$

$$Y_2 = 17.5 - 1.75x_1 + 2.05x_2 - 3.04x_3 - 5.67x_1x_2 - 2.92x_1x_3 + 3.02x_2x_3$$

$$Y_3 = 1.728 - 0.043x_1 + 0.038x_2 - 0.063x_3 + 0.058x_4 - 0.133x_1x_2$$

Table 2

Conditions of preparation of EHMM PS samples $1e$—$8f$

x_i^*		-1	1
	Input variable		X_i
x_1	Mass of OIPP I	0.4 g	0.8 g
x_2	Volume of the solution of Chelaton III	0.5 cm³	1.5 cm³
	Volume of the solution of FeSO₄	0.5 cm³	1.5 cm³
x_3	Volume of the solution of Slovasol 2430	3.0 cm³	6.0 cm³
x_4	Polymerization temperature	30°C	40°C

* The level of factor $x_i = (X_i - X_0)/I_i$, where X_i and X_0 are the corresponding values of the input variable and I_i is its single interval.

Table 3

Values of the monomer conversion, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$ of EHMM PS samples $1e$—$8f$

Experiment e, f No.	Output parameters		
	$y_{1e,f}$ Monomer conversion mass %	$y_{2e,f}$ $\bar{M}_w \cdot 10^{-6}$	$y_{3e,f}$ $\bar{M}_w/\bar{M}_n$
1	32.1, 31.5	14.2, 13.6	1.61, 1.70
2	57.8, 54.8	28.8, 25.9	1.91, 2.02
3	38.8, 40.4	24.5, 21.4	2.05, 2.05
4	43.4, 42.7	14.6, 14.9	1.59, 1.55
5	66.7, 68.9	8.84, 9.79	1.59, 1.64
6	65.5, 68.1	9.93, 9.38	1.65, 1.64
7	45.3, 45.8	29.4, 29.4	1.83, 1.84
8	79.8, 81.6	9.64, 13.1	1.59, 1.65

where Y_1 is the monomer conversion expressed in mass %, $Y_2 = \bar{M}_w \cdot 10^{-6}$, and $Y_3 = \bar{M}_w/\bar{M}_n$.

Rotatable factor experiment

The next planned experiment was chosen in agreement with the results of the preceding planned experiment, considering the intention of minimizing the

Table 4

Conditions of preparation of EHMM PS samples *1—20*

x_i		−1.682	−1	0	1	1.682
				X_i		
x_1	Mass of OIPP *II*	0.348 g	0.450 g	0.600 g	0.750 g	0.852 g
x_2	Volume of the solution of Chelaton III	0.46 cm³	0.60 cm³	0.80 cm³	1.00 cm³	1.14 cm³
	Volume of the solution of FeSO₄	0.46 cm³	0.60 cm³	0.80 cm³	1.00 cm³	1.14 cm³
x_3	Volume of the solution of Slovasol 2430	2.5 cm³	3.5 cm³	5.0 cm³	6.5 cm³	7.5 cm³

polymolecularity of the polymer. The preparation conditions of EHMM PS samples *1—20*, according to the planned experiments (Table 1), are given in Table 4. The polymerization temperature was 30°C and the time of polymerization was 20 min. The achieved monomer conversions, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$ are given in Table 5. Numerical evaluation of data in Table 5 led to the following second-order regression equations

$$Y_1 = 29.8 + 5.15x_1 + 1.16x_2 + 8.12x_3 - 0.70x_1x_2 + 3.15x_1x_3 - $$
$$- 1.25x_2x_3 - 1.31x_1^2 - 0.47x_2^2 + 1.00x_3^2 \tag{1}$$

$$Y_2 = 10.6 - 0.06x_1 - 0.15x_2 - 0.07x_3 - 0.30x_1x_2 - 0.23x_1x_3 - $$
$$- 0.15x_2x_3 + 0.88x_1^2 + 0.82x_2^2 + 0.86x_3^2 \tag{2}$$

$$Y_3 = 1.552 + 0.011x_1^2 + 0.007x_2^2 + 0.007x_3^2 \tag{3}$$

Table 5

Values of the monomer conversion, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$ of EHMM PS samples *1—20*

Experiment No.	Output parameters		
	y_1 Monomer conversion mass %	y_2 $\bar{M}_w \cdot 10^{-6}$	y_3 $\bar{M}_w/\bar{M}_n$
1	16.0	13.0	1.59
2	21.8	15.0	1.54
3	19.2	14.1	1.58
4	26.1	13.0	1.59
5	26.9	14.3	1.57
6	49.2	13.5	1.56
7	29.0	12.9	1.59
8	44.6	12.8	1.57
9	20.2	12.8	1.58
10	31.9	12.3	1.59
11	25.2	12.2	1.57
12	31.6	12.6	1.58
13	19.4	12.3	1.58
14	45.7	12.7	1.57
15	30.2	10.8	1.59
16	29.8	10.5	1.53
17	29.3	10.5	1.56
18	29.5	10.5	1.53
19	29.2	10.5	1.53
20	31.0	11.1	1.57

