Properties of extremely high molecular weight polystyrene in solution

V. Chrástová, D. Mikulášová, J. Lacok and P. Citovický
Department of Chemical Technology of Plastics and Fibers, Slovak Technical University, Bratislava, Czechoslovakia

(*Received* 20 *June* 1980; *revised* 24 *November* 1980)

Extremely high molecular weight polystyrenes with a $\bar{M}_w$ in the range 10.8×10^6 to 2.2×10^7 were prepared by emulsion polymerization initiated with a heterogeneous initiator at 30°C, which has a 'living character'. Samples of polystyrene were characterized by light scattering and viscometry in toluene and benzene at 25°C, and in θ-solvent cyclohexane at 34.8°C. Also determined were the relationships of mean-square radius of gyration $<s^2>$ (m^2) and the second virial coefficient A_2 (m^3 mol kg^{-2}) on the molecular weight, which for toluene and benzene are described in equations: Toluene (25°C) $<s^2> = 1.59 \times 10^{-23}\ \bar{M}_w^{1.23}$; $A_2 = 4.79 \times 10^{-3}\ \bar{M}_w^{-0.63}$; Benzene (25°C) $<s^2> = 1.23 \times 10^{-22} \bar{M}_w^{1.20}$; $A_2 = 2.59 \times 10^{-3}\ \bar{M}_w^{-0.59}$. The parameters in the Mark–Houwink–Sakurada equation were established, for extremely high molecular weight polystyrene in toluene and in benzene, at 25°C into the form giving for $[\eta]$(m^3 kg^{-1}): $[\eta] = 8.52 \times 10^{-5}\ \bar{M}_w^{0.61}$; $[\eta] = 1.47 \times 10^{-4}\ \bar{M}_w^{0.56}$. The mentioned relations, as well as the obtained values of Flory paramater ϕ_0 and of ratio $[\eta]/\bar{M}_w^{0.5}$ were compared with solution properties of high molecular weight polystyrene with narrow molecular weight distribution prepared by anionic polymerization by Fukuda *et al.*

INTRODUCTION

A number of papers[1-3] have already been published on the method of high molecular weight polystyrene preparation by heterogeneously initiated emulsion polymerization. From these studies it was found that the polymerization thus initiated has a 'living character', which is reflected in the growth of molecular weight with increasing conversion. Moreover the prepared polymer has extremely high molecular weight and relatively narrow molecular weight distribution[1,4].

In the present study, the possibility of preparing a series of high molecular weight samples with increasing molecular weight by properly controlled polymerization without subsequent fractionation has been utilized. The samples of this series, with $\bar{M}_w$ in the range of 10.8×10^6 to 2.2×10^7 were characterized by viscometry and light scattering in two good solvents, toluene and benzene as well as in θ-solvent, cyclohexane.

The results on molecular-weight characteristics obtained in this work were compared with data published in the literature[5,6] for high molecular weight polystyrene prepared by anionic polymerization.

EXPERIMENTAL

Preparation

High molecular weight polystyrene was prepared by emulsion polymerization according to the method described in a previous paper[1] where the purity of used materials was also specified.

The polymerization system consisted of an initiator—oxidized powdered isotactic polypropylene (content of hydroperoxide was 1.87×10^{-2} kmol 0_2 m$^{-3}_{\mathrm{emul}}$), an activator—3,6-diaza-1,8-octanediamine (3.3×10^{-3} kmol m$^{-3}_{\mathrm{emul}}$), an ionic emulsifier—Mersol H with am empirical formula $CH_3-(CH_2)_{16}SO_3Na$ (4.0×10^{-2} kmol m$^{-3}_{\mathrm{emul}}$) and styrene (1.45 kmol m$^{-3}_{\mathrm{emul}}$).

After the polymerization, the emulsion was isolated from the initiator by filtration. Polystyrene was precipitated from the emulsion by methanol and was purified from the residue of the polymerization system. The conversion was expressed in w/w per cent of the initial amount of styrene. The polymer samples, which were selected for the measurement of solution properties, were purified by repeated precipitation in toluene–methanol. The ratio $\bar{M}_w/\bar{M}_n$ for polystyrene thus prepared was determined by a modified g.p.c. method and was not higher than 1.4.