Discussion

The values of $\bar{M}_w/\bar{M}_n$, in the second step of the minimizing cycle (Table 5), were between 1.53 and 1.59, and the local minimum of the polymolecularity of EHMM PS samples $1—20$ ($\bar{M}_w/\bar{M}_{n,\,calc} = 1.552$) fell in the centre of the rotatable factor experiment (eqn (3)). However, it seems that the relatively narrow interval of the $\bar{M}_w/\bar{M}_n$ values was accompanied by a relatively narrow interval of $\bar{M}_w$ ($10.5 \times 10^6—15.0 \times 10^6$). Over this experimental interval ($\bar{M}_w > 15.0 \times 10^6$) it would be possible to extrapolate out of the range of the preparation conditions of EHMM PS samples $1—20$. Even more advantageous is to interpolate the preparation conditions of EHMM PS samples $1e—8f$, especially between experiments 4 and 7. Substituting 1 for x_2, and -1 for x_4, valid for both experiments, the calculated first-order regression equations are reduced to

$$Y_1 = 44.8 + 9.78x_1 + 10.7x_3$$

$$Y_2 = 19.6 - 7.42x_1 - 0.02x_3 - 2.92x_1x_3$$

$$Y_3 = 1.708 - 0.176x_1 - 0.063x_3$$

and by the conditions of experiments 4 and 7 ($x_1 = 1$, $x_3 = -1$ and $x_1 = -1$, $x_3 = 1$) the intervals of the $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ values are extended to $\bar{M}_{w,\,calc} = 15.1 \times 10^6—29.9 \times 10^6$ and $\bar{M}_w/\bar{M}_{n,\,calc} = 1.595—1.821$.

As a monomer more polar than styrene ($e = -0.800$) [16], polymerizable under similar conditions, methylmethacrylate ($e = +0.400$) [16] was chosen. The polymerization conditions of methylmethacrylate (3 cm^3) were the same as those given in Table 4 for $X_i = 0$. The monomer conversion, after 20 min of polymerization at 30°C, was 25.0 mass %.

The synthesized PMMA sample was characterized by gel permeation chromatography (g.p.c.) under conditions similar to those applied for the characterization of EHMM PS samples. In contrast to the procedure described previously [11] only three chromatographic columns, filled with gel of porosities of 5×10^5, 10^5, and 10^4 nm were used. Methyl ethyl ketone was used as the eluent. The concentration of the injected samples was 3 mg cm^{-3}.

A series of PS reference materials were used for calibration of the g.p.c. instrument. The molecular mass M ($M \equiv \bar{M}_w$) plotted against the elution volume v is shown in Fig. 1, above, where the experimental data are also given. To calculate [17] the plot of M vs. v, valid for PMMA under the same experimental conditions, the published constants of the Kuhn—Mark—Houwink equation for PMMA or PS in methyl ethyl ketone and at 25°C were used: $K = 7.1 \times 10^{-3}$ cm^3 g^{-1}, $a = 0.72$ [18] and $K = 1.95 \times 10^{-2}$ cm^3 g^{-1}, $a = 0.635$ [19]. From the normalized chromatogram $g^*(v)$ of the PMMA sample and the corresponding calibration curve M against v (Fig. 1, below) a value of 7.8×10^6 for M(peak) of the synthesized sample was found.
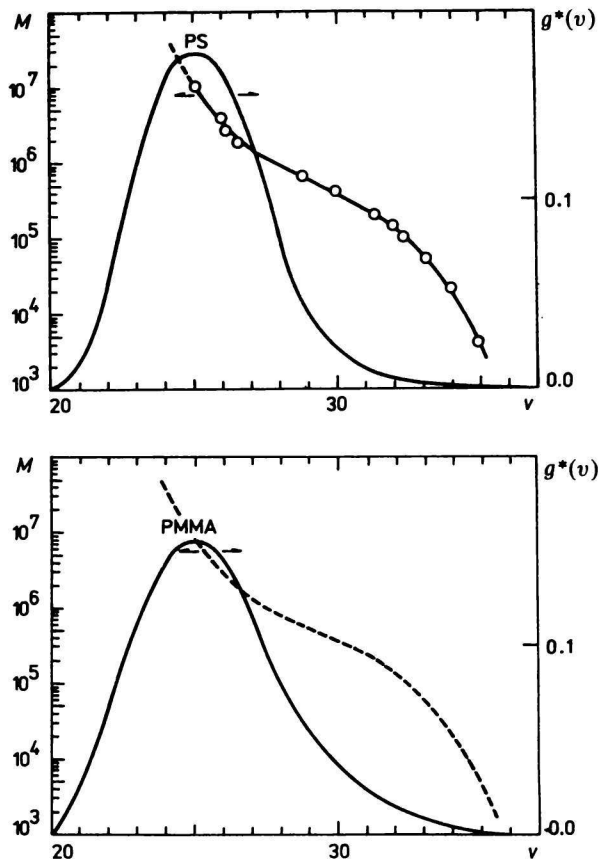
Fig. 1. Dependence of M vs. v for PS with experimental data (○), and the normalized chromatogram of PS reference material with $\bar{M}_w = 10.0 \times 10^6$ and $\bar{M}_w/\bar{M}_n \leqslant 1.15$ (above); the calculated plot of M vs. v for PMMA (— — —) and the normalized chromatogram of the synthesized PMMA sample (below).