Measurements in solution

Solvents. Analytical grade benzene and toluene were dried with $CaCl_2$, then refluxed over sodium metal and fractionally distilled before use. Cyclohexane for spectroscopy was used without further purification.

Light scattering. The intensity of light scattered from toluene and benzene solutions of the polymers was measured with a commercial Sofica photometer at 25°C, using unpolarized light of wavelength 5.461×10^{-7}m and calibrated with pure benzene. The specific refractive index increment dn/dc of polystyrene at 25°C was 1.12×10^{-4} m^3 kg^{-1} in toluene and 1.11×10^{-4} m^3 kg^{-1} in benzene. Measurements in cyclohexane were made under the same conditions at the temperature 34.8°C; the value of dn/dc was 1.71×10^{-4} m^3 kg^{-1} [7].

Polystyrene solutions in toluene and benzene were prepared by dissolving a weighed amount of polymer for

0032-3861/81/081054-04$02.00

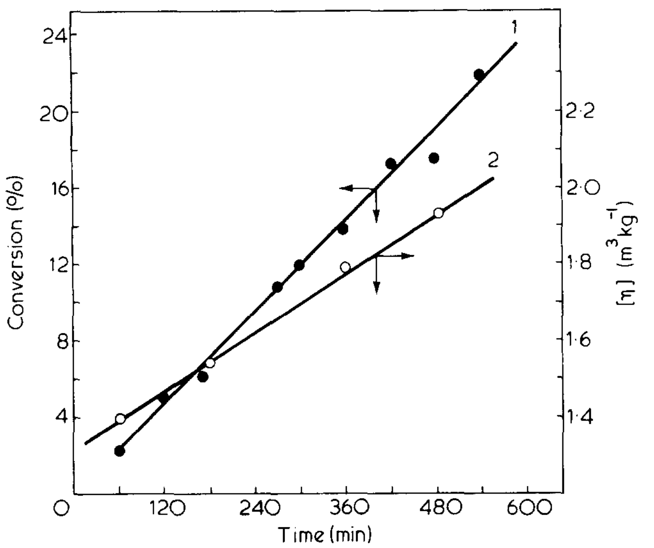

Figure 1 Dependence of % conversion (1) and [η] (2) on time, for heterogeneously initiated emulsion polymerization of styrene at 30°C

24 h without mixing and then the system was slowly shaken for 48 h at room temperature. Polystyrene in cyclohexane was dissolved in the same way in an ultrathermostat at 34.8°C. The purification of the solutions was carried out by filtrating the required amount of solvent through filter (G5) into a dust-free light scattering cell and then the polymer solution was passed through filter (G4). The concentration of solutions was established by weighing and was in the range of 0.15 to 0.70 kg m^3.

Light scattering measurements were carried out between 28° and 150°C; in the range of angles from 30° to 75° the increment was 5°. The data from light scattering measurements were evaluated on the EC 1010 computer by the simulation of Flory–Beuche equation[8] which includes quadratic terms.

$$\frac{Kc}{R_\theta}=\frac{1}{\bar{M}_w}+\frac{vx}{3\bar{M}_w}+\frac{v^2x^2}{36\bar{M}_w}+2A_2c+3A_3c^2+\ldots \qquad (1)$$

where R_θ is Rayleigh ratio, θ is the scattering angle, K is the optical constant which is equal to $2\pi^2\, n_0\,(dn/dc)/N_A\lambda_0^4$; c is the concentration (kg m^{-3}), λ_0 is the wavelength of the incident light in vacuo, $\bar{M}_w$ is the weight average molecular weight; A_2 and A_3 are the second and third virial coefficients respectively; $v=16\pi^2\langle s^2\rangle_z/\lambda^2$ and $x=\sin^2(\theta/2)$, where $\langle s^2\rangle_z$ is equal to z-average-mean-square radius of gyration and λ is the wavelength of light in the medium.