The results of the synthesis (monomer conversion 25.0 mass %) and of the g.p.c. analysis ($M(\text{peak}) = 7.8 \times 10^6$) of the PMMA sample are in a very good agreement with the calculated results of the synthesis (monomer conversion 29.8 mass %, eqn (*1*)) as well as with the g.p.c. distribution analysis ($\bar{M}_n = 6.83 \times 10^6 < M(\text{peak}) < \bar{M}_w = 10.6 \times 10^6$, eqns (*2*) and (*3*)) of the EHMM PS sample prepared under the same conditions. Comparing the shape of the normalized chromatogram $g^*(v)$ of the PS reference material ($\bar{M}_w = 10.0 \times 10^6$, $\bar{M}_w/\bar{M}_n \leqslant 1.15$, Polysciences Inc., Warrington, Penna) shown in Fig. 1, above, with $g^*(v)$ of PMMA (Fig. 1, below), the calculated value 1.552 seems to be real estimate also for $\bar{M}_w/\bar{M}_n$ of the synthesized (EHMM) PMMA sample.

References

1. Fukuda, M., Fukutomi, M., Kato, Y., and Hashimoto, T., *J. Polym. Sci., Polym. Phys. Ed. 12*, 871 (1974).
2. Šoltés, L., Mikulášová, D., and Hudec, I., *Chem. Zvesti 35*, 543 (1981).
3. McIntyre, D., Fetters, L. J., and Slagowski, E., *Science 176*, 1041 (1972).
4. Mikulášová, D., Citovický, P., and Chrástová, V., *Eur. Polym. J. 10*, 551 (1974).
5. Inoue, T., Shiibashi, T., and Kotani, T., *26th International Congress of Pure and Applied Chemistry*, p. 1438. Tokyo, 1977.
6. Inoue, T., Seminar *Super Chemistry*, p. 43. Osaka, 1979.
7. *Data Sheets, TSK Standard Polystyrene*, Toyo Soda Manufacturing Co., Tokyo, 1973.
8. *Data Sheets*, Polysciences Inc., Warrington, Penna, 1977.
9. Mikulášová, D., Citovický, P., Chrástová, V., and Štaudnerová, A., unpublished results.
10. Šoltés, L., *CSc. Thesis*. Slovak Technical University, Bratislava, 1977.
11. Šoltés, L., Berek, D., and Mikulášová, D., *Colloid Polym. Sci. 258*, 702 (1980).
12. Nalimov, V. V. and Chernova, N. A., *Statisticheskie metody planirovaniya ekstremalnykh eksperimentov*. Izd. Nauka, Moscow, 1965.
13. Rezinov, L. P., *Statisticheskie metody optimalizatsii khimicheskikh protsessov*. Izd. Khimiya, Moscow, 1972.
14. Sautin, S. N., *Planirovanie eksperimenta v khimii i khimicheskoi tekhnologii*. Izd. Khimiya, Leningrad, 1975.
15. Citovický, P., Šimek, I., Mikulášová, D., and Chrástová, V., *Chem. Zvesti 30*, 342 (1976).
16. *Polymer Handbook*, 2nd Edition. (Brandrup, J. and Immergut, E. H., Editors.) J. Wiley & Sons, New York, 1974.
17. Benoit, H., Grubisic, Z., Rempp, P., Decker, D., and Zilliox, J. G., *J. Chim. Phys. 63*, 1507 (1966).
18. Chinai, S. N., Matlack, J. D., Resnick, A. L., and Samuels, R. J., *J. Polym. Sci. 17*, 391 (1955).
19. Oth, J. and Desreux, V., *Bull. Soc. Chim. Belg. 63*, 285 (1954).