Viscometry. Viscometry measurements of polystyrene samples were carried out in benzene and toluene (at 25°C) and in cyclohexane (at 34.8°C) by a Saide–Deckert type viscometer[9]. On the basis of previous results[10] concentrations in the range of 0.15 to 0.06 kg m^{-3} were used. Kinetic energy corrections were not applied because viscometer had a flow-time of more than 100 s. Limiting viscosity numbers [η] were determined from two types of plots $(\eta-\eta_0)/\eta_0 c$ *versus* c and $[\ln(\eta/\eta_0)]/c$ *versus* c; η, η_0 are solution or solvent flowing times and c is the solution concentration. The values of [η] in good solvents were extrapolated to zero rate of shear.

RESULTS AND DISCUSSION

Before measuring solution properties of high molecular polystyrene attention was paid to its synthesis by heterogeneously initiated emulsion polymerization. Under already defined conditions[1] dependence of conversion percentage and [η] on the time of polymerization was investigated (*Figure 1*). It has been shown that throughout the whole time range investigated the conversion as well as [η] of the prepared polymer have grown.

Polystyrene prepared by heterogeneous polymerization was further characterized by viscometry and light scattering in toluene, benzene and θ–solvent cyclohexane.

The measurement of the light scattering intensity in relation to the angle of observation has shown that this dependence is approximately linear up to 75°. With angles higher than 90° deformation of the Zimm plot was observed (*Figure 2*). In order to avoid graphical extrapolation in obtaining basic data of light scattering, mathematical simulation of equation (1) was used on computer EC 1010 according to a modified Ross–Murphy programme[11]. It was shown that not even quadratic approximation of function according to equation (1) sufficiently reflects the course of experimentally obtained relation

$$Kc/R_\theta=f\left(\sin^2\frac{\theta}{2}+kc\right)$$

for high molecular weight polystyrene in the entire range of investigated angles. Other authors[12] also indicated relatively great difficulties in obtaining basic data from measurements of light scattering for samples with $\bar{M}_w$ higher than 10^7. They recommend extrapolation at low angles (up to 80°).

Considering the above mentioned facts we have evaluated the results obtained from measurements of light scattering by extrapolating the relation

$$Kc/R_\theta=f\left(\sin^2\frac{\theta}{2}+kc\right)$$

in the range of angles up to 75°. Obtained results of $\bar{M}_w$, $\langle s^2\rangle$, A_2 and [η] for series of polystyrene samples (type PS–M) in toluene and benzene are presented in *Table 1*.

On the basis of our results of A_2 (m^3 mol kg^{-2}) as well

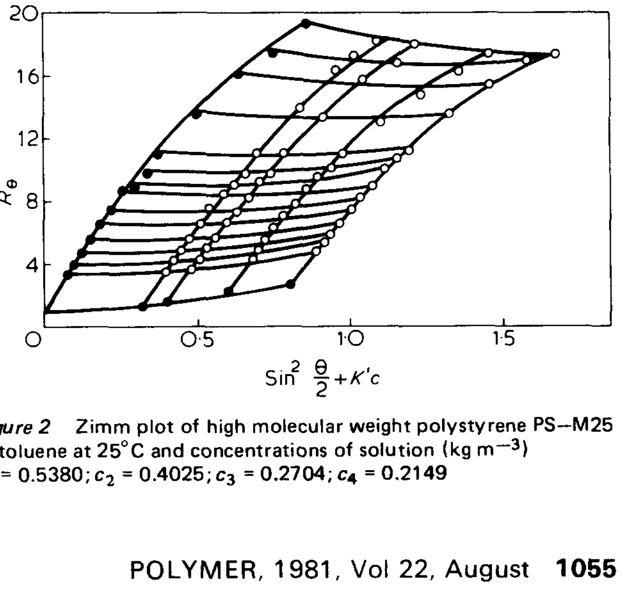

Figure 2 Zimm plot of high molecular weight polystyrene PS–M25 in toluene at 25°C and concentrations of solution (kg m^{-3}) c_1 = 0.5380; c_2 = 0.4025; c_3 = 0.2704; c_4 = 0.2149

Table 1 Results of scattering and viscometry measurements for high molecular weight polystyrene in toluene and benzene at 25°C

	Toluene, 25°C				Benzene, 25°C			
Sample Code	$\bar{M}_w \times 10^{-6}$	$\langle s^2 \rangle \times 10^{14}$ (m^2)	$A_2 \times 10^7$ (m^3 mol kg^{-2})	[η] (m^3 kg^{-1})	$\bar{M}_w \times 10^{-6}$	$\langle s^2 \rangle \times 10^{14}$ (m^2)	$A_2 \times 10^7$ (m^3 mol kg^{-2})	[η] (m^3 kg^{-1})
PS–M08	10.8	4.34	1.90	1.41	–	–	–	–
PS–M24	11.9	4.66	1.77	–	–	–	–	–
PS–M25	12.5	4.86	1.75	1.50	12.5	4.25	1.52	1.40
PS–M28	14.8	6.40	1.59	–	14.2	4.92	1.40	1.57
PS–M29	15.9	6.80	1.50	–	–	–	–	–
PS–M30	16.0	6.98	1.48	1.79	15.9	5.80	1.29	1.72
PS–M31	17.1	8.04	1.36	–	–	–	–	–
PS–M34	19.2	8.90	1.33	1.99	20.3	7.56	1.12	1.88
PS–M35	22.2	10.93	1.28	–	–	–	–	–

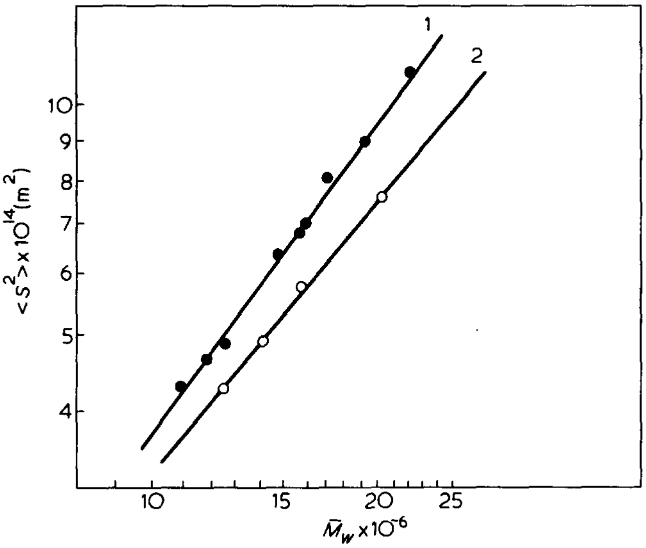

Figure 3 Double logarithmic plots of $\langle s^2 \rangle$ against $\bar{M}_w$ for polystyrenes in toluene (1) and in benzene (2) at 25°C

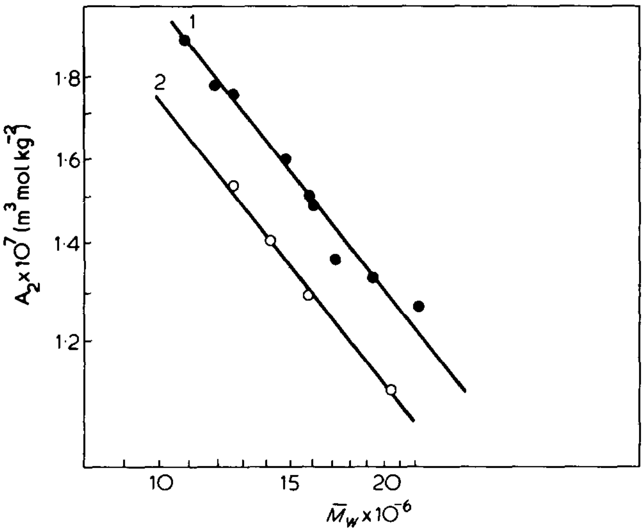

Figure 4 Double logarithmic plots of A_2 *versus* $\bar{M}_w$ for polystyrenes in toluene (1) and in benzene (2) at 25°C

as $\langle s^2 \rangle$(m^2) it may be said, that for extremely high molecular weight polystyrene toluene is a somewhat better solvent than benzene.

Double logarithmic relations of $\langle s^2 \rangle$ on $\bar{M}_w$ in toluene and in benzene at 25°C are presented in *Figure 3*. These relations can be described as in equations (2) and (3).

In toluene, 25°C:

$$\langle s^2 \rangle = 1.59 \times 10^{-23} \bar{M}_w^{\,1.23} \quad (2)$$

In benzene, 25°C:

$$\langle s^2 \rangle = 1.23 \times 10^{-22} \bar{M}_w^{\,1.20} \quad (3)$$

The squate of radius of gyration $\langle s^2 \rangle$ of high molecular polystyrene increases with molecular weight. A similar relation $\langle s^2 \rangle = f(\bar{M}_w)$ in benzene at 30°C has also been obtained by Fukuda *et al.*[5] for high molecular weight polystyrene prepared by anionic polymerization.

The second virial coefficient was another investigated parameter. Double logarithmic plot A_2 *versus* $\bar{M}_w$ in benzene and toluene is in *Figure 4*. This relation can be characterized by equations (4) and (5).

In toluene, 25°C:

$$A_2 = 4.79 \times 10^{-3} \bar{M}_w^{\,-0.63} \quad (4)$$

In benzene, 25°C:

$$A_2 = 2.59 \times 10^{-3} \bar{M}_w^{\,-0.59} \quad (5)$$

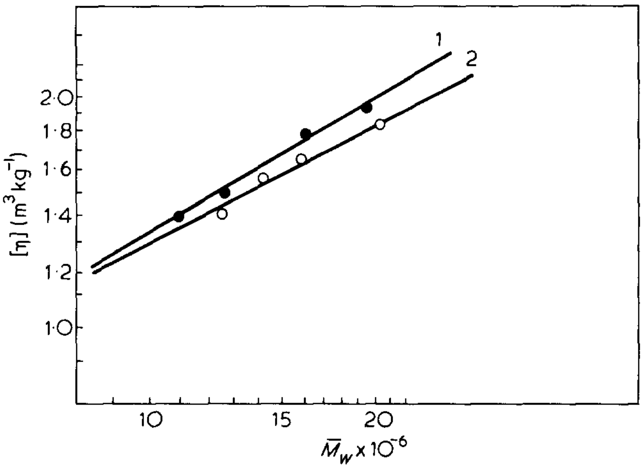

Figure 5 Double logarithmic plots of [η] against $\bar{M}_w$ for polystyrenes in toluene (1) and in benzene (2) at 25°C

In the entire range of molecular weights investigated the value of the second virial coefficient gradually decreased.

Unlike the published results[5] the A_2 in benzene, determined in this work, has somewhat lower values. The values determined in toluene were not higher than 1.9 $\times 10^{-7}$ m^3 mol kg^{-2}. This may be due to the fact that in the mentioned paper, characterized polystyrenes were of lower molecular weight (up to 13.4×10^6) and that the measurement was carried out in benzene at 30°C.

Table 2 Results of light scattering and viscometry measurements for samples PS–M25 and PS–M34 in cyclohexane at 34.8°C

Sample code	$\bar{M}_w \times 10^{-6}$	$\langle s^2\rangle_\theta \times 10^{14}$ (m^2)	$\langle s^2\rangle_\theta/\bar{M}_w \times 10^{21}$	$[\eta]_\theta$ (m^3 kg^{-1})	α* Toluene	α Benzene	$\bar{M}_w \frac{[\eta]_\theta}{0.5} \times 10^5$
PS–M25	12.5	1.28	9.19	0.31	1.94	1.82	8.76
PS–M34	20.5	1.71	8.69	0.39	2.28	2.10	8.60

* Expansion coefficient was estimated according to relation $\alpha = (\langle s^2\rangle)^{1/2}/(\langle s^2\rangle_\theta)^{1/2}$

The results for $\bar{M}_w$ and $[\eta]$(m^3 kg^{-1}) obtained in toluene and benzene at 25°C for high molecular weight polystyrene, presented in *Table 1*, enabled us to determine coefficients of Mark–Houwink–Sakurada equation (*Figure 5*).

In toluene, 25°C:

$$[\eta] = 8.52 \times 10^{-5} \bar{M}_w{}^{0.61} \tag{6}$$

In benzene, 25°C:

$$[\eta] = 1.47 \times 10^{-4} \bar{M}_w{}^{0.56} \tag{7}$$

Some samples of polystyrene with different molecular weights PS–M 25 and PS–M 34 were also characterized in θ–solvent. The results are presented in *Table 2.*

According to the Flory–Fox[13] relation, describing the dependence of $[\eta]$ on the ratio $\langle s_\theta^2\rangle/\bar{M}_w$ for linear macromolecules in θ-conditions

$$[\eta]_\theta = 6^{3/2}\varphi_0(\langle s_\theta^2\rangle/\bar{M}_w)^{3/2}\bar{M}_w{}^{1/2} \tag{8}$$

the value of the Flory parameter φ_0 was calculated. The average value of $\varphi_0 = 2.25 \times 10^{21}$ mol^{-1}, obtained from our results, is a little lower than that published by Flory (2.87×10^{21} mol^{-1}); however it is in relatively good agreement with the results[5] presented for high molecular polystyrene prepared by anionic polymerization (2.53×10^{21} mol^{-1}).

The ratio $[\eta]_\theta/\bar{M}_w{}^{0.5}$ (m^3 kg^{-1}) was calculated from the results of viscometry and light scattering measurements of samples in θ–solvent. Values (8.76×10^{-5} resp. 8.60×10^{-5}) so gained, which are presented in the last column in *Table 2*, are in good agreement with the corresponding value published by Fukuda[5] (8.77×10^{-5}), Yamamoto[6] (9.1×10^{-5}) and Berry[14] (8.4×10^{-5}).

From the results given in this paper it follows that even extremely high molecular weight polystyrene prepared by heterogeneous emulsion polymerization can be characterized in good and θ–solvents and the characteristics obtained are in good agreement with solution properties of polystyrene prepared by anionic polymerization. Besides this, heterogeneously initiated emulsion polymerization which has a 'living character' enables control of the polystyrene molecular weight by changing the time of polymerization.

ACKNOWLEDGEMENT

The authors express their thanks to Professor J. Beniska, Head of the Department of Chemical Technology of Plastics and Fibers, for his constant encouragement and valuable advice.

REFERENCES

1 Mikulásová, D., Chrástová, V. and Citovický, P. *Eur. Polym. J.* 1974, **10**, 551

2 Mikulásová, D., Chrástová, V., Citovický, P. and Horie, K. *Makromol. Chem.* 1977, **178**, 429

3 Chrástová, V., Mikulásová, D. and Citrovický, P. *Chem. Zvesti* 1978, **32**, 205

4 Mikulásová, D., Chrástová, V. and Citrovický, P. *CS Pat. No.* 159670 (1975)

5 Fukuda, M., Fukutomi, M., Kato, Y. and Hashimoto, T. *J. Polym. Sci. Polym. Phys. Edn.* 1974, **12**, 871

6 Yamamoto, A., Fujii, M., Tanaka, G. and Yamakawa, H. *Polym. J.* 1971, **2**, 799

7 Elias, H.-G., Etter, O. *Makromol. Chem.* 1963, **66**, 59

8 Flory, P. J. and Bueche, A. M. *J. Polym. Sci.* 1958, **27**, 219

9 Langhammer, G., Berger, R. and Seide, H. *Plaste u.Kautsch.* 1964, **8**, 472

10 Chrástová, V., Mikulásová, D., Citovický, P. and Lacok, J. Collection of Communications, Slovak Technical University (in press)

11 Ross-Murphy, S. B. and Kajiwara, K. *Eur. Polym. J.* 1975, **11**, 365

12 Orofino, T. A. and Wenger, F. *J. Phys. Chem.* 1963, **67**, 566

13 Fox, T. G. and Flory, P. J. *J. Phys. Coll. Chem.* 1949, **53**, 197

14 Berry, G. C. *J. Chem. Phys.* 1966, **44**, 4550, *ibid.* 1967, **46**, 1338